

Development of High-paintability Waterborne Primer Paint

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ABSTRACT

Waterborne primer paint is easily affected by temperature and has to be applied under certain temperature conditions, and so in order to save energy there is a need to expand the range of painting temperatures. To expand the range of painting temperatures, painting resin compositions were studied that can control changes in paint viscosity in relation to changes in paint solid content. By increasing the ratio of hydrophilic component of paint resin, it was discovered that the interaction of resin in the low solid-content range directly after application was strengthened and high viscosity was achieved, while resin phase transformation in the high solid-content range prior to drying was mitigated and low viscosity achieved, thus controlling changes in paint viscosity. This technique was used to develop paints, with the result that the range of painting temperatures, which was $\pm 3^{\circ}\text{C}$ with conventional paints, was expanded to $\pm 10^{\circ}\text{C}$.

1. Introduction

As Fig. 1 shows, the structure of automotive body paint consists of four films: e-coat, primer, basecoat and clearcoat. Of these, primer paint has three functions: providing a paint appearance, imparting chipping resistance and imparting weather resistance. As such, it plays a very important role in terms of the marketability and durability of the automotive body paint.

To prevent air pollution, the industry has shifted from solvent-based primer paints to waterborne primer paints in order to reduce emissions of volatile organic compounds.

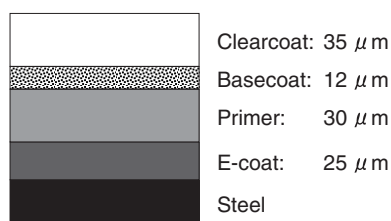


Fig. 1 Film structure of automotive body paint

However, waterborne primer paint is more easily affected than solvent-based primer paint by paint booth climate-control temperature and the coating object's temperature, so painting is done under controlled conditions in a narrow temperature range of $\pm 3^{\circ}\text{C}$. If waterborne primer is applied outside the current temperature range, sagging is likely on the low-temperature side, and poorer paint appearance is likely on the high-temperature side, leading to a loss of paint marketability under either condition. Therefore large-scale climate-control equipment is necessary in the paint booth and storage before the booth (Fig. 2), which increases energy consumption. Trial calculations indicate that energy consumption from climate control in a waterborne paint booth may be about 60% higher as compared to a case using solvent-based primer⁽¹⁾.

What is needed to save energy is a waterborne primer paint that can be applied over a wide temperature range similar to that allowed by solvent-based primer, without sacrificing paintability. Because paint's application properties vary widely according to changes in the coating object's temperature, painting materials were developed with a focus on coating object temperature.

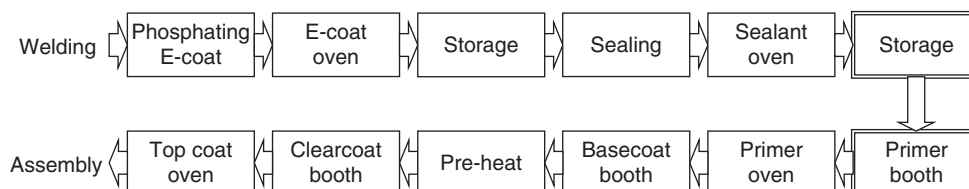


Fig. 2 Outline of body paint process

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2. Current Issues

Because solvent-based primer paints use organic solvents as thinner, one can control how much of these solvents is volatilized during painting, even if the temperatures of the paint booth and car body vary, by carefully selecting the type of organic solvent. This enables one to maintain a uniform application solid content in the paint at a wide temperature range, thus making it easy to do painting work and adjust paint appearance. Therefore, painting processes that use solvent-based paints allow a wide range of tolerable temperatures of paint booths and of car bodies, which are affected by ambient temperature and dryer heat exhaust.

Figure 3 shows body temperature changes in a condition that the temperature is not adjusted in storage before the primer paint booth. When car bodies are put inside the primer paint booth, their temperatures vary over a range of 20°C, from a low of 18°C in winter to a high of 38°C in summer.

Waterborne primer paints, on the other hand, use water as thinner, which takes greater evaporation energy than organic solvents and therefore evaporates less at low temperatures. Additionally, since there is not a choice of type as there is with organic solvents, one cannot control water evaporation at high temperatures, so it is challenging to control the paint's application solid content. Therefore, it is necessary to control water evaporation by controlling the coating object's temperature within a narrow range during painting and thereby maintain a uniform application solid content.

