State of the Art in Precoated Steel Sheet for Automotive Body Materials in Japan

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The history of precoated steel usage as car body materials in Japan is reviewed first. Japanese steelmakers developed galvannealed steel, duplex Zn–Fe coated steel, Zn–Ni coated steel and organic composite coated steel. All of them have been widely used. Recently, electrolytically Fe–Zn plated galvannealed steel and 1µm thick organic painted Zn–Ni electroplated steel have been applied. They have not only excellent corrosion resistance, but also good paintability, formability and weldability. Car body corrosion is classified into cosmetic corrosion and perforation. Newly clarified mechanisms for these two are explained. As for current research subjects, the development of inorganic and organic dispersion coating, Zn–Mn plating, galvannealed steel by vapor deposition, and vapor phase deposited Zn–Mg coating are described. Surface roughness control, application to vibration damping sheet, adhesive bonding, and the adaptation to lightweight cars are also important subjects to be studied now.

KEY WORDS: precoated steel; automobile; corrosion resistance; paintability; formability; weldability; image clarity; adhesive bonding; lightweight car.

1. Introduction

Many authors¹⁻⁴) have already published reviews on precoated steel sheets for automotive use in Japan. Since then, the technology of corrosion protection has made steady progress. Good corrosion resistance is now one of a car's strong selling points. The percentage of precoated sheet panels used in a body-inwhite is now estimated as 60-90 % for export cars and about 40 % for domestic cars, and it is increasing. In the future, all panels of export cars will be precoated except for the roof. Some European manufacturers are producing good corrosion resistant cars with 100 % Zn-plated panels.

In Japan, more than 10 million metric tons of Zn plated steel sheet are produced in a year. Of that total, in 1988, about 2.3 million tons were for automotive use. Pure Zn plated-, Zn-Fe alloy coated-, Zn-Ni alloy coated- and organic composite coated steels are 4 main kinds.

In this paper, the history of automotive steel usage is first overviewed. Then the corrosion mechanism of car bodies, the classification and performance of precoated steels, research in this field and future trends will be reviewed, especially concentrating on corrosion problems. Corrosion is caused by de-icing salt, marine atmosphere and acid rain. Among these, de-icing salt is the most important and has been the most precisely studied.

2. History of Precoated Steels for Automotive Bodies

Fig. 1 shows the secular change of precoated steels

used for car bodies. The use of de-icing salt in North America and Canada increased very rapidly from 1950 to 1970. As a result, the corrosion of car bodies was actualized around 1960 in these regions. In the early 1960's American car manufacturers started to apply Zn coated steel sheets for from-theoutside unvisible body parts, such as floor, in order to suppress corrosion. Since 1963, when the hot dip galvanized rocker panel showed an excellent durability, Zn plated sheets have been used as visible part panels, such as doors and fenders. In 1972, the application of Zincro Metal (zinc chromated and Zn rich primed sheet) began.

In Japan, with the increase of car exports to North America, automobile manufacturers developed considerable interest in the corrosion problem. Electrogalvanized steel was applied first in 1974 for the bodyin-white of an export car. In 1977, a steelmaker developed galvannealed sheet with a good performance and started to supply it for body panels.

In 1978, the Canadian Government introduced the famous Canadian Code, which is an anticorrosion code establishing minimum levels of corrosion protection to be provided for all vehicles sold in Canada. Japanese car manufacturers were forced to design export vehicles which fulfill the requirements of the Canadian Code, because the United States also observed the Code. They raised the amount of precoated steels to be used in body-in-white rapidly around 1980, for example 47 % for export cars and 16 % for domestic cars in 1982.⁵) In 1983, a more severe Scandinavian Code was introduced in Europe, which required 3 years cosmetic corrosion free and 6 years perforation free.

