

Updated Pretreatment Technologies for Automotive in Japan

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Recently, to avoid global warming, reduction of CO₂ generation has been demanded. Each car manufacture takes positive actions for improvement in fuel consumption by various kinds of countermeasures, e.g. improving engine efficiency, using alternative fuels, lightening the car body. Regarding lightening of the car body, aluminum alloys and high tensile strength steels has been gradually adopted as lightweight materials. However, such materials are normally not easy to be treated with zinc phosphate system. Focusing the pre-treatment processes, low temperature phosphate system could be demanded for energy saving. This time, new surface conditioning process for lightweight materials and low temperature phosphate system shall be discussed.

Keywords: surface conditioner, zinc phosphate

1. Introduction

Zinc phosphate coating plays an important role in protecting car bodies from corrosion. We have been repeatedly making improvements to the zinc phosphate treatment process in order to satisfy the increasingly sophisticated requirements of car bodies. At present, Ni and Mn are contained to the zinc phosphate coating and the substrate surface is covered evenly with fine crystals to provide a highly satisfactory coating performance. Furthermore, the zinc phosphate treatment method has also been improved, with the most common type of treatment being a dip treatment at the low temperature of 43 °C. Lower temperature phosphate treatment at 35 °C has already been commercialized in many lines in Japan. A surface conditioning treatment is indispensable prior to conducting a low temperature dip type zinc phosphate treatment. Ti colloid aqueous solution is being used as a surface conditioner prior to the zinc phosphating process. The Ti colloid is highly effective as a surface conditioner, however, the stability of the colloid is low, and therefore it is necessary to drain and replenish the bath little by little during processing. We have succeeded in developing a completely new type of surface conditioner. The new surface conditioner possesses excellent stability as well as a phosphatability which far surpasses the former chemicals. Here we report on test data which compares the functions of the newly developed liquid surface conditioner (PREPALENE

X : PL-X) with the conventional surface conditioner (PREPALENE Z : PL-Z).

2. Development of Zinc Phosphating Technology

2.1 Development History of Phosphating Treatment

Since the commercialization of zinc phosphate treatment, the focus of improvements has been on lowering the treatment temperature and reducing the treatment time.^{1),2),3)} For example, although it was not a zinc phosphate treatment, the early iron phosphate type surface treatments required a treatment time of two hours and the treatment temperature was close to boiling point. Later

Table 1. Development history of phosphating treatment

Year	Items	Process time	Process temp.
1906	Iron phosphate	2-2.5h	Boiling temp.
1909	Zinc phosphating	1h	
1929	Cu modified zincphosphate	10min	
1931	Oxidizing agent added	5min	65-93 °C
1934	spray process	60-90s	
1943	Jernstadt salt in use		65-70 °C
1979	Immersion type for CED	120s	50 °C
1985	Lower temp. type	120s	35 °C
1993	Lower temp. & sludge type	120s	35 °C

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on, a phosphate treatment with zinc added was developed and improvements to this technology began in earnest around the 1930s. Table 1 shows examples of improvements.

2.2 Lower Treatment Temperatures

The reaction rate of the zinc phosphate treatment is determined by the temperature, concentration and solution flow of the treatment bath and the higher each of these conditions, the faster the reaction. For Japanese industry, which has experienced two oil shocks, the lowering of the treatment temperature has been an important goal and currently the degreasing process can be done at 40 °C and the zinc phosphate treatment at 35 °C. The solution flow is determined by the equipment capacity and increasing the solution flow would often involve equipment improvements that may be costly, so this is a difficulty. We have been able to maintain the reaction rate, which is lowered by the lowering of the temperature, by optimizing the composition of the zinc phosphate bath.⁴⁾ As shown in Fig. 1, we maintain the phosphatability by increasing the zinc concentration and lower the free acidity.

2.3 Less Sludge Technology

Furthermore, it simultaneously became possible to lower the volume of sludge generated in the zinc phosphate coating formation. As the volume of sludge generated in the zinc phosphate treatment depends on the substrate etching volume, it became possible to reduce the sludge volume by reducing the etching volume through lowering the free acid. It depends on the substrate type however we have been able to reduce sludge by 10~30%.

