Progress of Automotive Precoated Sheet Steels*

By Shigetoshi ISHIHARA**

I. Introduction

The Japanese production of four-wheel vehicles peaked with some 11.7 million units in 1981. About 50% of these automobiles were exported abroad, chiefly to cold regions like North America and Europe. In 1981, Japan’s automotive industry consumed 10,671,000 tons of plain carbon steel, and uncoated and coated steel sheets accounted for 62% and 12% of this consumption, respectively, as shown in Table 1.

For automobiles in general and passenger cars in particular, four prime social needs have been highlighted: (1) alleviation of exhaust gas pollution, (2) assurance of passenger safety, (3) fuel economy and (4) improvement of automobile durability. From a point of view of steel, the need (1) calls for exhaust system material that can withstand corrosion at high temperatures. The needs (2) and (3) can be filled by the strength enhancement and weight reduction of automobile bodies, which in turn necessitates the use of higher-strength and lighter-gage hot-rolled sheets for wheels and other components, and cold-rolled and precoated sheets for bodies. To conserve oil resources, alcohol and other alternative fuels have appeared and created an exacting demand for new fuel tank material. For the need (4), automobile body corrosion is the largest problem and attack by deicing salt spread on the highways of North America and Europe in winter is the severest. In this field, it is necessary to improve the phosphatability of sheets and to coat sheets with more adequate protective material.

Of the automotive steels mentioned above, this report takes up precoated sheet steels, classifies them into automobile body corrosion-resistant steel, fuel tank steel and heat-resistant steel according to application, and discusses their developmental background, present status and future problems. There also are available prepainted steel sheets for inner panels, another category of precoated steel, vibration-damping steel sheets for noise abatement around the engine, and steel-sandwiched plastic sheets, studied now as material for weight reduction in U.S.A. etc., but these materials are omitted here. The progress of the processes that have enabled the manufacture of these products is reviewed in the last section.

II. Precoated Steels for Prevention of Automobile Body Corrosion

I. Actual Condition of Automobile Body Corrosion

The body corrosion of automobiles has become a general problem in the world in recent years, especially so in North America where large amounts of deicing salt are spread on the highways in winter. Autobody corrosion is particularly severe in the Snow Belt or Great Lakes areas of North America, the eastern to northeastern states of U.S.A. and the Quebec Province of Canada. In these regions, there are heavy snowfalls in winter, large cities are concentrated and vehicular traffic volumes are large, so that deicing salt is used in large quantities to ensure mobility on the highways. The U.S.A. uses by far the largest amount of deicing salt in the world (9 million tons in 1970). From 1969 to 1970, the usage of deicing salt reached 1.37 million tons in Canada and 1.40 million tons in Britain. In Japan, a deicing compound mainly composed of calcium chloride is spread, but its usage is very small. The Okinawa area of Japan, the coastal regions of the Middle and Near East and the Gulf States of U.S.A. are subject to sea salt particles and constitute relatively severe corroding environments for automobiles. The distribution of automobile corroding environments in the world is shown in Fig. 1. The change in deicing salt usage on the highways of U.S.A. is given in Fig. 2. The usage of deicing salt sharply increased from 2 million tons in 1960 to 9 million tons in 1970 and has been on the increase thereafter. As the usage of deicing salt has increased, automobile corrosion has become a serious problem in various parts of U.S.A. Figure 3 illustrates the relationship between the number of years to body perforation and the usage of deicing salt in cities in Canada and U.S.A.

Investigations of many automobiles run on the highways have yielded the following findings:

<table>
<thead>
<tr>
<th>Bar, shape, plate, pipe, etc.</th>
<th>Hot-rolled sheet</th>
<th>Cold-rolled sheet</th>
<th>Precoated sheet</th>
</tr>
</thead>
<tbody>
<tr>
<td>26%</td>
<td>12%</td>
<td>50%</td>
<td>12%</td>
</tr>
</tbody>
</table>

* Received March 29, 1983. © 1983 ISIJ
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A few types of characteristic corrosion are developed in many automobiles.

Most automobiles have common causes of corrosion.

Main types of corrosion are limited to certain areas of specific automobiles.

Each car model has a particular distribution of corrosion damage.

Corrosion that occurs in automobiles may be classified into crevice corrosion, deposit attack, galvanic corrosion, pitting and general corrosion as shown in Table 2. Automobile body corrosion is mainly accounted for by corrosion that results from the deposition and collection of salt and dirt in pockets, dents and joints between panels or hemmed parts. Corrosion in hemmed parts calls for special care, because it leads to perforation from the inside to the outside of the hemmed parts. Another significant type of corrosion is scab or filiform corrosion that occurs when the paintwork is damaged or worn away by flying gravel spread together with deicing salt on the road surface. This type of corrosion, also called cosmetic corrosion, has become the focal point of rust protection as the beautiful appearance of automobile exterior has assumed more importance in recent years.

2. Elucidation and Simulation of Corrosion Phenomenon

Establishment of rational measures for automobile corrosion protection calls for a three-step approach. In the first step, a corrosion test method is established that can accurately correlate the corrosion of automobiles on the marketplace to specific corrosive conditions and judge the corrosion in a short time. The second step involves the basic analysis of automobile corrosion and the development of protective measures. More specifically, the corrosion behavior of automobile steel sheet under the paint film is grasped, the corrosion behavior of steel sheet used unpainted is analyzed, and the results obtained are utilized in the development of automotive corrosion-resistant sheet steel. The final stage involves the establishment of an optimum corrosion protection system composed of (1) corrosion-resistant steel, (2) chemical treatment and painting and (3) carbody structure design. This section introduces a few interesting facts about the first and second steps. Corrosion protection will be touched upon in another section.