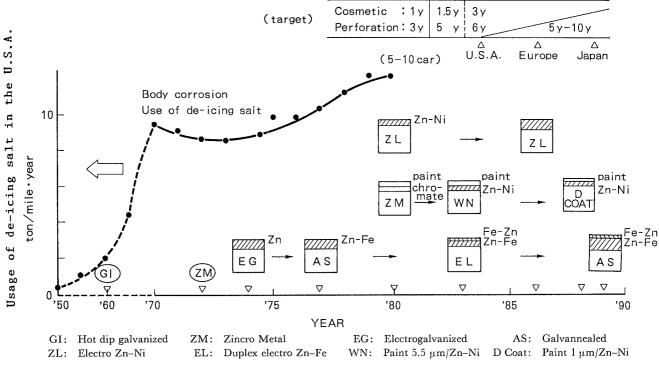


Fig. 1. History of precoated steel application to automobiles in Japan.

In accordance with the above-mentioned situation, Japanese steel manufacturers made great efforts to develop new precoated steels having higher performances than the ones being used at that time. Three different kinds were invented by refining the long-standing galvanized steel and/or Zincro Metal. They are: duplex Zn-Fe alloy electroplated steel ($20 \text{ g/m}^2 + 3 \text{ g/m}^2$), Zn-Ni alloy electroplated steel ($20-30 \text{ g/m}^2$), and organic composite coated steel (Zn-Ni base, 15 g/m²). They not only have an excellent corrosion resistance but also good press formability and weld-ability. Moreover, they are not too expensive.

About the middle of the 1980's, American automakers prolonged the target years of corrosion-free to 10-5, which means 10 years of perforation free, 5 years of cosmetic corrosion free. They tried to improve corrosion resistance by using a lot of Zn coated steel. In 1984, at the SAE (Society of Automotive Engineers) Exposition, Chrysler made public its T-Wagon whose body-in-white was made of hot dip galvanized steels except for the roof. The percentage of galvanized steel reached 88 %.⁶) Influenced by this technical trend, Japanese automakers gradually increased the usage of precoated steel. The coating weight of the Zn or Zn-alloy layer was also increased.

In 1989, several Japanese automakers made public their 10–5 cars by applying either galvannealed steel with 60 g/m² or organic composite coated steel with 30 g/m² of Zn–Ni. However, they are not fully satisfied with these materials. Work toward improvement is underway among steelmakers.

3. Corrosion Mechanism of Car Bodies

3.1. General

Car body corrosion is caused by de-icing salt, ma-

rine atmosphere and acid rain. Among these three factors, de-icing salt is the most influencial and has been widely studied.

Corrosion is classified into two main categories, cosmetic type and perforation. The former means red rust formation, paint blistering and delamination of visible parts, all of which start from paint damage or defects. The latter means penetration of panels, which often occurs at the hemming part of assembled panels.

Previous papers discussed corrosion mechanism in general.^{3,7-10)} In this paper, newly obtained results will be explained.

3.2. Cosmetic Corrosion

These days both-side zinc coated steel is generally used for body outer panels. If the outside paint film has been damaged during car driving, underfilm corrosion starts from the paint defect and propagates under the paint film. As zinc is a less noble metal compared with iron, it is attacked preferentially at an early stage and, as a result, a corrosion layer develops parallel to the surface, as is shown in Fig. 2.

Oxygen is supplied through the paint defect and a local cell is formed, where the corrosion front acts as an anode and the substrate near the paint defect acts as a cathode.^{8,11,12} The corrosion mechanism is shown in Fig. $3.^{11}$ At the extreme front, zinc is oxidized in the anodic reaction and becomes zinc chloride.¹³ Then it is converted into zinc hydroxide or oxide. After the metallic zinc has been consumed, the steel substrate begins to have an anodic reaction. As iron corrosion product is larger in volume than metallic iron, a volume increase occurs, which lifts up the paint and results in blistering or delamination.