Figure 4 shows the results of altering the coating object's temperature and confirming changes in a current waterborne primer paint's application solid content, between one minute after spraying and five minutes after, when drying starts.

The figure shows that the difference in application solid content at 23°C - 28°C (the current waterborne primer paint's range of painting temperatures) has been minimized. When the range is expanded to 18°C - 38°C (similar to the painting temperature range of solvent-based primer), the application solid content is low at 18°C

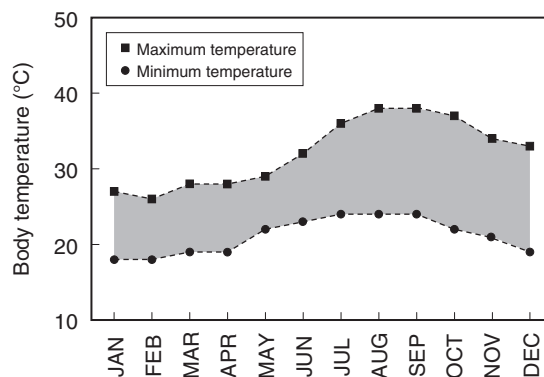


Fig. 3 Annual body temperature

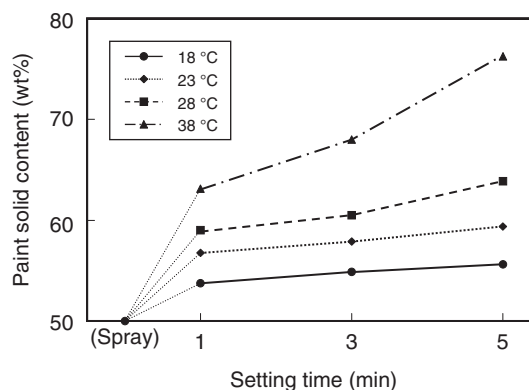


Fig. 4 Paint solid content versus setting time

immediately after painting, and there is subsequently little change in application solid content. Therefore, the state of low viscosity continues, making the paint flow easily and producing paint sagging. At 38°C, the application solid content is high starting immediately after painting, and it rises subsequently, so there is high viscosity and flow is lost; paint appearance is poorer because uneven places that occur on the paint surface during painting do not get smoothed out. Thus, waterborne primer paints do not have a stable application solid content over a wide temperature range and do not allow the marketability that solvent-based primer paints do under the same temperature conditions.

There is also a method of limiting application solid-content changes that result from temperature changes, by mixing paint and water inside the painting machine based on the coating object's monitor temperature⁽²⁾, but this is not considered to provide sufficient adjustment because the application solid-content change is too great at 38°C. Additionally, a method has been considered that alters the relationship between application solid content and paint viscosity by adding a viscosity adjuster to the paint. However, in addition to temperature changes over the course of a year, those over the course of a single day are not insignificant, making paint adjustment and control during the painting process complex and thus disadvantageous in terms of human errors.

To reduce energy consumption from climate control and achieve the same level of paintability as with solvent-based primer paint when there are fluctuating temperatures, viscosity characteristics are needed that minimize changes in viscosity even if there are great changes in application solid content.

3. Materials Development Concept

The following targets were set for materials development, accounting for environmental needs and productivity.

- (1) Be able to reduce temperature controls in the painting process
- (2) Make complex production process control unnecessary

These perspectives were taken in the study as the stance on materials development.

4. Techniques for Achieving the Targets

The relationship between current waterborne primer paint's application solid content and viscosity is shown in Fig. 5. The shaded area in the figure represents the paintable range, in which the minimum viscosity at which sagging does not occur at 18°C (application solid content 55%) and the maximum viscosity that achieves the target paint appearance at 38°C (application solid content 76%) are confirmed in advance. Because the viscosity is insufficient at 18°C and excessive at 38°C, it is necessary to adjust the viscosity for both low-application solid content and high-application solid content.

Since it uses minute particle hydrophobic resin as the main resin, waterborne primer paint has two mechanisms for increasing viscosity. One mechanism for increasing viscosity is resin particle interaction at low-application solid content (below 65%), while the other is resin phase transformation at high-application solid content (above 65%). Therefore, the study of techniques for achieving the primer paint was divided into two ranges: the low-application solid-content range and high-application solid-content range.