1. Automobile Corrosion Test Methods

At present, a new automobile corrosion-resistant sheet steel is adopted after its performance is verified by car running tests on salt-covered proving grounds or highways. These tests are usually conducted for confirming the usability of a new automobile corrosion-resistant sheet steel, rather than for developing a new automobile corrosion-resistant sheet steel, and are limited in scope to the comparative study and selection of new materials. Laboratory corrosion tests with steel specimens or automobile parts play a more important role in the development stages of autobody corrosion-resistant sheet steels. In order to accurately perform the evaluation test of body corrosion-resistant sheet steel, the analysis of the corrosion mechanism involved and the comparison and selection of new materials, it is necessary to set optimum laboratory corrosion test conditions and sample shapes, to establish a rational test method that can properly judge the corrosion of automobiles on the highways,
and to quantitatively grasp and evaluate the properties required of automotive corrosion-resistant sheet steels.

Figure 4\(^1\) shows weather conditions in Chicago, a central city in the Snow Belt. In winter in Chicago, the temperature is \(1 \degree C\) to \(-10 \degree C\) and the relative humidity is 80 \% or more. In urban areas like Chicago, heating is liberally provided and in garages, automobiles are exposed to warm and dry conditions. Automobiles are also exposed to various polluted industrial atmospheres (dust and sulfur dioxide gas, for example) that constitute more corrosive environments.

The way corrosive agents collect and corrode various parts of an automobile is shown in Fig. 5.\(^5\)

As described above, the automobile is corroded on the market mainly when it is repeatedly exposed to dry and wet and warm and cool conditions with salt, dirt and water collected in the hemmed parts. In addition, the hemmed parts are difficult to electro-deposit primer and are coated with no paint at all. The cyclic corrosion test (CCT) and dip and dry (D & D) test were developed by considering all of these factors. Figure 6 gives typical CCT results.\(^6\) CCT is a combination of salt spray test (SST) and cooling-heating cycle test and is more effective than SST or the cooling-heating cycle test alone. SST or the cooling-heating cycle test alone is unable to properly reproduce the corrosive environment on the market. It is necessary to determine the shape of test specimens and the condition of corrosion test cycles by considering the structure of hemmed parts, the deposition and collection of salt, dirt and water, and the drying and humidifying and cooling and heating conditions of test specimens.

It should be also noted that corrosion simulation testers\(^7\) (Photo. 1) for the corrosion test of automobile parts like doors and automobile corrosion test chambers\(^3\) (Fig. 7) are built so as to more accurately reproduce corrosive environments on markets.

2. Basic Analysis of Automobile Corrosion

Elucidation of the automobile body corrosion mechanism is an important prerequisite to ascertainment of the future direction of automobile corrosion protection, but has just gotten under way in combination with corrosion under the paint film and corrosion-resistant sheet steel.

Table 2. Type of corrosion and commonest cause of corrosion in various car components.

<table>
<thead>
<tr>
<th>Component</th>
<th>Material</th>
<th>Type of corrosion</th>
<th>Cause</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chassis</td>
<td>Sheet steel</td>
<td>Crevice corrosion</td>
<td>Moisture and road dirt entering members, gaps, welds, etc.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>General corrosion</td>
<td>Damage to paintwork from flying stones</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Deposit attack</td>
<td>Gravel wearing away protective surface coating</td>
</tr>
<tr>
<td>Spring mountings</td>
<td>Sheet steel</td>
<td>Crevice corrosion</td>
<td>Moisture and road dirt filling gaps and pockets formed by reinforcements round the mounting</td>
</tr>
<tr>
<td>and other force-</td>
<td></td>
<td>General corrosion</td>
<td></td>
</tr>
<tr>
<td>transmitting</td>
<td></td>
<td>Deposit fatigue</td>
<td></td>
</tr>
<tr>
<td>mountings</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Floor sections</td>
<td>Sheet steel</td>
<td>General corrosion</td>
<td>Moisture collecting under carpets and in gaps, especially along edges</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Crevice corrosion</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Deposit attack</td>
<td></td>
</tr>
<tr>
<td>Wings</td>
<td>Sheet steel</td>
<td>Pitting</td>
<td>Damage to paintwork from flying stones. Gaps and shelves where road dirt traps moisture</td>
</tr>
<tr>
<td></td>
<td></td>
<td>General corrosion</td>
<td>Gravel wearing away protective surface coating</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Crevice corrosion</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Deposit attack</td>
<td></td>
</tr>
<tr>
<td>Doors</td>
<td>Sheet steel</td>
<td>General corrosion</td>
<td>Water collecting in inadequately drained door constructions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Crevice corrosion</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Deposit attack</td>
<td></td>
</tr>
<tr>
<td>Brake pipes</td>
<td>Zinc-coated steel tube</td>
<td>Galvanic corrosion</td>
<td>The zinc coating corrodes exposing the thin layer of copper</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pitting</td>
<td>Galvanic corrosion occurs where there are pores in the copper</td>
</tr>
<tr>
<td>Bumpers</td>
<td>Steel with decorative</td>
<td>Pitting</td>
<td>Road dirt and exhaust fumes accelerating the corrosion process</td>
</tr>
<tr>
<td></td>
<td>chrome-nickel coatings</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Anodized aluminium</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4. Weather conditions of Chicago.
Corrosion under Paint Film

In corrosion under the paint film, metal ions dissolve at anodes (damaged points, paint film defects, abnormal spots in the paint film, etc.) and a cathodic reaction (reduction of oxygen) takes place around the anodes, sharply increasing the pH of the solution. As a result, the paint film is damaged and peeled under the action of the strong alkali.

