

Development of Lead Free E-coating with Low Cost Anti-rust Pigments

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ABSTRACT

A new electrocoating has been developed as part of the ongoing efforts to move towards the use of lead-free cationic electrocoatings as an auto body primer. The new e-coat dispels concerns, such as increased cost and inferior rust protection due to the absence of lead, and will be able to be easily introduced to automotive production lines. Several technologies were necessary for this development: new corrosion inhibitors essential for rust protection; improvement of the performance of the base resin of the paint film; methods to control the viscosity of the deposited film, in order to prevent deterioration of the workability and the appearance of the paint; and optimization of pigment mixture to control costs.

1. Aims and Agenda of this Research

The demand to reduce the amount of environmentally harmful substances utilized in automotive manufacture is intensifying. This includes the inorganic lead compounds employed in the cationic E-coatings, which are conventionally used as body coats⁽¹⁾. The aim of the research discussed in this paper was to create a lead-free E-coating, in order to further reduce the environmental impact for recycling of scrapped vehicles.

The lead component of existing coatings is added as an inorganic lead compound pigment. This pigment functions to prevent corrosion of the steel plate, and to act as a catalyst for the hardening reaction of the film during curing. If the amount of the lead component were simply reduced, both anti-corrosion performance and film hardness would decline.

Bismuth-based pigments are used in conventional lead-free E-coatings to replace the lead component, while ensuring that its functions are maintained. However, the higher price of this material increases the cost of the coat. This research project therefore adopted the following goals:

- (1) Environmental friendliness: Zero lead component.
- (2) Film performance: Identical anti-corrosion performance, physical performance, film smoothness, and durability to conventional coats.
- (3) Workability: Able to be introduced to existing coating lines.
- (4) Coating cost: Equivalent to or less than that of conventional coats.

2. Development of New Anti-corrosion Pigment

2.1. Functions of Conventional Anti-corrosion Pigments

The lead-based pigments utilized in existing cationic E-coats prevent corrosion by passivating the steel surface receiving the film, thus blocking the spread of rust, and by binding any corrosive agents entering the film (chloride ions, etc.) to prevent them from reaching the steel surface.

The mechanism of passivation by lead is as follows: the ionized lead component in the electro-coat solution is

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precipitated onto the substrate surface during electrolysis, forming a metal oxide film. This film shifts the surface potential of the substrate to the noble range, thereby functioning to maintain passivity⁽²⁾.

Bismuth-based pigments function in the same way as lead-based pigments, and are used as a replacement in conventional lead-free E-coatings. Measurements of corrosion currents on steel plates onto which lead and bismuth have been precipitated show that bismuth has a range of passive potentials virtually identical to that of lead⁽²⁾. Figure 1 shows the results of an evaluation of the anti-corrosion performance of films employing bismuth-based pigments in compound corrosion tests (CCT), and demonstrates that at least 1.5 wt% of bismuth must be added to achieve the same performance as a conventional coat. This is approximately the same as the amount of lead-based pigments added to E-coatings, but the higher cost of bismuth makes it economically unfeasible. The research project described here therefore developed a new and more economical pigment to replace bismuth-based pigments, and studied methods of reducing the amount of high-priced components utilized.