4.1. Increasing Viscosity in the Low-application Solid-content Range

Particulate hydrophobic resin is not uniformly distributed in paint, but rather is unevenly distributed in particulate form, and therefore when in low-application solid-content state the particles are separated from each other, the interaction is weak and viscosity is low. However, as the water evaporates and the application solid content increases, the particles draw closer to each other, stronger interaction occurs and viscosity increases (Fig. 6(a)). To help ensure sagging resistance, a method of increasing viscosity with a viscosity adjuster has been used⁽³⁾ as a technique to supplement particle interaction,

so that application solid content is increased by about 5% and sufficient viscosity is achieved. However, if the low-application solid-content viscosity is increased by viscosity adjuster, the viscosity of the high-application solid-content range discussed next is simultaneously increased, so it is challenging to get a viscosity balance between the low- and high-application solid-content ranges.

The optimization of hydrophilic resin was considered as a technique for increasing resin interaction to increase viscosity in the low-application solid-content range. Since hydrophilic resin dissolves in water and is spread out in linear form, it keeps a close distance to particulate hydrophobic resin, and it is expected this will encourage resin interaction, increasing viscosity in low-application solid content (Fig. 6(b)).

4.2. Decreasing Viscosity in the High-application Solid-content Range

An increase in the viscosity in the high-application solid-content range is the result of the main component of the paint transforming from an aqueous phase to an oil phase (phase transformation)⁽⁴⁾. An aqueous phase consists of water and hydrophilic resin dissolved in that water, whereas an oil phase contains hydrophobic resin, which does not dissolve in water, dispersed in particulate form. In the low-application solid-content range, the particles of the hydrophobic resin are distributed at low concentration in an aqueous phase. For this reason, the fluidity of the aqueous phase is not inhibited and the paint has a low viscosity, but as the water evaporates, the particle concentration increases, paint fluidity is inhibited and viscosity increases⁽⁵⁾. As more water evaporates, the main component of the paint becomes an oil phase with aqueous phase particles dispersed within it, lowering the viscosity (Fig. 7).

In current waterborne primer paints, only a narrow range of temperature conditions is allowed when painting, which controls increases in application solid content, so there has not been sufficient study of viscosity in the high-application solid-content range. The application of hydrophilic resin has been considered

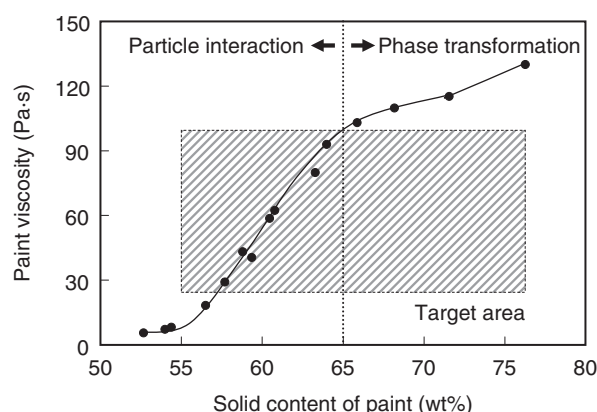


Fig. 5 Current paint viscosity versus solid content

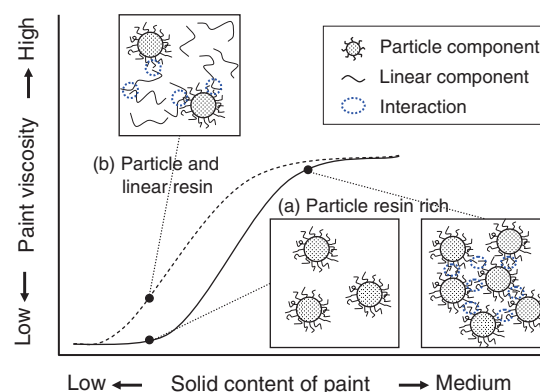


Fig. 6 Interaction between particle resin and linear resin at low solid content

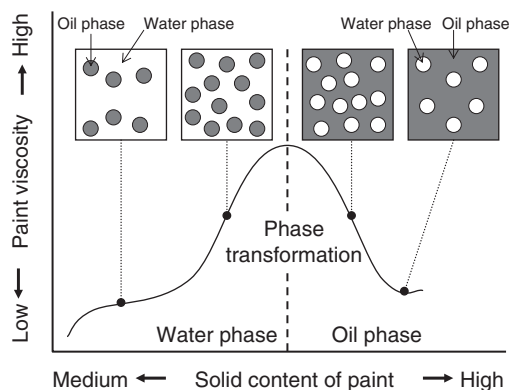


Fig. 7 Phase conversion and paint viscosity at high solid content

as a method for controlling viscosity increase in the high-application solid-content range prior to phase transformation. Hydrophilic resin dissolves in water and does not form particles, so no phase transformation occurs and viscosity is not increased. However, with hydrophilic resin alone, it is impossible to get an increase in viscosity in the low-application solid-content range necessary to ensure sagging resistance.