Application of precoated sheet steel is considered as a measure against corrosion under the paint film. The work of Meguro et al. is one of the interesting studies in this field. They report that the protective action of the paint film becomes a problem on outer body panels and that galvannealed sheet steel and prepainted sheet steel are excellent from this standpoint. Some test results are presented in Fig. Few papers have been published on the process of perforation from inside. This type of perforation is an issue for future research.

Corrosion Resistance of Precoated Sheet Steel in Unpainted Condition

Oka et al. related the corrosion resistance of zinc-alloy-coated sheet steel to the stability of the Zn(OH)₂ film formed on the zinc alloy coating. They described that the change of Zn(OH)₂ into ZnO is retarded by the addition of such alloying elements as aluminum, magnesium, nickel, cobalt and manganese and that even when ZnO is formed, alloying elements like aluminum magnesium, nickel, cobalt, iron and
manganese act to lower the electrical conductivity of ZnO and to enhance the corrosion resistance of the steel. This theory is extremely interesting as suggesting the development policy of zinc-alloy-coated sheet steels. The effects of these alloying elements on the stability of Zn(OH)₂ are shown in Table 3.⑧

3. Trend of Automobile Body Corrosion Protection

The Canadian Federal Government established the Canadian Anti-corrosion Code shown in Table 4 as the target quality of automotive corrosion protection and called on automakers to upgrade the corrosion protection of automobile bodies. The world’s automakers are considered to have successfully complied with the Canadian Code recently. Some manufacturers are aiming higher and striving to offer a five-year guarantee against cosmetic corrosion and a ten-year guarantee against perforation corrosion in 1985, for example.⑨

Against this background, carmakers are systematically pushing corrosion control measures in all aspects from the adoption of corrosion-resistant steel sheets to the improvement of chemical treatment and painting to the upgrading of body construction as described below:

1) Improve body construction to prevent the collection of salt and muddy water that cause automobile corrosion
2) Apply wax and sealer to prevent the entrance of salt and muddy water—largest factors responsible for corrosion
3) Heavily coat easy-to-corrode parts with suitable paint, such as zinc-rich paint
4) Change the phosphating method from spray phosphating to dip phosphating
5) Adopt cathodic electrodeposition primer of excellent performance as undercoat
6) Adopt highly corrosion-resistant materials, such as precoated sheets.

These measures are shown in Table 5. Substantial progress has been made against perforation corrosion through the efforts of automobile-related industries, but more effective measures are urgently required against cosmetic corrosion.

Figure ⑩,⑪ shows the changes in the production of passenger cars in Japan and the usage ratio of precoated sheet steels. These precoated sheet steels are chiefly galvannealed steel, Zincrometal and electro-galvanized steel and are shown to have suddenly increased in usage since 1977. These statistics are all

Table 3. Zn(OH)₂ stabilizing elements.

<table>
<thead>
<tr>
<th>Rust composition</th>
<th>Element added</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-rust</td>
<td>Fe Al Mg Ni Co Mn</td>
</tr>
<tr>
<td>Zn(OH)₂</td>
<td>- - + + + + + +</td>
</tr>
<tr>
<td>ZnO</td>
<td>+ + - - - - + +</td>
</tr>
<tr>
<td>+ : Present</td>
<td>- : Not present</td>
</tr>
</tbody>
</table>

Table 4. Canadian anticorrosion code.

<table>
<thead>
<tr>
<th>Model year</th>
<th>Required corrosion resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No outer panel corrosion</td>
</tr>
<tr>
<td>1978~1980</td>
<td>At least 1 year or 40,000 km</td>
</tr>
<tr>
<td>1981 and after</td>
<td>At least 1.5 years or 60,000 km</td>
</tr>
</tbody>
</table>

Table 5. Progress of automobile body corrosion protection system.

<table>
<thead>
<tr>
<th>Year</th>
<th>1970</th>
<th>1975</th>
<th>1980</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design of body construction</td>
<td>Construction to allow no collection of salt and muddy water, reduction in number of closed and narrow parts, improvement in underbody construction</td>
<td>● Improvement in throw of chemical conversion coating and electrodeposition primer (current holes, water drain holes, air vent holes)</td>
<td>● Application of wax and sealer</td>
</tr>
<tr>
<td>Painting technology</td>
<td>Anodic primer ED</td>
<td>Cathodic primer ED</td>
<td>Chemical conversion coating ● Spray process ● Slipper dip process Dip process</td>
</tr>
<tr>
<td>Adoption of precoated sheet steel</td>
<td>Rapid increase in Zincrometal usage</td>
<td>One-side galvanized steel+Zincrometal</td>
<td>Zinc alloy electroplated steel (particularly in Japan)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Positive action against cosmetic corrosion (Ultrasmooth of Armco, etc)</td>
<td></td>
</tr>
</tbody>
</table>
concerned with compact and subcompact cars. The usage ratio of precoated steel exceeds 30% in some of the automobiles of enhanced rust protection for North America and other overseas markets.