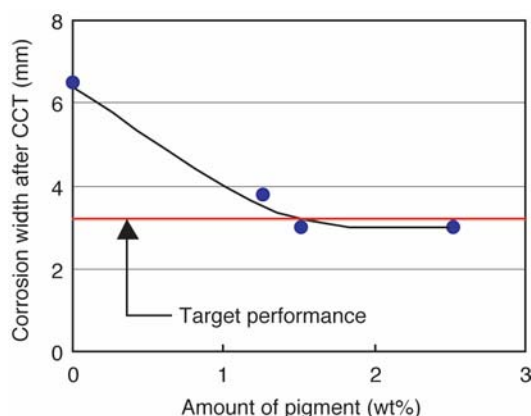


Fig. 1 Effect of concentration of bismuth pigment on anti-corrosion performance

2.2. Development of a New Anti-corrosion Pigment

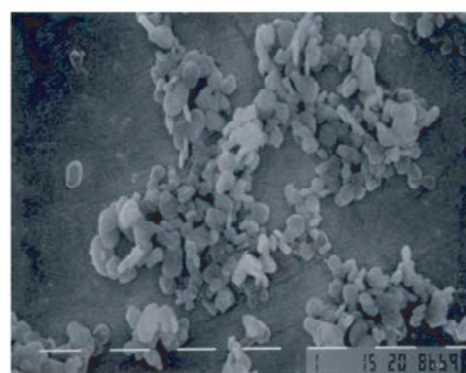
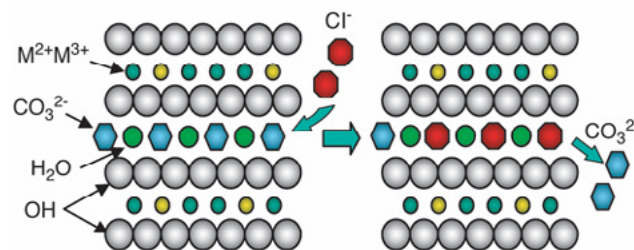
Layered double hydroxides with layered crystal structures, such as graphite, display the ability to selectively absorb ions into their structure, a phenomenon known as intercalation. Research focused on a method of inhibiting rust by utilizing this function to prevent corrosion-promoting ions from reaching the substrate surface.

Having determined the viability of a substance capable of intercalating anions such as chloride ions as a corrosion inhibitor, considerations of chemical stability in the coating, ability to bind chloride ions, and suitability for electro-deposition led to the selection of a hydrotalcite-based pigment termed new pigment A. A model of a crystal structure displaying intercalation and an electron micrograph of new pigment A are shown in Fig. 2. The general formula for hydrotalcite is $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}_{x/n} \cdot mH_2O]^{x-}$. Hydrotalcite is composed of positively charged layers of divalent (M^{2+}) and trivalent (M^{3+}) metals. Between the layers there are anions (A^{n-}), which cancel the charge. These interlayer ions can be exchanged with other ions. New pigment A intercalates chloride ions by exchanging with the carbonic acid ions making up its interlayer anions.

Figure 3 shows the results of a comparison between the chloride ion absorbency of new pigment A and a

conventional lead-based pigment. The new pigment was shown to possess a higher level of chloride absorbency than the conventional pigment.

Substances with a similar derivation to new pigment A are used as stabilizers in PVC resins and anti-oxidants in pharmaceuticals, and have not displayed any environmentally harmful effects.



SEM image $\times 7500$

Fig. 2 Intercalation function (above) and SEM image of rust-inhibiting pigment 'A'

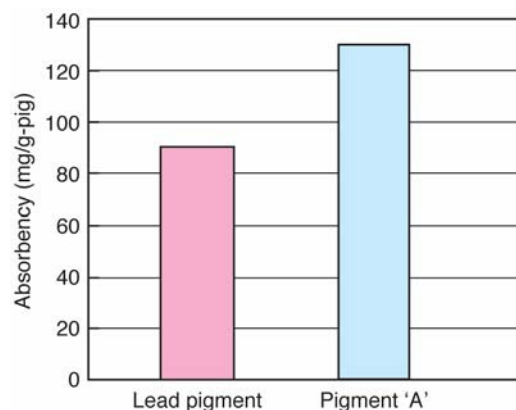


Fig. 3 Chloride absorbency of anti-corrosion pigments

The pH buffering performance of the new pigment in the acid domain (low pH domain) was studied in order to determine its effectiveness as a corrosion inhibitor. To study the pH buffering performance of various pigments, 2.0 wt% of each was added to 0.01 N solutions of hydrochloric acid, agitated, and left at 20 °C for 48 hours, after which the pH was measured. The results of these tests are shown in Fig. 4. New pigment A bound 3.3×10^{-3} mol/g of chloride ions, a figure close to the 4.0×10^{-3} mol/g predicted from studies of intercalation.