Because viscosity increase during phase transformation depends on particle concentration, a method was considered that reduces the hydrophobic resin that turns into particles and increases the hydrophilic resin that turns into the aqueous phase component. This makes it possible to reduce the particle component while keeping the amount of resin component uniform, so control over phase transformation viscosity can be expected.

Based on the above, the technique of increasing viscosity at the low-application solid-content range and the technique of decreasing viscosity at the high-application solid-content range coincide with each other, as they both reduce the hydrophobic resin component and increase the hydrophilic resin component of the resin.

5. Results of Viscosity Behavior when Resin Ratio Changed

Current waterborne primer paints consist of two kinds of resin: polyester resin and melamine resin. In the case of both polyester resin and melamine resin, a choice can be made between a hydrophilic and hydrophobic type. Samples of hydrophilic and hydrophobic components of each resin were produced in the ratios shown in Table 1, with the solid content varied and viscosity measured.

5.1. Polyester Resin's Hydrophilic/Hydrophobic Component Ratios

Viscosity was measured using Samples 1-4, which varied the polyester resin's hydrophilic/hydrophobic component ratios from 75:25 to 100:0. The results are given in Fig. 8.

Table 1 Resin formulation of test sample

Sample	Polyester		Melamine	
	Hydrophilic	Hydrophobic	Hydrophilic	Hydrophobic
Sample-1	75	25	—	—
Sample-2	82.5	17.5	—	—
Sample-3	90	10	—	—
Sample-4	100	0	—	—
Sample-5	56.2	18.8	7.5	17.5
Sample-6	56.2	18.8	12.5	12.5
Sample-7	56.2	18.8	16.5	8.5

In the low solid-content range, an increase in viscosity was observed as the polyester resin's ratio of hydrophilic component rose. However, when the hydrophilic component reached 100% (Sample 4), there was no increase in viscosity. The results indicate that in the low solid-content state, in the hydrophobic component that occurs as particles in the paint, there is little interaction, but by increasing the ratio of hydrophilic component, which spreads out in linear form, interaction becomes stronger and viscosity increases. Also, in the case of hydrophilic component alone, there is no strong interaction from hydrophobic component particles, and the interaction in the hydrophilic component is weak, so viscosity does not easily increase. These facts indicate that in the low solid-content range, mixing a hydrophobic component and hydrophilic component with each other and increasing the ratio of hydrophilic component can increase resin interaction and increase viscosity.

In the high solid-content range, it is recognized that increasing the ratio of hydrophilic component will reduce viscosity, but viscosity increases are not completely controlled. It is thought that, although an increase in the ratio of hydrophilic component causes the concentration of particle component to be reduced, the particle component remains, and therefore the point at which viscosity increase begins shifts to the high solid-content side, only to delay the viscosity increase.

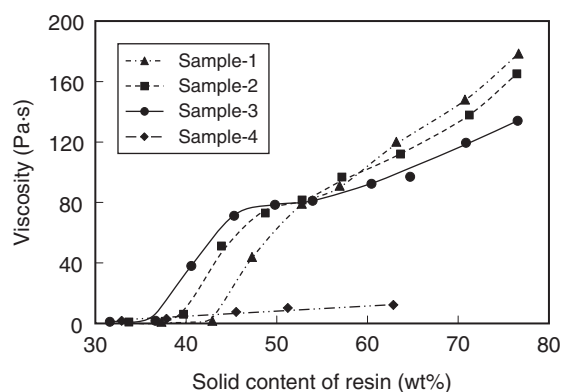


Fig. 8 Resin viscosity when polyester ratio changed

5.2. Melamine Resin Hydrophilic/Hydrophobic Component Ratios

Viscosity was measured using Samples 5-7, which varied the melamine resin hydrophilic/hydrophobic component ratios from 30:70 to 66:34. The results are given in Fig. 9.