This tendency is especially conspicuous in U.S.A. where a vast corrosion environment develops in winter. The steep increase in the consumption of Zincrometal since 1975 as shown in Fig. 10[12] attests to the positive adoption of precoated sheets for corrosion protection of automobiles. Since 1975 or 1976, one-side galvanized steel with heavy coating weight has been used together with Zincrometal. In Europe, painting and wax injection are employed as main means for automotive corrosion protection, but the usage of precoated steels is on the rise.

4. Automotive Corrosion-resistant Sheet Steels

1. Properties Required and Types of Corrosion-resistant Sheet Steel

Automakers differ in opinion about the selection of corrosion-resistant sheet steels, but the following can be said:

1) Adoption of corrosion-resistant steel, like galvannealed steel that proves most effective when painted
2) Adoption of precoated steel that exhibits corrosion protecting ability in very difficult-to-paint areas or in nearly unpainted conditions. Precoated steel is subdivided into heavily zinc-coated steel and prepainted steel like Zincrometal
3) An intermediate philosophy between those described in 1) and 2) above.

Although they differ in application standards, corrosion-resistant sheet steels for automobile bodies should meet the following requirements:

(1) Corrosion-resistant performance is sufficient and compatible with the ideas mentioned above. If priority is given to painting, chemical treatability, paintability like cratering resistance and paint adhesion are important properties.
(2) Press formability is good.
(3) Weldability is good.
(4) Surface appearance is particularly good for outer panel applications.

Optimum automotive corrosion-resistant sheets should be used for specific automobile parts. Figure 11[13] illustrates application examples of corrosion-resistant sheets.

Many corrosion-resistant sheet steels are developed to satisfy the requirements (1) to (4) above. They may be classified as follows:

(1) Zinc-coated sheet steels
   - Hot-dip galvanized sheet
   - Galvannealed sheet
   - Electrogalvanized sheet
   - Zinc-alloy-electroplated sheet
(2) Prepainted sheet steels
   - Zincrometal, etc.

These types of corrosion-resistant precoated sheets are roughly compared as to their performance in Table 6.[10] Their specific characteristics are introduced below.

2. Hot-dip Galvanized Sheet Steel

Hot-dip galvanized sheet steel is the most proven precoated steel in the world and has been long used in the inner panels and structural members of automobiles.

Manufactured by the hot-dip coating process, galvanized steel with heavy coating weight can be easily obtained and can be guaranteed against perforation for as long as ten years. As the hot-dip galvanizing process was initially difficult to provide surface nature suitable for outer body panels and to produce one-side coated sheets, hot-dip galvanized steel was limited in automobile parts for which it could be successfully used. Since around 1976, when National Steel Corp. of U.S.A. started the manufacture of Unikote and Armco Inc. commenced the production of one-side galvanized sheet by the meniscus concept, galvanized sheets began to be used in large quantities for the enhanced rust protection of the inside surface of outer body panels, mainly by carmakers in U.S.A. The subsequent progress of one-side hot-dip galvanized sheet steel manufacturing processes will be discussed in detail in Chapter V. Recently, one-side hot-dip aluminized sheet steels have also been developed.[14]

Two-side hot-dip galvanized sheet steels with improved surface appearance have been developed[15,16] and are being applied for exposed automotive parts. In this way, the recent trend is toward positive action
against cosmetic corrosion.

3. Galvannealed Sheet Steel

Galvanized and then heat treated to allow the zinc coating to completely alloy with the base metal, galvannealed sheet steel is a precoated sheet product that has excellent paintability and weldability. Japanese automakers have been traditionally using galvannealed sheets, and American counterparts are beginning to use them as well, because they exhibit high corrosion resistance in combination with painting.

In general, one-side galvannealed sheets are used for large outer panels and two-side galvannealed sheets for inner panels. Recently, sheet products, which are intermediate between hot-dip galvanized and galvannealed sheets and are coated with zinc on one side and with a Zn-Fe alloy on the other, are being adopted by American carmakers to protect their cars against cosmetic corrosion for five years and against perforation corrosion for ten years.

4. Electrogalvanized Sheet Steel

Electrogalvanized sheet steel has many features, among which are good formability ascribable to the base sheet, beautiful appearance suited for outer panels and ease of one-side coating. On the other hand, it is not satisfactory with respect to corrosion resistance in the painted condition, as indicated by susceptibility to blistering.

As the corrosion environment of automobiles increases in severity, sheets with heavy zinc coating weight are required to provide sufficient corrosion resistance. It is disadvantageous in terms of manufacturing cost to produce sheets with heavy zinc coating weight by the electroplating process and for this reason, electrogalvanized sheets are being replaced by other precoated sheet products. The Carosel process developed by U.S. Steel Corp. of U.S.A., however, can electrogalvanize a heavy zinc coating of 15 μ (equivalent to G90) per side^19 and sheets electrogalvanized by this process are accepted by the country’s automobile industry.

5. Zinc Alloy-electroplated Sheet Steel

A zinc alloy-electroplated steel is the sheet product that has electrogalvanized steel’s problems of poor paintability and high cost with heavy coating weight solved by providing high corrosion resistance with light coating weight through addition of alloying elements to the zinc coating while utilizing the advantages of the electroplating process.