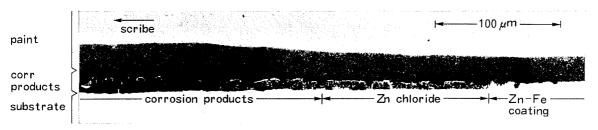
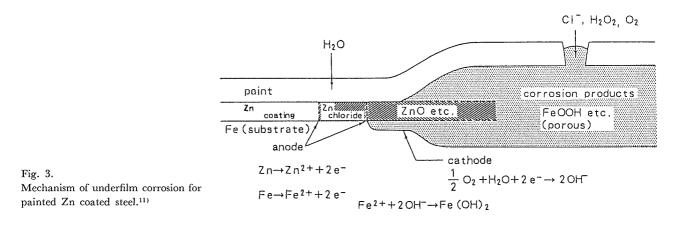


Fig. 2. Microscopic observation of paint blistering of galvannealed steel after a half year weathering test with 5 % NaCl solution spray once a day except for weekend.



3.2. Perforation

Perforation is often observed at the hemming part of assembled panels, such as doors, hoods and quarter panels. A hem has a small gap, which is very difficult to be covered with paint. And moreover, if water penetrates, it stays for a long period.

Cross sections of corroded door hems from a 10-year field-drive car are shown in Fig. $4.^{14)}$ There are 4 remarkable points.

(a) The outer panel, not the inner panel, gets perforated.

(b) Perforation progresses from inside to outside.

(c) Corrosive substances are supposed to come to the gap not only from the top but also from the hem edge.

(d) The gap becomes wider because of rust growth.

From these points, the perforation mechanism of a door hem can be estimated as follows:

(1) Initiation

Water and salt are supplied from the window glass *etc.*, to the gap. If adhesive, inner sealer or wax is insufficient, they stay there and start corrosion. Or, the hem edge is first attacked and corrosive substances reach the gap through it.

(2) Propagation

The gap surface, where paint thickness is zero or small, becomes easily corroded. Because of the temperature difference between the atmosphere and the gap inside, the outer panel surface dries up much slower than the inner panel surface, and dewing may even occur. Therefore, the former is attacked much faster than the latter.

(3) Perforation

Once a hole has been formed in the outer panel, corrosive substances are supplied through that hole

Fig. 4. Cross-sectional observations of corroded door hems from a 10-year field drive car.¹⁴ Three different positions from one door were investigated.

and it will grow quickly in size.

(4) Deformation Rust growth deforms the hem.

4. Classification of Precoated Steels for Car Body

Precoated steels can be classified into 4 categories: hot dipped, hot dipped & electroplated, electroplated, and electroplated & painted. Table 1 gives the summary of these steels being properly used for car bodies. In Table 1, hot dipped & electroplated steel and electroplated & 1 μ m thick painted steel, have been recently put into practical use.

Category	Designation	Precoat layer	Coating weight (g/m² per one side
Hat dinned	Pure Zn	Zn	60-120
Hot dipped	Galvannealed	Zn-Fe	30-90
Hot dipped & electroplated	Duplex	Fe-15Zn/Zn-Fe, Fe-P/Zn-Fe	3/45-90
Electroplated	Pure Zn	Zn	10-30
	Duplex Zn-Fe	Fe-15Zn/Zn-15Fe	3/20
	Zn-Ni	Zn-11Ni	20-40
Electroplated & painted	Organic composite	Organic film/Zn-11Ni	l μm/20-30
	Organic composite	Organic film/Zn-11Ni	$5.5 \mu m / 15$

Table 1. Precoated steel being properly used for car body in Japan.

5. Performances of Precoated Steels

5.1. Corrosion Resistance

5.1.1. Cosmetic Corrosion

As a car body is exposed to the environments of salt, high humidity, drying, freezing, *etc.*, in the field, corrosion test is usually carried out in cyclic conditions (CCT). Many kinds of CCT have been proposed.³⁾ Principally, CCT is a combination of salt spray and repetition of wet & dry. One example of CCT is given in Table 2.³⁾

Figs. 5 and 6 show the effect of zinc or zinc alloy coating weight on the red rust onset and the underfilm corrosion resistance, respectively.¹⁵⁾ The increase in coating weight improves both resistances remarkably.