In the low solid-content range, there was an increase in viscosity as the ratio of hydrophilic component rose, but the viscosity increase effect was small compared to that of polyester resin. The chemical structure of melamine resin is smaller than that of polyester resin and does not spread out as much in the paint, so it is thought that the viscosity increase effect is smaller because the structure has less influence on interaction between particles with a large distance between them.

In the high solid-content range, increasing the hydrophilic component markedly controls viscosity increase, and in Sample 7, with a hydrophilic/hydrophobic component ratio of 66:34, no viscosity increase was found up to a solid component of 65%. The hydrophobic component of melamine resin is stable in water and does not disperse; it is incorporated into particles that are the hydrophobic component of polyester resin, so it has no impact on particle concentration. However, the hydrophilic component can exist stably in water, so the aqueous phase increases and there is the effect of decreasing particle concentration. Also, the melamine resin's hydrophilic component has a low viscosity of 2.1 Pa·s, so it is thought that the viscosity increase is controlled by the decline in aqueous-phase viscosity.

Following the above, in the low solid-content range, paint viscosity was increased by increasing polyester resin's ratio of hydrophilic component and thereby increasing polyester resin interaction. In addition, in the high solid-content range, it was confirmed that paint viscosity is reduced by increasing melamine resin's ratio of hydrophilic component and thereby lowering particle concentration and lowering aqueous-phase viscosity. It was found that by adjusting the ratio of hydrophilic resin component, it is possible to adjust viscosity in the low and high solid-content ranges.

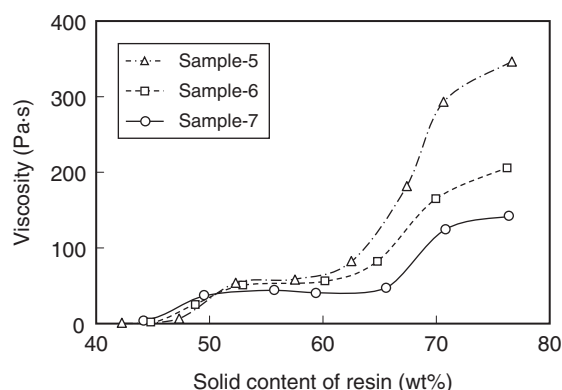


Fig. 9 Resin viscosity when melamine ratio changed

6. Developed Materials

Based on the results of confirming resin viscosity, waterborne primer paint was mixed with a hydrophilic/hydrophobic component ratio of 90:10 with polyester resin and a hydrophilic/hydrophobic component ratio of 66:34 with melamine resin.

The relationship between the developed waterborne primer paint's application solid content and viscosity is shown in Fig. 10. In this graph, the developed paint is represented by the solid line and the current paint by the broken line. Additionally, the shaded area of the figure indicates the region within the upper and lower limits of target viscosity to ensure sagging resistance and paint appearance. It was found that, compared to the current paint, the developed paint can achieve high viscosity in the low-application solid-content range and low viscosity in the high-application solid-content range. Also, whereas the current paint has a narrow-application solid-content range (57%-65%) from minimum to maximum viscosities, the developed paint has a wider range, from 55% (at body temperature 18°C) to 76% (at body temperature 38°C).

Using a test booth under actual line painting conditions, sagging resistance and paint appearance were comparatively demonstrated, using the developed paint and current paint. Sagging resistance was evaluated by applying a film of primer at an incline to panels with $\phi 10$ holes; the panel passed if it had sagging of no more than 5 mm at the bottom of the holes. The film thickness in this case was set as the sagging limit film thickness. Additionally, the paint appearance was evaluated by applying finish paint and subsequently using a Wavescan (BYK) orange peel meter, taking LW of 1.2 mm to 12 mm wavelength as the parameters.

Results of confirming sagging resistance with varied coating object temperatures are shown in Fig. 11. At 18°C, the current paint has a limit film thickness of 26 μm , making it challenging to paint, but the developed paint has outstanding painting properties, with a limit film thickness of 45 μm . Whereas the lowest paintable temperature is 23°C with the current paint, it is 18°C with the developed paint.