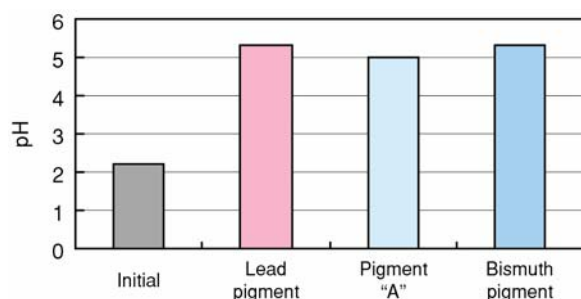


Fig. 4 pH buffering capacity of pigments

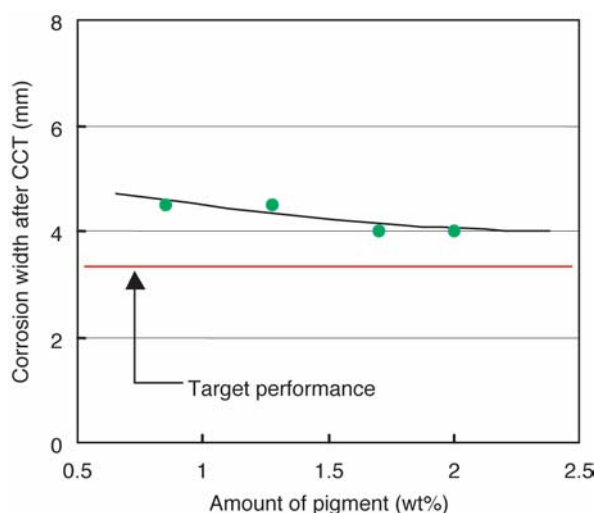


Fig. 5 Anti-corrosion performance of pigment 'A'

Prototype E-coats were formulated using new pigment A, and its corrosion inhibition performance was evaluated in compound corrosion tests. Cold-rolled steel (CRS) plates were utilized as the test substrates, and were E-coated after galvanization with zinc phosphate. A knife cut was made in the coat, and the width of the area of corrosion after CCT was measured. Figure 5 shows the results of these tests. The corrosion inhibition performance of new pigment A was inferior to that of conventional films employing lead-based pigments, and it was judged that increasing the amount of the pigment added to the coat would not enable it to reach target performance. A bismuth-based pigment was therefore mixed with new pigment A to supplement its corrosion inhibition

performance. Study focused on optimizing the ratio of the pigments to achieve a balance of performance and cost.

The results of these studies led to the development of a mixture of 1.28 wt% new pigment A as the main ingredient and 0.43 wt% bismuth as a secondary ingredient. This ratio of pigments equaled the corrosion inhibition performance of lead-based pigments. New pigment A, in combination with improvements made to the base resin to be discussed below, enabled film performance to be maintained despite the reduction of the bismuth content to 0.29%, 80% less than used in conventional films employing bismuth-based pigments. Figure 6 shows the results of a test in which coated cold-rolled steel sheets were immersed in 5% salt water at 55 °C for 240 hours.

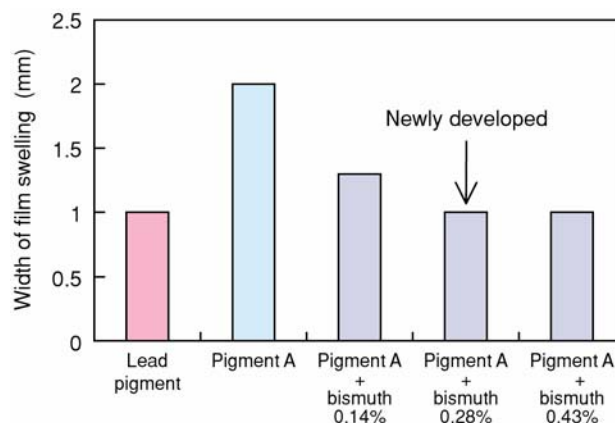


Fig. 6 Effect of ratio of pigment 'A' and bismuth pigment as demonstrated by hot salt water immersion test

3. Improvement of the Base Resin

Existing cationic E-coat films employ a bisphenol A-type epoxy resin as the base resin. The ends of the molecules of this resin are amino-denatured to render them water-soluble, and side chains with a flexible molecular structure are attached as a plasticizing component.

A cross-linking agent with an isocyanate reaction base is included as a component in the coating to enable the resin molecules to form cross-links in the baking process after electro-deposition of the film in the tank, ensuring that it becomes sufficiently hard (Fig. 7).

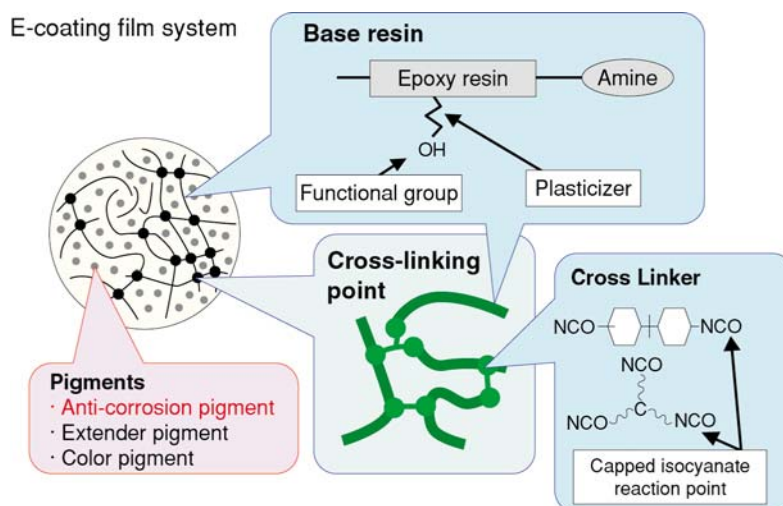


Fig. 7 E-coating film system consisting of pigments, epoxy-based resin and cross-linking resin

