

New Liquid Surface Conditioner for Low-Temperature Phosphating System Aimed at CO₂ Emission Reduction

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ABSTRACT

A new liquid surface conditioner has been developed to improve phosphate coating quality and enable a low-temperature phosphating system designed to reduce CO₂ emissions during the pretreatment processes of automobile production. Phosphate film is formed by a phosphating treatment that provides corrosion resistance for the steel plates that make up auto bodies. In the vehicle body, pocket-shaped structures such as side sills and wheel arches are likely to collect muddy water and from rust. Regarding anticorrosion quality assurance, particular attention must be paid to these pocket structures, in which phosphating solution flows slowly, and a lower solution-volume-to-surface-area ratio contributes less to the phosphating reaction. For this reason, with the conventional liquid surface conditioner, a low-temperature phosphating system can not coat substrate surfaces sufficiently, which would result in lower corrosion resistance. The new liquid surface conditioner developed in this research improves the phosphate coating quality of substrate surfaces using smaller seed particles, each of which has greater electrostatic charge to improve the stability of the dispersed particles. A combination of the new surface conditioner and a low-temperature phosphating agent has resulted in a low-temperature phosphating system that forms sufficient phosphate coatings even in pocket sections and ensures excellent anticorrosion performance. This system can lower the temperature of phosphating treatment without compromising anticorrosion performance and, in the process, makes it possible to meet CO₂ reduction targets.

1. INTRODUCTION

Much evidence of global environmental destruction and abnormal weather has been reported since the beginning of the 21st century. Under such circumstances, many industries, including automotive, have been focusing on the issue of reducing environmental impact. A particularly pressing issue is the reduction of CO₂ emissions. Efforts are being made towards this, for instance, in the framework of the Kyoto Protocol to prevent global warming. The automotive industry is required to reduce CO₂ emissions in two respects: CO₂ exhaust while driving and CO₂ discharged during the vehicle manufacturing processes. Setting its own targets to reduce CO₂ emissions, Honda has been developing energy saving technologies for production processes as well as technologies to improve vehicle fuel economy. In the body pretreatment process, energy saving can be achieved, for example, by shorter processes or lower treatment temperatures. Lowering the treatment temperature decreases the energy necessary for heating up chemical solutions, reducing CO₂ discharges in the process. There are two pretreatment processes that require heating: one is the degreasing process for removing oil and stains from base materials, and the other is the phosphating process for forming phosphate film on substrate surfaces. Some technologies are known to lower the treatment temperature by optimizing phosphating compositions or treatment conditions. At present, however, there has been little discussion on the relation between the issue of vehicle corrosion prevention and technology to lower temperatures. This paper presents a method of providing low-temperature zinc phosphating treatment designed to ensure corrosion resistance of auto-bodies. It also reports the results of studies on the effectiveness of this method in reducing CO₂ emissions.

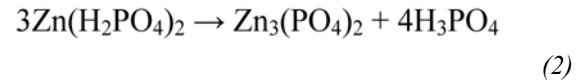
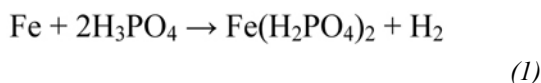
2. CURRENT ANTICORROSION MEASURES AND THE CHALLENGE OF REALIZING LOW-TEMPERATURE PHOSPHATING

2.1. CURRENT ANTICORROSION MEASURES

Regarding the rustproof quality of the body structure, particular attention must be paid to pocket sections, such as side sills and wheel arches, where corrosion is likely to occur. When vehicles drive on roads sprinkled with snow melting agents and muddy splashes containing salt, the pocket sections become entrapped with salt solutions causing a harsh corrosive environment. To solve this problem, measures were taken to improve corrosion resistance by applying an electrodeposition coating (e-coating) with uniform film thickness. The foundation of this e-coating is provided by a phosphate coating. Phosphate coatings play an important role in increasing adhesion between the e-coat and the substrate to provide excellent anticorrosion performance. To achieve this performance, phosphate film must completely cover the substrate surface leaving no spots without phosphate crystal deposition. Accordingly, in the studies of low-temperature phosphating treatment, consideration must be given to the e-coating quality and phosphate coatings inside the pocket structures exposed to a severe corrosive environment.

