# Lubricant Coating Film for Zinc-plated Steel Sheets

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## Abstract

For the improvement on the formability of zinc coated steel sheets for automotive use, very thin manganese-phosphorus type lubricant film has been studied and developed. In order to confirm the influences of the film on the car manufacturing process, the lubricant film was precisely studied. The results of the study show that the film improves the formability and gives no advers influence on the automotive manufacturing process and has good anti-corrosion properties after painting.

### 1. Introduction

Zinc-plated steel sheets are used as corrosion-resistant steel sheets for the automotive industry. However, since the plating layer of zinc is soft, and thus it often sticks to forming dies during press forming work, it sometimes leads to poor quality of formed products, which does not occur with cold-rolled steel sheets. Various lubrication treatment methods have been studied recently for improving the pressformability of the zinc-plated steel sheets.<sup>1-7)</sup>.

A corrosion-resistant steel sheet for automobiles is subjected to a long period of use as a final product after passing through the following fabrication processes: press forming, assembly by welding, degreasing, chemical treatment, electro-deposition painting, intermediate coating, and finish coating. Therefore, besides having good lubrication at press forming, it is essential for a lubricating film for the galvanized steel sheets not to adversely affect the processes after the press forming and the durability of the car body components that the steel sheets are made into. The authors looked for a lubricating coating film satisfying the above requirement, and developed an inorganic coating film of a Mn-P system<sup>8</sup>.

This paper describes, based on authors' examinations, the structure and lubricating properties of the developed Mn-P inorganic coating film and its effects on the fabrication processes after press forming.

#### 2. Test Methods

#### 2.1 Specimens

Two kinds of specimens were prepared by coating the surfaces of electro-galvanized steel sheets (Zn coating weight per side 60 g/m<sup>2</sup>, hereinafter referred to as the EG sheets) and galvannealed steel sheets (Zn coating weight per side 45 g/m<sup>2</sup>, hereinafter referred to as the GA sheets) with the Mn-P coating films so that the deposition amount of each of Mn and P was within a range from 0 to 50 mg/m<sup>2</sup>. **2.2 Analysis of Coating Film** 

The lubricating coating film was analyzed by X-ray diffraction, SEM observation, EPMA, XPS, and GDS.

#### 2.3 Lubricating Properties

The lubricating properties of the film were evaluated by measuring a coefficient of sliding resistance through an L-shape draw-bead test<sup>9)</sup> using the above specimen steel sheets after coating them, additionally, with 1 g/m<sup>2</sup> of rust-preventive oil.

#### 2.4 Spot-weldability

Continuous-spot-weldability was tested using Cu-Cr electrodes (type DR) having a tip diameter of 6 mm under the conditions of an electrode force of 1,960 N, a welding time of 12 cycles at 60 Hz, and a retention time of 40 cycles at 60 Hz. The lower limit of the nugget diameter was set at  $4\sqrt{t}$  (t: sheet thickness).

#### 2.5 Chemical Treatment Properties

The specimen steel sheets were subjected to an immersion type phosphate treatment for 2 min, and then the crystal structure of the phosphate coating film was observed with an SEM and its deposi-

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#### tion amount was measured.

### 2.6 Corrosion Resistance after Paint Coating

Test pieces for the water-resistance adhesion test and salt spray test were prepared by applying to the specimen steel sheets an epoxy paint 20  $\mu$ m in thickness by cationic electro-deposition and then an intermediate and a finish coating for automobiles, each 35  $\mu$ m in thickness. In the water-resistance adhesion test, the test pieces were immersed in distilled water at 40°C for 240 h, then the paint coating was cross cut into 2 mm × 2 mm grids, and the area percentage of the coating remaining after peeling with an adhesive tape was measured. In the salt spray test, the paint coating was cross cut in X, each stroke being 70 mm in length, then the test pieces were subjected to salt water spray for 600 h, and the maximum blister width on one side of a cross-cut line was measured.

### 3. Test Results

## 3.1 Analysis of Coating Film

**Photo 1** shows the SEM photomicrographs of the EG sheets before and after the application of the lubricating film; in the image after the application of the lubricating film, the film was not detected by the SEM and the crystal structure of the Zn plating layer was little affected by the film.