Zinc alloy composition also influences the underfilm corrosion, as is seen in Fig. 7.¹⁶) Zn-Fe deposits with 5–15 % Fe demonstrate the best performance among Zn-Fe alloys. This is one reason why Zn-Fe coated steels used for car bodies have 8–15 % Fe.

5.1.2. Perforation

Perforation is mainly found at the lapped part of a hem. Therefore, the corrosion test is often carried out in CCT using lapped-panel specimens. Fig. 8 shows the result of such an experiment.¹⁶ Zinc or Zn alloy coated steel with a higher coating weight gives a better performance. These days, automakers are changing to a higher coating weight than before in order to achieve long car service life.

As shown in Figs. 9^{17} and 10^{18} , alloy composition also has some effect. Considered from these figures, 10-20 % Fe and 11-13 % Ni, respectively, are the most suitable regions. Zn alloy coated steels with these compositions are now widely used.

Organic composite coated steel with Zn–Ni layer and 1 μ m thick organic film demonstrates an excellent corrosion resistance before painting. Test results are given in Fig. 11.¹⁹ This type of steel is also applied in Japan.

5.1.3. Cratering Property

In a car production line, assembled bodies are cathodically electroprimed (C-ED). Depending upon the priming conditions, C-ED film gets a lot of point defects called craters. These craters not only damage the surface appearance, but also cause corrosion. Therefore they are to be avoided.

Tabie 2. One example of CCT (Cyclic Corrosion Test) conditions.³⁾

→Salt spray	35°C	4 h
↓ Drying	70°C	2 h
↓ Humidifying	RH 60 % 49°C	2 h
↓ Freezing	RH 95% −20°C	1 h
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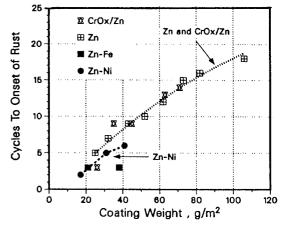


Fig. 5. Relationship between time to onset of red rust at the scribe and the coating weight of unpainted steels in a laboratory cyclic test.¹⁵

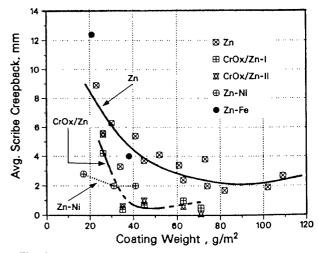
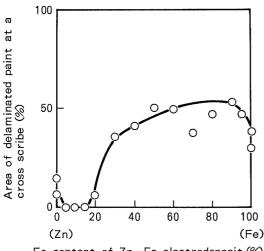
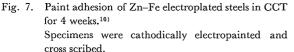
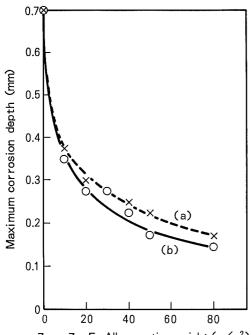


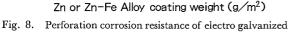
Fig. 6. Influence of the coating weight on the underfilm corrosion in a laboratory test for 30 cycles.¹⁵⁾



Fe content of Zn-Fe electrodeposit (%)



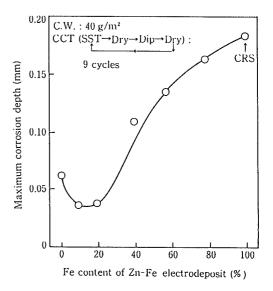




steel(a) and Zn-15%Fe electroplated steel(b) with various coating weights in CCT for 84 cycles.¹⁶ Lapped panel specimens were used.

As is shown in Fig. 12, Zn-Fe coatings with low Fe content are apt to get cratering,²⁰⁾ and lowering the applied voltage reduces the number of craters. In a priming bath where the electrolysis voltage is low, Zn-low Fe alloy coated steel can be painted without craters. However, the number of such baths is small.