Most of sludge is being buried at landfill still now, however cost of landfill for this type of sludge becomes higher and number of landfill space is getting limited. Therefore, several recycling methods for sludge have been studied

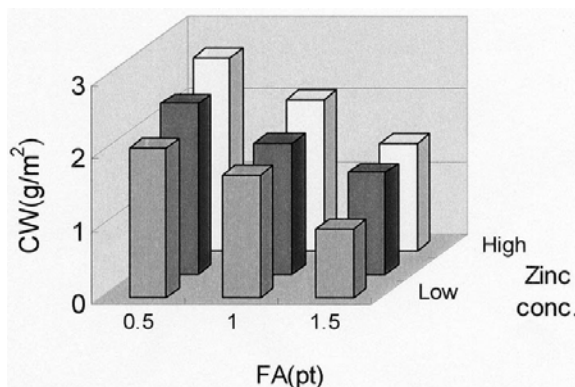


Fig. 1. Effect of zinc concentration and free acidity on coating weight on CRS at 35°C

and have become practical.^{5),6)}

Currently in Japan, the number of auto body lines with phosphate treatment operating at 35 °C is increasing and we expect that the low temperature/less sludge type zinc phosphate treatment will become the standard.

3. New Surface Conditioning Chemical (pl-x)

The characteristics of this new surface conditioner were presented at the SAE2001 World Congress.⁷⁾ The new surface conditioner possesses excellent stability as well as a phosphatability, which far surpasses the former chemicals. A significant characteristic of the improvements was the elimination of variations in the effectiveness of the surface conditioner due to variations at the time of production including water quality, stability over time, drag-in of degreasing chemicals, pH variations.

3.1 Image of the Growth of Zinc Phosphate Crystals

PL-X increases the dispersion stability of fine phosphate salt particles which are the surface conditioning component and remains unaffected by a number of factors which may occur on an actual line. By causing the adsorption of fine particles on the surface of the substrate, PL-X causes the formation of a large number of micro-cells and crystal nuclei and furthermore shortens the zinc phosphate treatment time by epitaxial matching.

Fig. 2 shows an image of the growth of zinc phosphate crystals comparing development surface conditioner with conventional.

3.2 Stability of surface conditioner particle

After a 10 days shutdown of a customer's line over summer, the customer was able to continue using the chemical without discarding and renewing, and achieved an equally good coating quality.

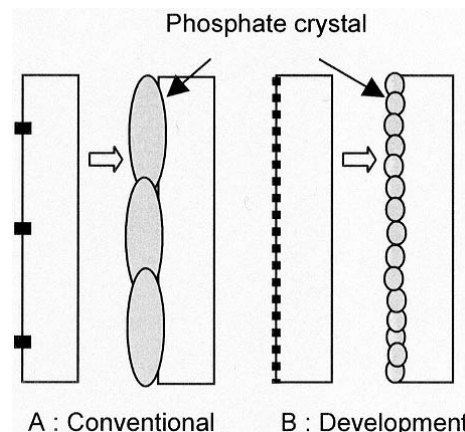


Fig. 2. Image of growing process of phosphate coating formation

Fig. 3 shows the appearance of crystals in the zinc phosphate coating after adjusting the concentration of Mg ions in the surface conditioner bath to various levels. In case of PL-Z, effectiveness of the surface conditioner is deteriorated by Mg ion in the bath. As the results, zinc phosphate coating crystals become larger. By contrast, with PL-X, the surface conditioner remains effective even if the concentration of Mg is increased.

Fig. 4 shows influence of Mg contamination on particle size of surface conditioner. In the case of the PL-Z, as the concentration of Mg in the bath is increased, particle size become larger. Particle size of PL-X keeps equal size if the concentration of Mg is increased. They are the similar tendency of crystal sizes on Fig. 3.