Zinc alloy-electroplated sheet steels have been recently developed, mainly in Japan. Table 7 lists the zinc alloy-electroplated sheet steels that are now under development or already manufactured commercially in Japan. Of these steels, the single-layer Zn-Ni alloy coated steel and the Zn+trace Co+trace Cr alloy coated steel are aimed at improving corrosion resistance by adding alloying elements to the zinc coating. The Zn–Fe alloy coated steel is designed to

<table>
<thead>
<tr>
<th>Press formability</th>
<th>Cold-rolled</th>
<th>Hot-dip Zn coated</th>
<th>Hot-dip Zn-Fe coated</th>
<th>Zn-Fe electroplated</th>
<th>Zn-Ni electroplated</th>
<th>Zinc-rich paint coated</th>
<th>Organic composite coated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weldability</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
</tr>
<tr>
<td>Corrosion resistance in unpainted condition</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
</tr>
<tr>
<td>Corrosion resistance in primer ED condition</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
</tr>
<tr>
<td>Corrosion resistance in top-coated condition</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
<td>⊘</td>
</tr>
<tr>
<td>Coating weight or thickness</td>
<td>—</td>
<td>90 g/m²</td>
<td>45 g/m²</td>
<td>20 g/m²</td>
<td>20 g/m²</td>
<td>13 μm</td>
<td>10 μm</td>
</tr>
</tbody>
</table>

SST: salt spray test, CCT: SST+cooling-heating cycle test, D & D: dip and dry test
Overall evaluation of rust and blister
◎ Very good, ○ Good, △ Slightly poor, × Poor

<table>
<thead>
<tr>
<th>Zinc alloy electroplated sheet steel</th>
<th>Steelmaker</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-Ni base</td>
<td>Nippon Steel Corp., Sumitomo Metal Industries, Ltd., Kawasaki Steel Corp.</td>
</tr>
<tr>
<td>Zn-Fe (single layer or two layers)</td>
<td>Nippon steel Corp., Nippon Koken K.K.</td>
</tr>
<tr>
<td>Zn(Zn-Ni, Zn-Cr/Zn-Ni, Zn–Fe/Zn-Ni (two layers)</td>
<td>Kobe Steel, Ltd.</td>
</tr>
<tr>
<td>Zn+trace Co+trace Cr</td>
<td>Nippon Koken K.K.</td>
</tr>
</tbody>
</table>
obtain performance equal to or better than galvannealed steel has. Of deep interest are two-layer zinc alloy coated sheets aimed at higher corrosion resistance. The two-layer Zn–Cr/Zn–Ni alloy coated steel is intended to further increase corrosion resistance, and the two-layer Zn–Fe alloy coated steel and the Zn/Zn–Ni alloy coated steel are designed to upgrade paintability as well as to enhance the corrosion resistance of the alloy coating itself. For the Zn/Zn–Ni alloy coated steel, the upper layer of pure zinc applied to a coating weight of about 3 g/m² improves the adhesion of cathodic electro-deposited primer after warm water immersion. In the case of the two-layer Zn–Fe alloy coated steel and Zn–Fe/Zn–Ni alloy coated steel, an upper layer of Zn–Fe alloy coating with a high Fe content has enabled: (1) formation of alkali-resistant chemical conversion coating; (2) prevention of craterform defects in the cathodic primer being electro-deposited; and (3) improvement in the wet adhesion of the cathodic electrodeposited primer film. Coupled with the protective action of the inner layer, these features help two-side zinc alloy-electroplated sheets to protect car bodies not only against perforation corrosion but also against cosmetic corrosion.

Test results of deep interest obtained for two-layer zinc alloy-electroplated sheet steels are given in Figs. 12 and 13. The zinc alloy-electroplated steels are of the light coating weight type and thus, have readily formable and weldable coatings and are expected to afford very high corrosion resistance when combined with body construction improvement and wax injection.

6. Prepainted Sheet Steel

Zincrometal is a special zinc-rich paint coated sheet steel developed for autobody corrosion protection, and is a two-layer prepainted sheet product with a Zincromet coating applied on a Dacromet coating. Zincrometal is manufactured on two-coat two-bake coating lines and thanks to ease of manufacture and good performance, is produced and used in the world.

Zinc- or zinc alloy-coated sheets and prepainted sheets represented by Zincrometal have been used to date as automobile body corrosion-resistant materials. Zinc-coated steel has an advantage of sacrificial protection, but is not sufficiently resistant to corrosion when the zinc coating is thin. Prepainted steel, on the other hand, is low in sacrificial protection, is susceptible to rusting from film defects and to paint flaking during press forming, and does not have satisfactory weldability. In this way, both zinc-coated and paint-coated sheets each have improvements to be made.

Recently, a new type of prepainted sheet is being developed in Japan to make up for these disadvantages of conventional products. It is an organic composite-coated sheet steel that has an improved paint applied on a thin Zn–Ni alloy-electroplated sheet. The effects of this steel's alloy coating weight and paint film thickness are shown in comparison with Zincrometal in Fig. 14.

In Europe, Inmozinc of Inmont GmbH is famous as a new type of prepainted sheet steel.

Prepainted sheets are adopted by automakers who attach importance to the corrosion resistance of difficult-to-paint parts such as hemmed parts and enclosed parts.