The research discussed here studied potential improvements to the resin from the dual perspectives of achieving improved blocking performance and reducing costs. However, no major changes were made to the epoxy resin backbone, with research focusing instead on adding multi-functional groups and adjusting the proportion of plasticizer to improve base resin performance. This would supplement the functioning of the corrosion-inhibiting pigment and the hardening catalyst, and enable lead-based pigments to be eliminated.

Various methods were predicted to enable improvement of the blocking performance of the film: Reducing the amount of isocyanate used in cross-linking, increasing the molecular weight of the base resin to increase the glass transition temperature (T_g), increasing the ratio of functional groups, and reducing the plasticizer content.

To increase the ratio of functional groups, the conventionally used single-function base resin was replaced with a resin with more than three functional groups. This increased the cross-linking reactivity of the resin, compensating for the loss of the lead component as a hardening catalyst. Figure 8 shows a conceptual diagram of the multi-function base resin.

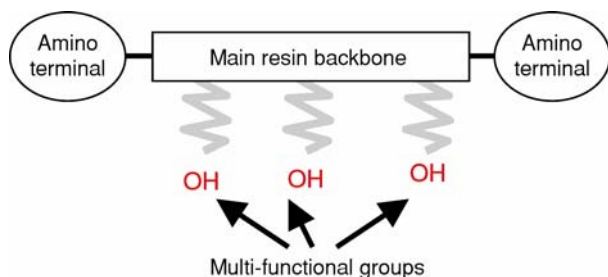


Fig. 8 Base resin with multi-functional groups

Tests were conducted to determine the effect of changes in plasticizer content on the performance of the coating. Ratios of 3-9% of plasticizers with flexible molecular side chains of varying lengths were added to the base resin and blocking performance and corrosion inhibition performance was studied.

Figure 9 shows the effect of the amount of plasticizer in the film on oxygen infiltration, as one measure of film performance. 9% plasticizer is added to the resins employed in conventional films; the reduction of this amount to 3% in the new film has enabled a 15% improvement in blocking performance.

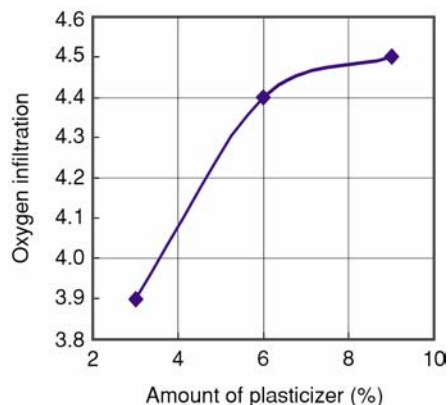


Fig. 9 Effect of plasticizer on barrier performance

Comparisons of the width of swelling in the film from a knife cut after immersion in 55 °C 5% hot salt water for 240 hours confirm that the reduction of the amount of plasticizer has increased the adhesiveness of the film (Fig. 10).

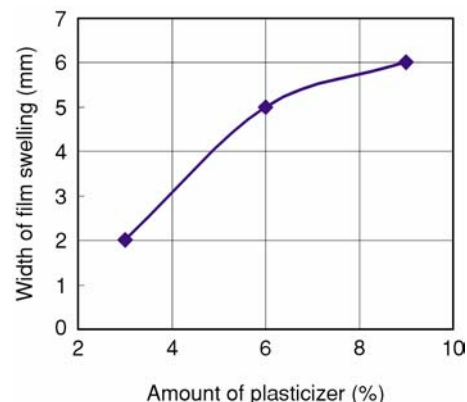


Fig. 10 Effect of plasticizer on adhesion performance in HSW test

4. Increasing Applicability of the Coat

Blemishes occurred in the finished coat when the new E-coat with a resin plasticizer content of 3% was used to coat an alloyed welded galvanized steel plate.