Galvannealed steel, which shows an excellent perforation resistance, has a poor cratering property, as can be estimated from its Fe content. By covering its surface with an Fe-15%Zn coat by electroplating, its cratering property has been improved.²¹ Consequently, its usage has been increasing rapidly among



C.W.: Coating weight.

Fig. 9. Influence of Zn-Fe alloy composition on the corrosion behavior in a CCT.¹⁷⁾

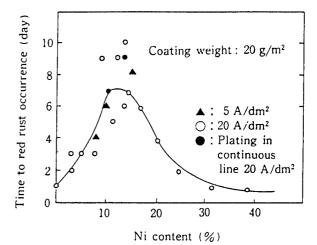
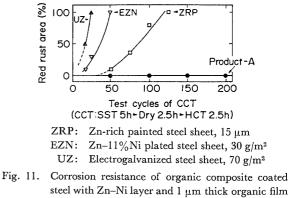
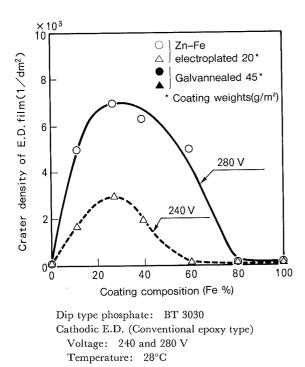


Fig. 10. Influence of Zn-Ni alloy composition on the corrosion behavior in salt spray test.¹³⁾ Specimens were prepared under various plating conditions.



if. Correston resistance of organic composite coated steel with Zn–Ni layer and 1 μm thick organic film (Product-A) in comparison with other steels in a CCT.¹⁹
 Unpainted specimens were used.

Japanese automakers. In the case of organic composite coating, the organic layer is designed to have no priming defect.



Electrode distance: 15 cm Cathode/anode area ratio: 1/4 Fig. 12. Influence of Zn-Fe alloy composition on the cratering property.²⁰

5.2. Formability

5.2.1. General

Generally speaking, precoating makes the formability of steel sheet worse. There are two significant aspects. The first is the narrowing of the available range of blank holding force in a press line, due to the deterioration of the mechanical properties of the substrate and to the change of surface lubricity.

The use of Ti- or Nb-added low-C steel as the substrate can avoid the lowering of *r*-value in hot dipping treatment. And the use of lubricants can improve the lubricity.

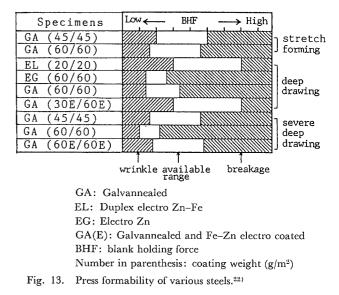
The second is the exfoliation of precoated materials, such as Zn, Zn alloy and organic substances, in a press forming process. The exfoliated materials stick to the dies or punches and cause press defects, called pimples, on the sheet. This phenomenon is called powdering, flaking, or build-up.

Recently, the formability of precoated steels has improved greatly by applying an Fe-rich upper layer or a thin organic film on the top of these steels. In this paper, these new technologies are reviewed.

5.2.2. Available Range of Blank Holding Force

Fig. 13 summarizes the results of the press forming tests.²²⁾ Three different modes were chosen. They are: stretch forming (hood inner), deep drawing (fender), and severely deep drawing (rear floor). Galvannealed (denoted as GA), galvannealed & Fe-Zn electroplated (GA with E), duplex Zn-Fe electroplated (EL) and pure Zn electroplated steel (EG) were used as specimens.

In the stretch forming mode, no difference was observed between galvannealed steels with 45 and 60



g/m². However, in the drawing mode increasing the coating weight considerably narrowed the available press range. This is thought to be brought about by the change of surface lubricity due to the formation of Zn–Fe ζ -phase on the galvannealed surface.²³⁾ It is very difficult to avoid the ζ -phase formation in the galvannealing process when the coating weight is high. In the case of pure Zn electroplated steel, a pure Zn layer easily sticks to the die or punch and causes problems.