2.2. CURRENT ANTICORROSION MEASURES

The state of phosphating solution (stirred or unstirred) and its solution-volume-to-surface-area ratio differ greatly between outer panels and pocket sections. Because these factors affect phosphating reactions, differences also occur in the phosphate film formed by the chemical reaction between the substrate surface and the solution. In this paper, the solution-volume-to-surface-area ratio refers to the ratio between the weight of the chemical solution and the area of the surface under the phosphating treatment. Chemical reactions between iron substrates and zinc phosphate are given by [equations \(1\) and \(2\)](#). Increased amounts of H_3PO_4 , in [equation \(1\)](#), and $\text{Zn}(\text{H}_2\text{PO}_4)_2$, in [equation \(2\)](#), are supplied from the solution to the reaction interface as a higher flow rate is produced by stirring, which leads to a greater volume of solution supply to the surface area. In this condition, zinc phosphate crystals $\text{Zn}(\text{H}_2\text{PO}_4)_2$ precipitate in greater amounts, as indicated by [equations \(1\) and \(2\)](#) which express equilibrium reactions.



Phosphating of outer panels occurs at a higher flow rate and a higher solution-volume-to-surface-area ratio, that is, conditions favorable to the precipitation of phosphate crystals. On the other hand, crystal precipitation is more difficult in pocket structures where the solution flows at a lower rate and has a lower solution-volume-to-surface-area ratio.

[Fig. 1](#) shows the relation of phosphating treatment time versus coating weight in both stirred and non-stirred states. The data was obtained by phosphating a mild steel sheet at a temperature of 35 °C and a flow rate equivalent to that on outer body panels. [Fig. 2](#) shows the SEM (scanning electron microscope) images of phosphate film formed after 120-second treatment under the same conditions. As shown in [Fig. 1](#) and [Fig. 2](#), the coating weight increased slowly in the non-stirred condition. Because the phosphating reaction was slow and did not complete after the 120-second treatment, the steel sheet surface was not fully coated with phosphate crystal deposits, leaving some bare spots. On the other hand, when the solution was stirred and flowed at a rate equivalent to that on outer panels, the surface was sufficiently coated with phosphate film after 120 seconds. Based on this result, phosphating conducted at a low flow rate is thought to have caused poor coating of the substrate surface. In pocket structures, coating quality is feared to deteriorate further because the solution-volume-to-surface-area ratio is lower. Thus, to lower the temperature of phosphating treatment, we had to take on the challenge of improving phosphate coating quality in phosphating conducted with a non-stirred solution and at a lower solution-volume-to-surface-area ratio, that is, conditions equivalent to those in auto-body pocket structures.

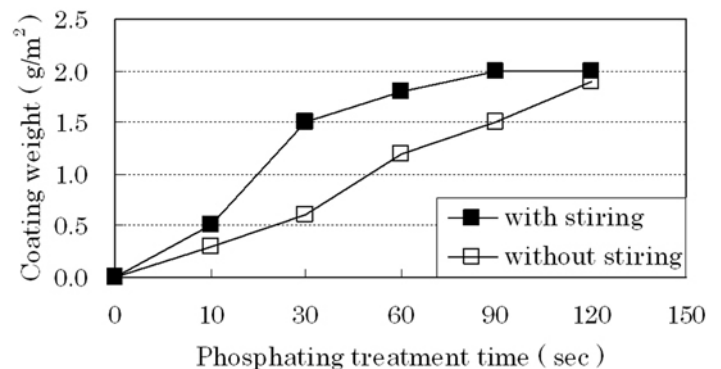


Fig. 1. Phosphating treatment time vs. coating weight in stirred and non-stirred states