Fig. 5 shows the results of zeta potential on the particles. The results show that the zeta potential of PL-X is lower

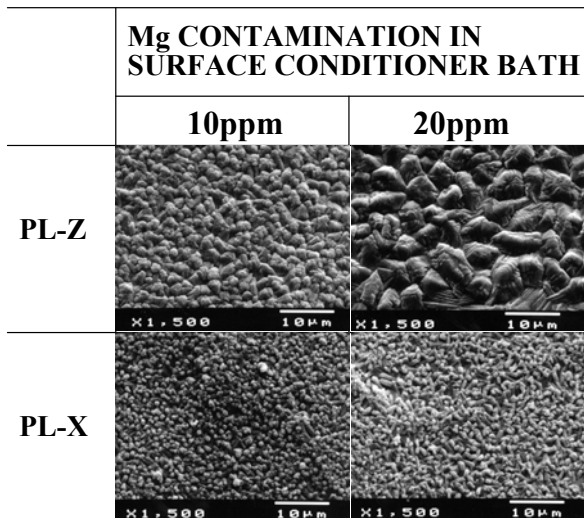


Fig. 3. Influence of Mg concentration in surface conditioner on crystal size

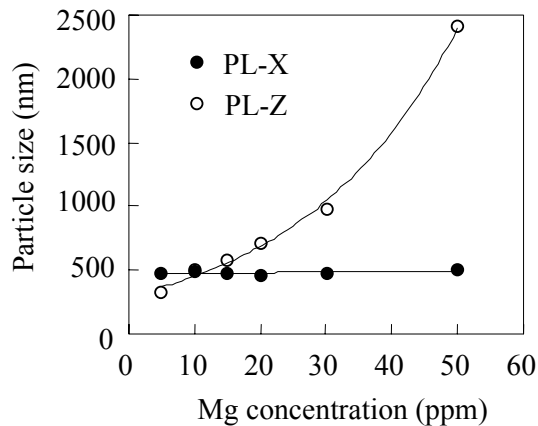


Fig. 4. Influence of Mg concentration on particle size of surface conditioner

than PL-Z. Both particles have similar particle size and are negatively charged, but the charge amount of PL-X is larger. Accordingly, the particles in PL-X remains stable in the bath solution more than PL-Z due to the electrical repulsion from the higher negative charge. It can also be observed that as the pH is getting lower, the charge amount becomes smaller. The particles have lost their electrical repulsion aggregate, and as the results, the effectiveness of the surface conditioner deteriorates and the crystals become larger. Similarly, in the case of high concentrations of Mg in the bath, the charge of the particles is canceled by the Mg ions, which are multicharged cation.

Fig. 6 shows the schematic diagram of repulsion of the surface conditioner. As mentioned above, PL-X can keep high stability even under lower pH value and higher Mg level. With the PL-Z, depending on the quality of the water available, it is necessary to use ion-exchanged water for the bath make-up and replenishing due to the instability