An electroplated Fe–Zn layer on the top of galvannealed steel remarkably widens the available press range, as can be seen in Fig. 13. The hard Fe–Zn layer works as a kind of lubricant. Galvannealed & Fe–Zn electroplated steel is now widely used in Japan.

Fig. 14 gives the press formability of Zn–Ni electroplated & 1 μ m thick organic painted steels (OF-1 to -3) in comparison with other steels.²⁴⁾ Organic composite coated steel (OF) showed almost the same available press range as cold rolled steel (CR). Its formability is better than other precoated ones tested. This type of steel is also often applied in Japan.

5.2.3. Exfoliation of Coating Layer

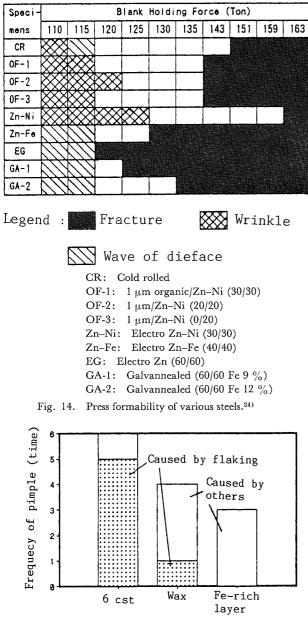
An Fe–Zn overlayer on galvannealed steel considerably decreases the pimples caused by flaking, as is shown in Fig. $15.^{23}$ It is more effective than other methods such as lubricant 6 cst and wax. This is a result of successive fender pressings.

An organic film on Zn–Ni layer has the same effect. Fenders were press formed from various steels and tape peel tested. Fig. 16 gives the results.²⁴ Organic film (OF-1 to -3) reduces the coating exfoliation of the Zn–Ni layer.

5.3. Weldability

In the body assembling process spot-, arc-, gasand laser-welding are applied. Precoated steels have worse weldability than cold rolled steel. There are many reasons for that. Zinc plating needs a large spot welding current, because zinc melts easily and, as a result, widens the nugget diameter. Both zinc and organic film react with the spot welding tip and damage it. The Zn layer brings about blow holing in arc welding due to its high vapor pressure.

For the sake of good weldability, a thin precoating



6 cst and wax: Lubricants

Fig. 15. Effect of Fe-rich upper layer on galvannealed steel in decreasing the press pimples caused by flaking.²³⁾

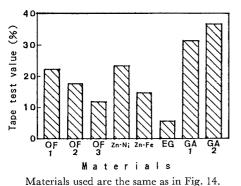


Fig. 16. Tape test results for press formed fenders made of

various precoated steels.24)

layer is preferable. However, the coating thickness of car body steels has been increasing in order to prolong car service life. Although the existing precoated steels can be welded, automaker engineers are not fully satisfied with their weldability. Efforts must be made to improve it.

6. Current Research Subjests

6.1. Development of New Precoated Steels

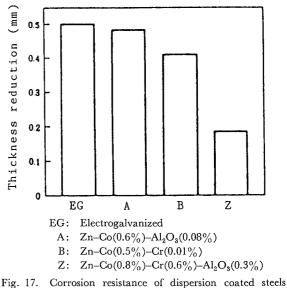
The corrosion resistance of Zn or Zn alloy coating can be improved by adding other elements or compounds. Electro-dispersion plating of inorganic substances such as Al_2O_3 , SiO_2 and $BaCrO_4$ has been carefully studied.²⁵⁻²⁷⁾ In this process, small particles of such substances are dispersed in Zn or Zn alloy plating solutions and electrolysis is carried out. As these particles adsorb ions in the solution on their surface, they migrate to the cathode, discharge electricity of the adsorbed ions and deposit on it together with Zn or Zn alloy.