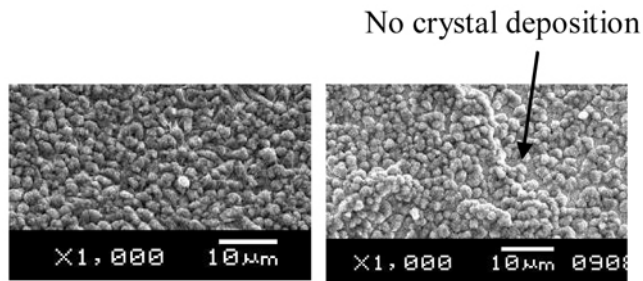


Fig. 2. SEM images of phosphate coatings after 120-second treatment

To promote crystal precipitation during the phosphating reaction and improve coating quality, there is a method that decreases the phosphate concentration in the solution in order to lower acidity to a pH value at which the reaction in [equation \(2\)](#) occurs. This makes it possible to promote the precipitation of phosphate crystals by providing little pH fluctuation. The crystal precipitation is enhanced also by increasing the zinc concentration in the solution to a saturation level. This method, however, has disadvantages in a narrower acidity control range that results in a less stable solution, as well as a higher cost due to an increase in the zinc concentration. Thus, excessive adjustments of neither acidity nor zinc concentration are desirable.

Accordingly, in this research, we used an existing phosphate solution without changing its specifications too much, considering the fact that its composition and treatment conditions have already been optimized. Instead, to improve the coating quality of the phosphate film, we developed a new liquid surface conditioner material (hereafter referred to simply as a new surface conditioner) that is used in the preconditioning process of phosphating treatment and has a substantial influence on the phosphating reaction.

3. METHOD FOR REALIZING A LOW-TEMPERATURE PHOSPHATING TREATMENT SYSTEM

3.1. DEVELOPMENT CONCEPT BEHIND NEW SURFACE CONDITIONER

A surface conditioner is used in the body pretreatment process to seed the substrate surface with particles to trigger a phosphating reaction. While phosphating is a chemical reaction, surface conditioning is an adsorption reaction, which is unaffected by the flow rate of a phosphating solution. Regarding a zinc-phosphate-type liquid surface conditioner currently in use, improvements made to various functions were reported some time ago ⁽¹⁾. In this study, a

new surface conditioner was developed to improve the coating quality of phosphate film. The developed conditioner contains zinc phosphate as the main ingredient. [Fig. 3](#) shows a model of the targeted phosphate coating. This figure illustrates the coating states of the conventional and new conditioners to show the difference on the substrate surface phosphated with a non-stirred solution

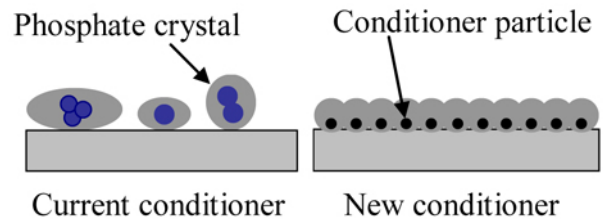


Fig. 3. Pocket-area phosphate models-new and current conditioners

The conventional conditioner model shows that seed particles for starting a phosphating reaction are sparsely distributed. As shown in Section 2 of [Fig. 2](#), the coating formed with this conditioner had poor quality in the non-stirred state in which the phosphating reaction was slow. Accordingly, the target of the new surface conditioner was to increase the number and distribution density of seed particles so that more fine phosphate crystals would deposit on the substrate surface for a better coating.

3.2. DEVELOPMENT CONCEPT BEHIND NEW SURFACE CONDITIONER

To increase the number and distribution density of seed particles on the substrate surface, it is necessary to increase the concentration of the surface conditioner and make its particles smaller. [Fig. 4](#) shows the solution concentration versus the coating weight of the phosphate film formed at a temperature of 43 °C, using the conventional surface conditioner. [Fig. 5](#) depicts SEM micrographs of phosphate films formed at each concentration.

[Fig. 4](#) shows that the coating weight decreases with an increase in the concentration of the surface conditioner solution. [Fig. 5](#) shows that phosphate crystals become finer as the concentration becomes greater. However, when the concentration is 3.0 g/L or above, the increase in coating weight levels off. Also the reduction in phosphate crystal size becomes less obvious. Therefore to get finer phosphate crystals, it is necessary to miniaturize seed particles and make the distribution denser.