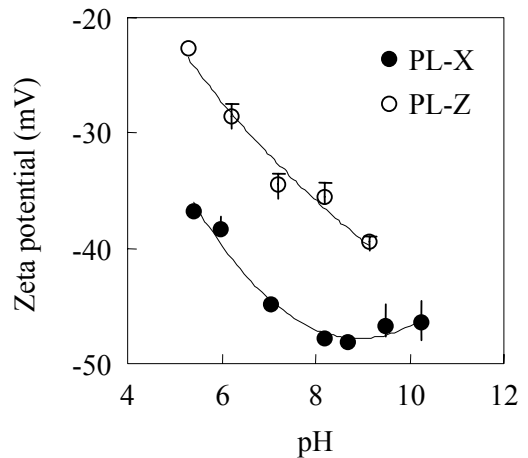


Fig. 5. Relation between pH of surface conditioner bath and Zeta potential

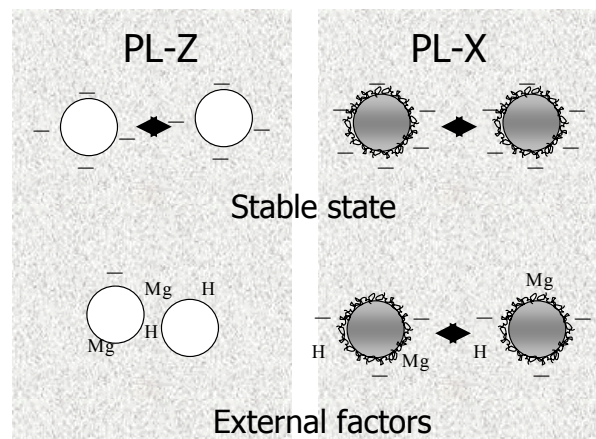


Fig. 6. Schematic diagram of repulsion of the surface conditioner

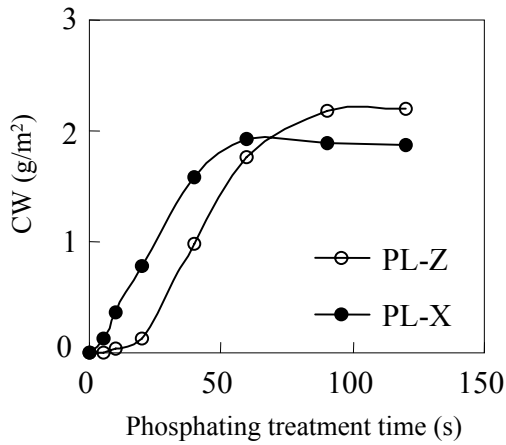


Fig. 7. Effect of surface conditioner on phosphatability (Substrate : CRS)

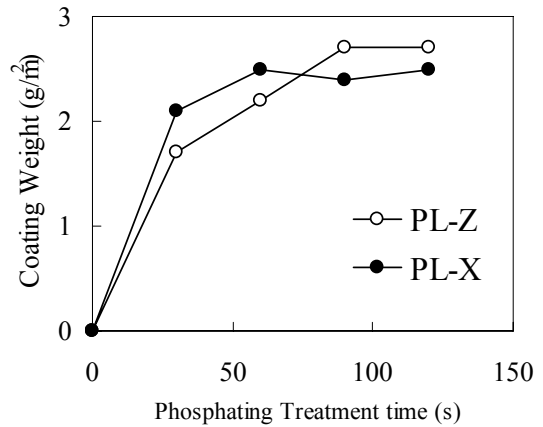


Fig. 9. Effect of surface conditioner on phosphatability (Substrate : high tensile strength steel)

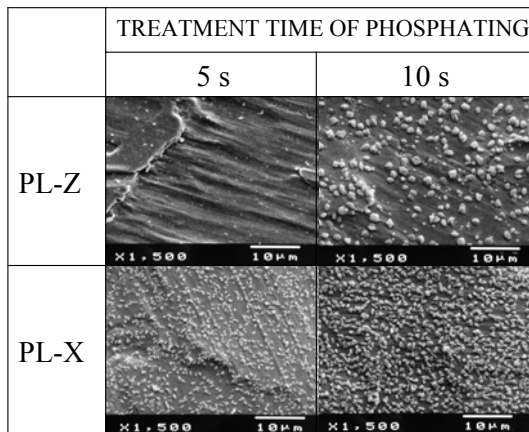


Fig. 8. Photo image of phosphate coating at various phosphating treatment time

of the Ti colloid. However with PL-X, it is possible to use the water available in virtually all regions of Japan.

3.3 Reduction of Phosphate Treatment Time

Fig. 7 shows the relationship between the coating weight and the zinc phosphate treatment time on CRS, which had been treated with PL-Z and PL-X. The c by using PL-X is completed by approx. 60 seconds.

Fig. 8 shows the appearance of crystals in the zinc phosphate coating. Phosphate generation at the beginning of the reaction is remarkably faster than PL-Z.

3.4 Improving Phosphatability of New Lighter Substrates for Automobiles

Regarding lightening of the car body, aluminum alloys and high tensile strength steels has been gradually adopted as lightweight materials. However, such materials are normally not easy to be treated with zinc phosphate system.

It has been necessary to improve the phosphatability for these substrates.

Fig. 9 shows the relationship between the coating weight and the zinc phosphate treatment time of high tensile strength steel, which had been treated with PL- Z or PL-X. The standard coating weight with PL-X is reached after a treatment time of approx. 60 seconds, and the rate at the beginning of the phosphating reaction was remarkably fast.