The corrosion behavior of Zn–Co–Cr–Al₂O₃ dispersion coated steel is shown in Fig. 17.²⁵) Codeposition of 0.3 % Al₂O₃ reduces the thickness loss in salt spray test remarkably. SiO₂ and BaCrO₄ have the same effect. According to X-ray diffraction measurements, the addition of these substances helps the formation of ZnCl₂·4Zn(OH)₂, which exerts a corrosion preventive action.²⁸)

Zn-organic polymer dispersion coating by electroplating is also studied. The dispersed polymer is said to especially improve paint adhesion.²⁹⁾

Zn-Mn coated steel has an excellent corrosion resistance in a salt spray test (SST), as is shown in Fig. $18.^{30}$ γ -Mn₂O₃ is formed in SST, which suppresses the cathodic reaction.

Galvannealed steel can be produced by the zinc vapor deposition process with after-heating. This steel has the same corrosion resistance as that produced by a hot dip method. However, the former



3. 17. Corrosion resistance of dispersion coated steels without painting in comparison with other steels in salt spray test for 720 h.²⁵

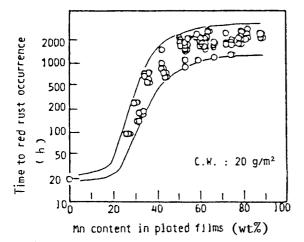


Fig. 18. Corrosion behavior of unpainted various Zn-Mn electroplated steels in salt spray test.³⁰⁾

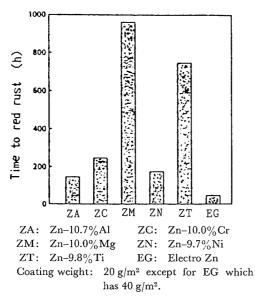


Fig. 19. Corrosion behavior of unpainted Zn alloy vapor deposited steels.³²⁾

shows a much better press formability than the latter. 31

Vapor phase deposition enables the preparation of a variety of Zn alloy coatings. Fig. 19 gives the corrosion behaviors of vapor deposited Zn-Al, Zn-Cr, Zn-Mg, Zn-Ni and Zn-Ti coatings.³²⁾ Among them, Zn-10%Mg demonstrates the best performance.

However, none of the above mentioned new Zn alloy coated steels has been put into practical use, because of either high cost or unsolved problems in mass production.

6.2. Surface Roughness Control

There are many factors which determine the value of a car. Recently, image clarity has become one of these important factors. Although the image clarity of a car is determined mainly by the thickness and the quality of the paint, the surface roughness of the substrate steel also exerts a great influence.

The surface roughness is composed of waves with various lengths and intensities. The influence of each

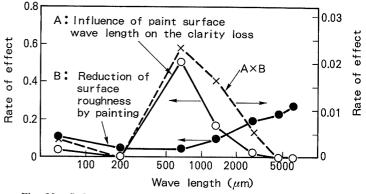


Fig. 20. Influence of steel surface wave length on the image clarity after painting $(A \times B)$.³³⁾

wave on the image clarity is given by Fig. 20 which was obtained with the help of Fourier Analysis.³³⁾ Short length waves are attenuated by painting. Long length ones have little influence on the image clarity. Wave lengths from 500 to $4\,000\,\mu\text{m}$ are important. According to Nishimura *et al.*, the flat area portion of the surface also has to be considered.³⁴⁾

Efforts are being made to reduce the intensity of steel surface waves with 500 to $4\,000\,\mu\text{m}$ of length in order to realize a good image clarity after painting. The surface roughness of precoated steel for outer body panels is controlled by the cold- and skinpass rolling.

6.3. Vibration Damping Steel Sheet

Low noise and low vibration of car body are also important factors to determine its value. Vibrationdamping steel, which is made of 2 lapped sheets with a thin resin film between them, has been developed.³⁵) The application of this steel to body panels is well in progress.