5. Future Problems

For rust and corrosion protection of automobile bodies, corrosion-resistant sheet steels are widely adopted in U.S.A. and Japan, and are increasingly employed in Europe. In U.S.A., zinc-coated sheets with heavy coating weight are used as main precoated sheets, but in Japan, where corrosion resistance in the painted condition is made much of, galvannealed sheets and zinc alloy-electroplated sheets are applied more extensively than plain zinc-galvanized sheets. Generally in U.S.A., galvanized strip is phosphated
and then chromated in a chromic acid bath. This practice is known to be effective in facilitating the adhesion of paint to the galvanized steel.\textsuperscript{24,25}) In Japan, the latter chromate treatment is not performed due to the problem of environmental pollution. Here may lie the reason for the difference in the selection of corrosion-resistant sheet steels between Japan and U.S.A. Therefore, efforts against cosmetic corrosion appear as Ultrasmooth of Armco Inc. and PAINT-TITE B of Inland Steel Co. in U.S.A., and develop as two-layer zinc alloy-electroplated sheet steels in Japan as already described. The directions these two trends will take are expected to be determined on the whole from various viewpoints, such as higher strength and better formability and weldability required of future automotive steel sheets.

Another important point as regards the development of automobile body corrosion-resistant sheet steels is the quantitative clarification of properties required of such materials. In this respect, it is desirable that automakers have their corrosion control ideas based on common premises. If a common corrosion test method is universally employed at least for corrosion-resistant steel sheets in the automotive industry, the development of new corrosion-resistant materials will be encouraged greatly.

III. Precoated Sheet Steels for Fuel Tanks

The fuel tank is an important component indispensable for the automobile to run safely and smoothly. Fuel tank material must meet the following quality requirements:

1. It is chemically stable against the fuel and does not form corrosion products that may plug the fuel line.
2. It is highly resistant to corrosion in the severely corrosive environment where it is subject to the attack of salt, muddy water and flying gravel.
3. It can be easily fabricated to make a strong fuel tank.

1. Fuel Tank Materials

Terneplate,\textsuperscript{26}) which is a sheet steel hot-dip coated with an alloy of lead and tin or terne, combines the high strength of the steel with the excellent corrosion resistance and formability of the Pb–Sn alloy and is a major material for fuel tanks. Fuel tanks made of terneplate rarely develop pinhole corrosion on the inside due to water trapped in the fuel, but corrosion products are not large enough to plug the fuel line. Fuel tanks are exposed to severe environments where their outside surfaces are subjected to the impact of flying gravel and sand and to the deposition of salt and muddy water. The Pb–Sn alloy is relatively soft, tough and strong against damage, so that the fuel tank does not severely corrode nor break to allow the fuel to spill. The good weldability and solder-ability of terneplate also facilitate the manufacture of fuel tanks.

Other fuel tank materials include electrogalvanized sheet steel, aluminum and plastics. Electrogalvanized steel is less expensive than terneplate and less harmful to the health of people, but is used less, because it is likely to produce white rust composed of zinc carbonate on the inside of the fuel tank and to plug the fuel line. Aluminum is effective in reducing the weight of fuel tanks, but is difficult to join or otherwise fabricate to make fuel tanks and is thus used on limited types of automobiles. Plastic fuel tanks made of high-density polyethylene are used for special automobiles and some passenger cars in U.S.A. and Europe, because of lightweight and freedom from corrosion, but are not widely spread in the world.

Although various materials are applied for fuel tanks as described above, terneplate has the best cost performance and is used most for fuel tanks in the world.\textsuperscript{28})

2. Terneplate Manufacturing Technology

The skyrocketing of tin price in the 1970s compelled terneplate manufacturers to take countermeasures. The tin content of terneplate, which had been 14 to 15\% before the steep rise of tin price, had to be lowered to 10\% or less, and the development of low-tin terneplate became a critical problem.

To manufacture pinhole-free terneplate, it is necessary to form an Fe–Sn alloy layer at the interface between the terne coating and the base steel, as is commonly known. Decreasing the tin content makes the effective Fe–Sn alloy layer incomplete and lowers the performance of the terneplate. To make up for this disadvantage, various approaches were made in the manufacture of low-tin terneplate, such as intensifica-
tion of strip pickling prior to fluxing, selection of optimum flux and addition to the terne coating bath of alloying elements that easily combine with iron. These terneplate manufacturing practices, however, had many problems, such as reduced production efficiency and insufficient corrosion resistance.

Recently, a new low-tin terneplate manufacturing technology, called the nickel preplating process\(^\text{\textsuperscript{29}}\) and capable of solving the technological problems mentioned above, was developed in Japan. In this process, strip is first electroplated lightly with nickel, which readily reacts with the Pb–Sn alloy, and is then coated with terne in a 8% Sn–Pb alloy bath. A fine-grained and tight Ni–Sn alloy layer is formed between the base steel and the terne coating, as shown in Photo. 2. The Ni–Sn alloy layer is effective in preventing the occurrence of pinholes and improving the adherence of the terne coating to the base steel. Since this process shortens the duration of the acid pickling step, high line speed is realized.

The electroplating process developed in West Germany for manufacturing low-tin terneplate\(^\text{\textsuperscript{30}}\) is also noteworthy. Under this method, fluoborate is used in the coating bath and strip is coated with a 7% Sn–Pb alloy on one side or two sides at high current density. The electroplated terne coating is claimed to be uniform, free from pinholes and highly corrosion resistant despite relatively thin coating thickness.