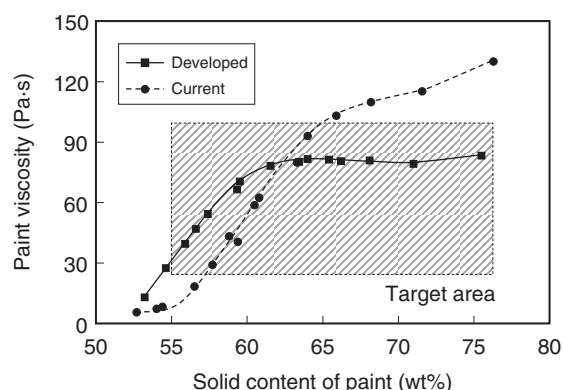


Fig. 10 Developed paint viscosity versus solid content

Next, results of confirming paint appearance with varied coating object temperatures are shown in Fig. 12. The viscosity of the current paint increases at 28°C or more, which makes smoothing properties insufficient, causing paint appearance to quickly diminish. In contrast, the developed paint has little increase in viscosity even if the application solid content is high, meaning that there is little change in paint appearance and an outstanding paint appearance can be achieved even at 38°C. Comparing the highest paintable temperature in terms of paint appearance, it is 28°C or below with the current paint, whereas the developed paint allows painting even at 38°C.

Based on the above, while it was necessary to control the current paint within a narrow temperature range in order to ensure paintability and paint appearance, it was found that the developed paint could be applied over the same temperature range as solvent-based primer paint. Further, whereas solvent-based primer paint had to be controlled by adjusting with thinning solvent, the developed paint works without any adjustment. Additionally, a check of paintability and paint appearance of the developed paint on an actual line produced good results that were similar to those in a test booth.

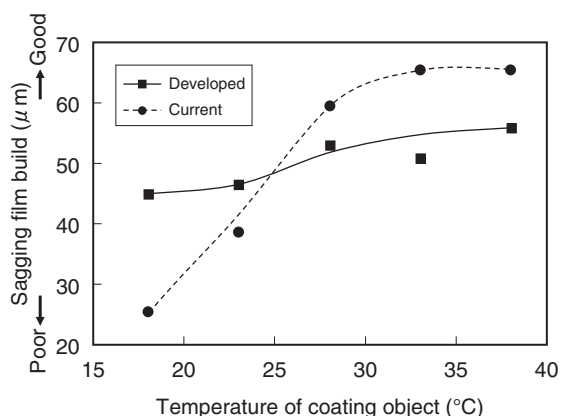


Fig. 11 Sagging film build versus temperature of coating object

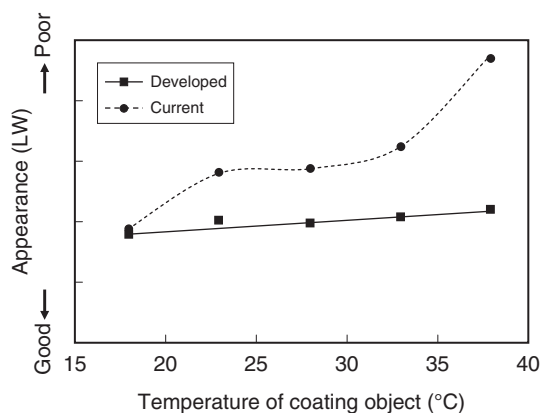


Fig. 12 Appearance versus temperature of coating object

7. Conclusion

New material was developed to ensure paintability and paint appearance of a waterborne primer paint over a wide temperature range by focusing on the ratio of hydrophilic component and hydrophobic component in polyester resin and melamine resin.

- (1) It was attempted to increase resin interaction and increase viscosity with low-application solid content and increase sagging resistance at low temperatures by increasing the ratio of hydrophilic component of polyester resin in the paint.
- (2) It was attempted to mitigate phase transformation and reduce viscosity with high-application solid content and increase paint appearance at high temperatures by increasing the ratio of hydrophilic component of melamine resin in the paint.

As a result, the temperature range of painting conditions could be expanded from the former $\pm 3^{\circ}\text{C}$ to $\pm 10^{\circ}\text{C}$. This made it possible to reduce energy consumption needed to keep the coating object at a constant temperature and reduce process control over temperature fluctuations. Additionally, since this technology can be widely applied to waterborne paints, not just waterborne primer paints, it is thought that expanding the application of the technology to basecoat, which increasingly uses waterborne paint, can further save energy in painting processes.

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