3.5 Improvement of Phosphatability of Inside of Box Structures

We treated actual parts and investigated the zinc phosphate coating appearance and coating characteristics of inside of box structures, and found that there was no rust and that fine crystals had formed.

Fig. 10 shows the appearance of crystals in the coating after processing using a range of agitation conditions in the zinc phosphate bath. With PL-X can be observed that

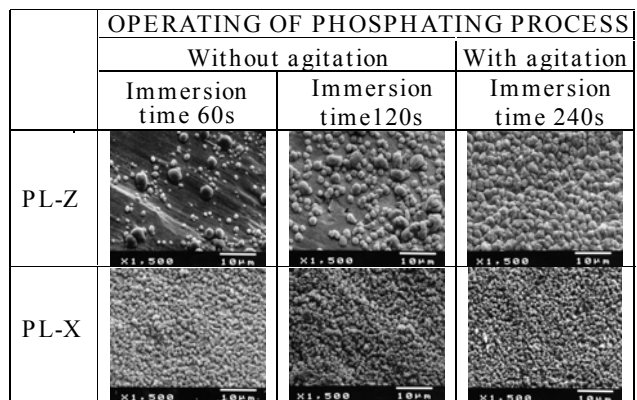


Fig. 10. Influence of Mg concentration in surface conditioner on crystal size

very fine zinc phosphate crystals form on the steel surface even without agitating the bath.

4. Cost Reduction

We have been able to realize cost reductions while maintaining performance by using a combination of the new surface conditioning chemical and a new zinc phosphate chemical. Our goal was to maintain paint performance by sufficiently covering the substrate surface with extremely fine zinc phosphate crystals and reduce the volume of phosphate chemical consumed in coating formation.

4.1 New Phosphate Chemical (PALBOND L3060 : PB-L3060)

By adding an organic chelating agent (OCA) to a tri-cationic type phosphating chemical base we can accelerate the phosphating reaction while reducing the coating weight on mainly cold rolled steel. Fig. 11 shows the coating characteristics of PB-L3060 and the conventional chemical on cold rolled steel.

It is clear that with the new chemical the crystals are finer and the coating weight lower. We have been unable

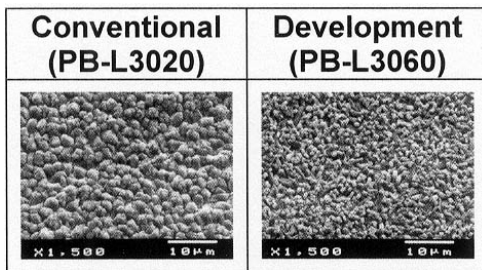


Fig. 11. Morphology of phosphate crystal

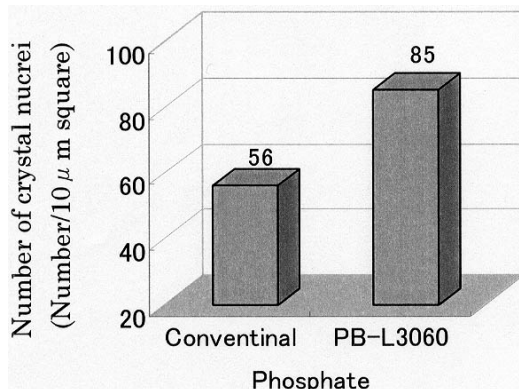


Fig. 12. Number of phosphating crystal nuclei on CRS (Phosphate treatment time 5s)

to confirm the details of the workings of the OCA, however, we believe that it allows the effective use of surface conditioner components adsorbed on the substrate surface as nuclei for the formation of zinc phosphate crystals.

Fig. 12 shows a comparison of the number of crystal nuclei at the very beginning stage of the phosphate treatment. Furthermore, we have been able to confirm the improvement in phosphate film appearance on inner side of actual auto body box parts.

4.2 Combination of PL-X and PALBOND L3060

Fig. 13 shows the coating characteristics that can be achieved with a combination of PL-X and PB-L3060. Significant changes in coating characteristics cannot be seen on the cold rolled steel however on Galvanneal (GA) and Hot Dip Galvanizing (HDG) we can see finer crystals and a significant drop in coating weight.