**Fig. 1** shows the GDS analysis result of the lubricating film applied to the EG sheet specimens. The deposition amount of each of Mn and P was 8 mg/m<sup>2</sup>. They were detected in the upper part of the Zn plating layer, and it was presumed that the concentration of P was higher in the outermost portion and that of Mn in the portion on the Zn plating side. It is seen from this result that the thickness of the lubricating film is 7 nm or so.

## **3.2 Lubricating Properties**

**Fig. 2** shows, regarding the EG and GA sheets, the influence of the deposition amount of the lubricating film over the coefficient of



Photo 1 SEM images of EG sheets



Fig. 1 GDS analysis result of lubricating coating film



Fig. 2 Influence of deposition amount of P on sliding resistance coefficient



Fig. 3 Surface conditions and analysis results of lubricating film before and after draw-bead test

sliding resistance. It is seen in the figure that the coefficient falls (lubrication is improved) rapidly as the deposition amount of P increases, and then it remains low stably, thereafter.

**Fig. 3** shows the conditions of the lubricating film applied to the specimen EG sheets (deposition amount of each of Mn and P: 8  $mg/m^2$ ) as observed with an SEM and analyzed by EPMA before and after the L-shape draw-bead test. It is understood from the figure that the continuity of the coating film is maintained after the drawbead test and that, while the decrease in the amount of Mn at the drawing was small, that of P was significant. Based on the above observation, it is presumed as follows: the layer rich in Mn on the Zn plating side prevents the Zn plating layer from sticking to the die during press forming work; on the other hand, a part of the outermost layer rich in P forms a solid-liquid lubricating layer together with the rust-preventive oil; and as a result, a good lubricating effect is realized in spite of the small film thickness of approximately 7 nm.

In consideration of the above result, the deposition amount of each of Mn and P of the lubricating film was set as follows for the tests described below:  $8 \text{ mg/m}^2$  for the EG sheets, and  $30 \text{ mg/m}^2$  for the GA sheets.

#### 3.3 Spot-weldability

**Fig. 4** shows the measurement results of the continuous-spotweldability of the EG and GA sheets. The number of consecutive spot welds was substantially the same with and without the application of the lubricating coating film, thus the film is considered not to affect the weldability of a steel sheet.

#### **3.4 Chemical Treatment Properties**

**Photo 2** shows the SEM photomicrographs of the surfaces of the EG and GA sheets with the phosphate treatment taken before and after the application of the lubricating film. The crystal structure of

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Fig. 4 Spot weldability (number of consecutive spot welds)



Photo 2 SEM images of chemical treatment films



Fig. 5 Water-resistance adhesion of paint coating

the phosphate coating film and its deposition amount were not affected by the application of the lubricating film, thus the film is considered not to affect the chemical treatment properties of a steel sheet. **3.5 Corrosion Resistance after Paint Coating** 

a) Water-resistance adhesion

**Fig. 5** shows the evaluation results of the water-resistance adhesion. No significant change of paint exfoliation was observed in either the EG or the GA sheets with and without the application of the lubricating film.

## b) Salt spray

**Fig. 6** shows the pain blister width from a cross cut line after 600 h of slat spray test. No significant change of paint blister width was



observed in either the EG or the GA sheets with and without the application of the lubricating film.

As a conclusion from the above two tests, the lubricating film is considered not to affect the corrosion resistance after paint coating.

#### 4. Summary

The authors studied the structure and lubricating properties of the coating film of a Mn-P system, which had been developed as a lubricating coating film for galvanized steel sheet products for automotive use, and its influences over the fabrication processes of the steel sheets after press forming work. The following findings were obtained as a result:

- (1) The lubricating coating film covers the whole Zn plating layer continuously in a thickness of some tens of nanometers, and is considered to have a multi-layered structure, wherein the concentration of P is higher in the outermost sub-layer and that of Mn in the sub-layer on the Zn plating side.
- (2) With regard to the effect of the coating film to enhance lubrication, the following are presumed. Whereas the sub-layer rich in Mn on the Zn plating side prevents the Zn plating layer from sticking to the die during press forming work, a part of the outermost sub-layer rich in P forms a solid-liquid lubricating layer together with the rust-preventive oil; and as a consequence, a good lubricating effect is brought about in spite of the small film thickness.
- (3) The lubricating coating film does not have any adverse effects on the weldability, chemical treatment properties, and corrosion resistance after paint coating of the steel sheets at the fabrication processes of an automobile body.

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