As for the protective effect of low-tin terne metal against salt-induced corrosion from the outside of fuel tanks, a study\(^\text{\textsuperscript{31}}\) was made of the electrochemical corrosion behavior of terne metal in salt water. According to the study results shown in Fig. 15, the corrosion rate is low when the tin content exceeds several percent. This finding provided the basis for the composition design of low-tin terneplate.

Chemical treatment after coating is also effective in preventing the pitting corrosion of low-tin terneplate and is studied for improvement. For example, the sealing mechanism\(^\text{\textsuperscript{32}}\) of phosphoric acid treatment became clear and helped to improve the corrosion resistance of low-tin terneplate.

3. Alcohol Fuel and Future Problems

Since the 1973 oil crisis, many countries have been actively pushing the development of alternative energy sources owing to the sharp rise in oil price and uncertainty about oil supply. In the field of automobile fuel, alcohol is considered the most promising alternative fuel and ethanol-gasoline mixtures are already marketed in Brazil, U.S.A. and France.\(^\text{\textsuperscript{33}}\) Methanol is field tested as automobile fuel in West Germany and Sweden.

Due to this situation, the effect of alcohol fuel on automotive material is investigated. Alcohol is reported to be corrosive to some metals.\(^\text{\textsuperscript{34}}\) Alcohol is hydrous and when soluble salts are present, accelerates the corrosion of automobile materials. When a small amount of water is introduced into a mixture of alcohol and gasoline, phase separation\(^\text{\textsuperscript{35}}\) takes place and the alcohol concentration increases in some parts of the mixture. When in contact with metallic material under heat, alcohol is subjected to oxidation and is liable to form corrosive acids or aldehydes. As these facts indicate, alcohol is more corrosive than gasoline. In either case, the corrosion mechanism of ferrous material in gasoline–alcohol–water mixture fuel or soured fuel calls for further research, and there is the need to develop materials that can adapt for various unconventional automobile fuels.

IV. Heat-resistant Precoated Steel Sheets

The automobile section where precoated steel sheet is used as heat-resistant material is represented by the exhaust system from the engine manifold to the tail pipe.

It was a long time ago that an interest was taken in the corrosion of the exhaust system, especially the muffler, in U.S.A.\(^\text{\textsuperscript{36}}\) There is now a similar move in Japan.

Muffler corrosion may be divided into external surface corrosion that results from the effect of rainwater, mud and deicing salt spread on the road surface to Fig. 15. Corrosion rates of various terne alloys in 5 % NaCl deaerated, 25°C.
prevent freezing and into internal surface corrosion that is caused by heating and condensation over a wide temperature range, as shown in Fig. 16.\textsuperscript{37}

Automakers select suitable materials for this application according to automobile models and parts by considering these corrosion factors as well as forming degree and cost. As shown in Fig. 17,\textsuperscript{38} it is a common practice to use stainless steel sheet on the high-temperature side of the exhaust system and to use different types of precoated steel sheet in combination on the low-temperature side. Of these materials, this chapter deals with aluminized steel sheet that belongs to the classification of heat-resistant material and for which many proposals have been made in recent years.

Characteristics of aluminized steel have been already introduced by many researchers. Oxidation weight gain at high temperatures, a typical property of aluminized steel, changes little up to 500 °C, as shown in Fig. 18.\textsuperscript{38} This is the reason why aluminized steel sheet is preferentially used as material for the exhaust system.

As exhaust systems advanced in terms of exhaust gas emission control, sound insulation, heat insulation, cost savings and other factors involved, the use of aluminized steel sheet came to be also specified for parts operating at over 500 °C, and various proposals were put forward to meet this demand.

One of such developments is an aluminized sheet steel with a suitable amount of titanium added to the base metal in order to ensure durability at 815 °C and to provide resistance to repeated heating and cooling.\textsuperscript{39,40} The oxidation weight gain of the steel is shown in Fig. 19, which suggests that the steel is applicable to parts operating at considerably high temperatures.

A material that features mechanical strength at over 540 °C is an aluminized sheet steel with niobium added to the base metal.\textsuperscript{41} Its high-temperature strength is shown in Fig. 20 as representative property. Its use is advanced for mufflers, support brackets and support straps to take advantage of this characteristics.

In Japan, aluminum sheet steels with excellent high-temperature properties imparted by adding an optimum amount of titanium\textsuperscript{42,43} or titanium and...
chromium\textsuperscript{43}) to the base metal are developed and already put on the market. As for the effect of titanium addition, noted most among the processes proposed, the presence of titanium eliminates carbon in solid solution in the steel. This is considered to facilitate the diffusion of aluminum and form not Fe-Al intermetallic compounds but Fe-Al solid solution, thereby retarding the flaking of the aluminum coating at elevated temperatures.

It is reported that of metal-coated steels, an Al-Zn alloy-coated steel is suited for automotive exhaust systems.\textsuperscript{44} The results of over three years of field test are given in Table 8. The Al-Zn alloy-coated steel outperforms the galvanized steel and is noted as a precoated sheet product that falls between the aluminized steel and galvanized steel in the application temperature range.

Various heat-resistant precoated sheet steels have been applied to automotive exhaust systems as described above. Particularly, aluminized sheets have been adopted for all parts of the exhaust system and substantially prolonged their service life.