Also as shown in Fig. 14., we have been able to demonstrate on an actual line that we can achieve an even zinc phosphate film on aluminum 6000 substrates under free fluoride concentration of normal phosphate conditions, which is around 50 ppm.

Corrosion Resistance

We have been able to confirm good corrosion resistance on lower coating weights than ever before. We conducted zinc phosphate treatment on a cold rolled steel panel on which we had conducted 5mm Erichsen extrusion and left it for 24 hours at 35 °C under 80%RH.

Fig. 15 shows photos of the resulting outer appearance.

	STEEL SUBSTRATES		
	CRS	GA	HDG
PL-Z			
PL-X			

Fig. 13. Morphology of phosphate crystal

	Conventional	Development
SEM Image (× 1000)		
C.W(g/m ²)	0.5	2.5

Fig. 14. Morphology of phosphate crystals on 6000 series Al

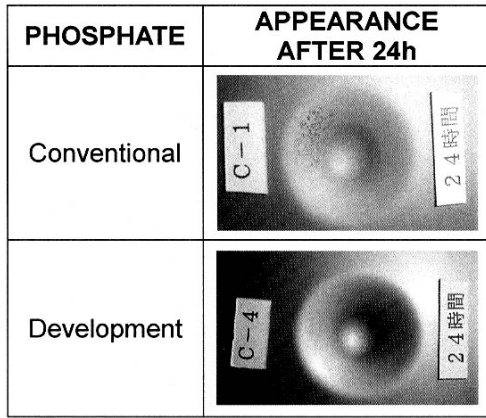


Fig. 15. Bare corrosion resistance of zinc phosphate coating

From this we believe that the corrosion resistance provided by zinc phosphate treatment does not depend on the coating weight but on the ratio of coverage of the substrate surface.

Fig. 16 shows a cross section photograph of zinc phosphate film crystals on cold rolled steel. As can be seen in Fig. 2, which is an image of crystal growth, fine crystals cover the substrate surface in a short time and the reaction is completed when the vertical growth is low. It indicates that the finer the crystals, the smaller the gaps between crystals and the lower the coating weight.

Corrosion Resistance after Painting

Fig. 17 shows the results of corrosion resistance after painting for our newest combination of chemicals. Regardless of the low coating weight, the paint performance achieved is at least as good or better when compared with conventional chemicals.

With this combination of the new surface conditioning chemical and zinc phosphate chemical we have been able to reduce running costs by 20%. We believe that this is one way we can pursue cost reductions in the future.

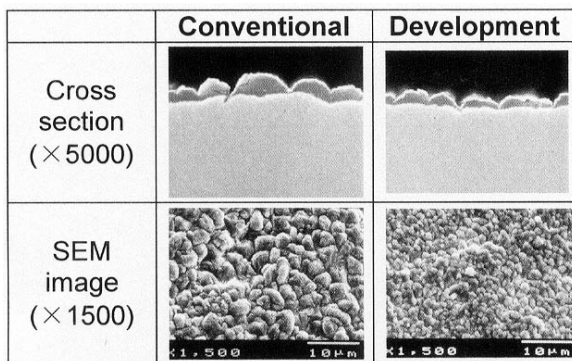


Fig. 16. SEM images of cross section of phosphate coating

	Conventional	Development
C.W(g/m ²)	2.3	1.5
Appearance		
Max blister width(mm)	2.1	2.2

Fig. 17. Paint performance newest phosphating system on CRS

5. Conclusion

Here we have explained just how much zinc phosphate technology has been improved over the nearly one century since it was first commercialized. Now we think you understand just what an important role zinc phosphate has played, as it is used on virtually every auto bodylines as a pre-treatment before painting. As we enter the 21st century a number of technical innovations are being initiated one after another, including environmentally friendly technologies, process shortening technology, and cost reducing technology to name but a few. We continue to believe that zinc phosphate technology has something to contribute to coating technology and hope to continue grappling with new developments.

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