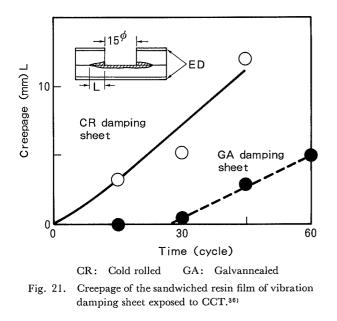
Recently, precoated steels have begun to be used as the lapped sheets for the sake of high corrosion resistance. Fig. 21 shows the resin film creepage in CCT (cyclic corrosion test).³⁶) Vibration-damping steel of GA (galvannealed steel) has a much better performance than that of CR (cold rolled steel).

6.4. Adhesive Bonding

Adhesive bonding may be applied to car body assembling in the future more and more, because it can improve body rigidness and fatigue strength. Single lap joints of various Zn coated steels were constructed using adhesive and the fracturing behaviors of the joints were measured with an Instron-type tensile tester. Results are given in Fig. 22.³⁷

As the adhesive is a viscoelastic substance, the test temperature has a great influence on the results. Lowering the temperature changes the fracture mode from adhesive type (adhesive/plating interface) to plating type (plating/substrate interface). The plating fracture is not desirable. However, when a test is carried out in a corrosive environment, the adhesive fracture dominates.

Test methods have to be developed which can well simulate field conditions.



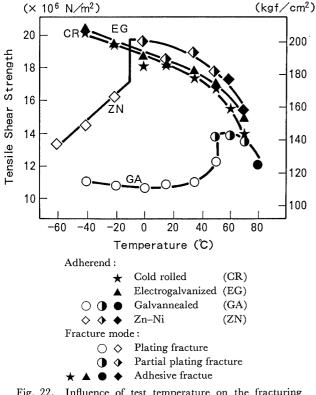


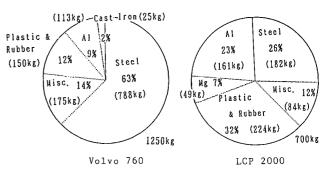
 Fig. 22. Influence of test temperature on the fracturing behavior of single lap joints made of various steels.³⁷
 Test was carried out using an Instron type tensile

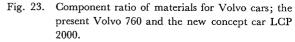
tester with a crosshead speed of 10 mm/min.

6.5. Adaptation to Lightweight Cars

Currently energy saving is a social demand. In the U.S.A., the Energy Policy Conservation Act was passed by congress and, since 1978, each carmaker has been producing automobiles having given fuel consumption rates in accordance with CAFE (Corporate Average of Fuel Economy). If, in the future, CAFE is changed to a more severe value, carmakers will be forced to develop lightweight cars.

Volvo, from Sweden, designed a concept car, called





the LCP 2000, weighing only 700 kg. The weight decrease of 550 kg is realized in comparison with the present Volvo 760. The component ratio of materials used is shown in Fig. 23. The steel ratio decreases from 63 to 26 %. The use of lightweight metals, such as Al and Mg, and of plastic and rubber has increased. Al and Mg may bring about new corrosion problems to precoated steels, especially when they come into an electric contact. A study of this will be necessary in the future.

7. Conclusion

Precoated steel was first applied to car bodies in Japan in 1974. Since then galvannealed steel, duplex Zn–Fe electroplated steel, Zn–Ni electroplated steel and organic composite coated steel have been put into practical use. The percentage of precoated steel in body-in-white has now reached 80 % for some models. In accordance with the 10–5 year corrosion prevention target, two kinds of steels have been newly developed. They are Fe–Zn electrolytically overcoated galvannealed steel with a coating weight of 60–90 g/m² and 1 μ m organic painted Zn–Ni electroplated steel with a coating weight of show an excellent corrosion resistance, good paintability, good formability and sufficient weldability.

The mechanism of car body corrosion for both cosmetic and perforation types was reviewed.

Efforts to develop new precoated steels are in progress. Inorganic or organic dispersion coating, new Zn alloy coatings by electroplating or vapor deposition process have several good properties. Surface roughness control, vibration-damping sheet, adhesive bonding and studies concerning lightweight cars are also important research subjects.

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