These blemishes are termed cratering, and show as pinhole imperfections in the film after baking and curing. Electrolysis during the coating process causes hydrogen gas bubbles to form on the surface of the substrate, and these gas bubbles enter the film. The application of high voltages causes electric discharges inside these bubbles, which in turn cause gelling of the surrounding resin. This gelling prevents the flow of heat across the surface when the film undergoes baking and curing, resulting in pinhole imperfections in the film. Figure 11 shows a schematic representation of the mechanism of cratering.

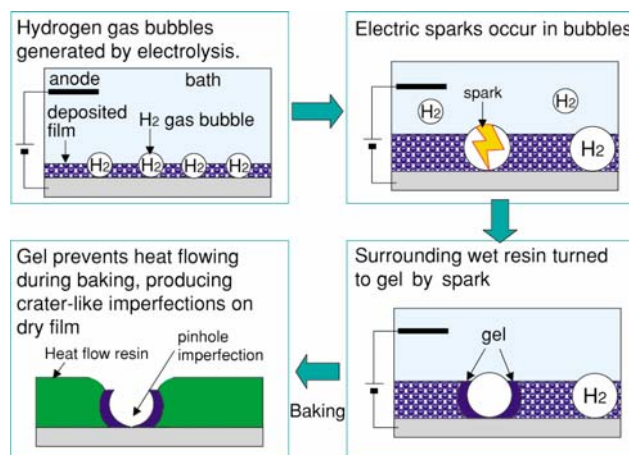


Fig. 11 Theory of occurrence of craters on GA substrate

The increased occurrence of cratering was believed to be due to the reduced plasticity of the base resin, which increased the viscosity of the precipitated resin, thus, reducing the ability of hydrogen gas to escape from the surface of the substrate. The plasticizer content of the base resin was therefore altered to adjust the viscosity of the precipitated resin in an attempt to promote the escape of hydrogen gas.

Increasing the plasticizer content to 4% enabled the achievement of a level of cratering performance equivalent to that displayed by conventional E-coats (Table 1). Anti-corrosion performance was also verified as being identical.

Table 1 Effect of plasticizer on GA cratering performance

	Conventional material	Newly developed material with 3% plasticizer	Newly developed material with 4% plasticizer
Critical voltage for occurrence of GA cratering	260 V	230 V	260 V

5. Film Performance

The newly developed E-coat was subjected to comprehensive film performance evaluations, including tests of physical characteristics focusing on smoothness, resistance to gravel chipping, resistance to impact, flexibility, and adhesiveness, and of chemical characteristics, such as chemical resistance, gasoline resistance, and suitability for use with a PCV plasticizer. The results of these tests demonstrated the performance of the newly developed coating to be equivalent to that of conventional coatings in all these areas.

To determine the suitability of the new coating to existing coating lines and facilities, additional tests included throwing power, applicability to the UF filters used in electro-coating facilities, resistance to contamination, ability to repel oil, suitability for the temperatures used over the specified period for oven baking, the amount of flux produced during baking, and reaction to buffing. Performance in these areas equaled that of conventional coatings, confirming that the new coating could be introduced to existing coating lines.

6. Cost

As a result of the employment of a low-cost anti-corrosion pigment and reduction in the cost of color pigments and other additives, the cost of the E-coating developed in this project is equivalent to or less than the cost of conventional E-coatings using lead-based additives.

7. Summary

Research to develop a lead-free E-coat employing a low-cost corrosion-inhibiting pigment produced the following results:

(1) Utilization of 1.28 wt% of a new corrosion-inhibiting

pigment and 0.28 wt% of a bismuth-based pigment to replace lead-based pigments, in combination with improvement of the base resin, has enabled the achievement of anti-corrosion performance equaling that of lead-based pigments.

- (2) Making the base resin multi-functional (more than three functional groups) has improved the blocking ability of the film. At the same time, utilizing a plasticizer content of 4% in the resin has improved GA cratering performance, enabling the achievement of a coating equivalent in quality to that of conventional films.
- (3) The newly developed film has equivalent durability to conventional films, and can be introduced to existing coating lines.
- (4) The cost of the new coating is equivalent to or less than that of conventional coatings.

8. Afterword

The current era is distinguished by a concern for the environment. The reduction in environmental pollutants, achieved in this research helps address this concern. At the same time, the new E-coat offers Honda's worldwide customers excellent rust-inhibition performance and superior vehicle exteriors, and is presently being introduced to the company's coating lines.

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