In line with these moves on the part of steelmakers, automakers have been carrying out various studies.\textsuperscript{37} These efforts have been directed to the determination of how to make up for weak points of aluminized steel, such as the damage which the aluminum coating invariably sustains during press forming, bending and welding and the presence of cut edges. Methods to prevent galvanic corrosion, crevice corrosion, exhaust gas condensation, etc., are under consideration.

Given the application of precoated sheets with high-strength steel or low-alloy steel used as the base metal as a result of thickness reduction, both steelmakers and automakers will have to clarify service properties required and accordingly perform research and development on steel types, coating conditions and application techniques so as to establish optimum exhaust systems for specific automobiles while working in closer cooperation than ever.

V. Progress of Precoated Sheet Steel Manufacturing Processes

Continuous sheet steel coating processes—hot-dip galvanizing, electroplating, and painting—have been very rapidly developed and commercially applied to meet diversifying needs for automotive precoated sheet steels.

1. Hot-dip Galvanizing Process

1. Improvement and Homogenization of Product Quality

Coating weight control by gas wiping has increased the line speed to a level of 200 m/min, permitted a free selection of light to heavy coating weights and enabled the manufacture of hot-dip galvanized steel with reduced variations in coating weight. That is, computer control of operating conditions, such as wiping pressure, and coating weight measured with a coating weight gage has allowed coating weight control with high accuracy.\textsuperscript{45,46}

As line speed and capacity increase, in-line annealing furnace heating capacity also increases, resulting in a length of as much as 200 m for a conventional horizontal furnace. It has been made clear that adoption of a vertical annealing furnace offers many advantages, among which are a substantial space savings, elimination of surface defects arising from furnace hearth rolls and improvement in coating adherence by the better strip surface cleaning action by the furnace atmosphere.

The quality properties especially required of hot-dip galvanized automotive sheet are improved surface appearance, surface smoothness and reduced dross deposit. Blanketing the wiping nozzle and pot bath surface with a nitrogen atmosphere is effective in suppressing the occurrence of dross. This nitrogen gas seal can decrease the deposit of dross on the product surface and improve the surface smoothness of the product. A representative example of such developments is the Ultrasmooth process developed by Armco Inc. of U.S.A. Although it is coated on two sides, the sheet steel hot-dip galvanized by this process is about to be used in U.S.A. for outer body panels to meet most stringent quality requirements.

Mechanical properties are an important group of sheet steel properties and automotive sheet steels are required to have a wide range of mechanical properties. It is very difficult to obtain various properties as required on a hot-dip galvanizing line equipped with a continuous annealing furnace. Recent years
have seen a marked advance to be made in property improvement through development of steels for continuous annealing grades and research of annealing heating cycles. When applying an optimum heating cycle to an actual operation, it is of utmost importance to accurately measure the strip temperature and to control annealing furnace combustion and cooling on the basis of the strip temperature measurement. Conventional strip pyrometers has no function of automatically compensating for the change in the emissivity \( \varepsilon \) of strip and did not perform satisfactorily. A new pyrometer, called the TERM pyrometer (Temperature and Emissivity measurement by Reflection Method), which can automatically compensate for the emissivity of strip, has been developed,47) making it possible to accurately and continuously measure the temperature of strip at the exit of the non-oxidizing furnace where its emissivity is particularly unstable. Figure 21 is a conceptual diagram of the TERM pyrometer and Fig. 22 shows an example of strip temperature control by the TERM pyrometer.

2. One-side Hot-dip Galvanizing Processes

As the need for automotive corrosion-resistant steel sheets has mounted, many one-side galvanized sheet steel manufacturing processes have been applied commercially after energetic research work. These processes may be roughly classified as follows:

1. Removal of zinc coating on one side:
   The zinc coating on one side of two-side galvanized steel may be removed by mechanical grinding47) or electrolytic stripping.48) These methods were practically applied first.

2. Masking:
   A stop-off film that does not react with molten zinc is formed on the strip side not to be galvanized before the strip is run through a plating pot and galvanized on the other side. The stop-off film may be formed by applying a stop-off agent or oxidizing the strip surface.

3. Supply of molten zinc to one side only:
   Molten zinc is supplied to only one side of strip. This method is subdivided as follows:
   (i) The position of the strip surface relative to the zinc bath surface is controlled with extreme accuracy, so that the molten zinc is deposited on the strip by its surface tension.
   (ii) The molten zinc is given motion, raised and deposited on the strip.
   (iii) The molten zinc is lifted from the bath surface by a revolving roll and coated on the strip.
   (iv) The strip surface not to be galvanized is mechanically covered to prevent contact with the molten zinc.49)

   Of the commercially applied processes and technologically noteworthy processes, representative pro-
cesses are described below.

For the method of forming a stop-off film in (2) above, selection of an optimum stop-off agent is important. The stop-off material to be used must have the necessary qualifications of masking performance, coatability, heat resistance, strippability and ability to ensure soundness of the strip surface after its removal, among other things. One steel maker\textsuperscript{50} has proposed a water slurry that has titanium or aluminum oxides or hydroxides added to a water glass-alkali-H\textsubscript{3}BO\textsubscript{4}-MgO system, while another steel maker\textsuperscript{51} has proposed a two-layer stop-off film with an inner coating of Mg\textsubscript{3}PO\textsubscript{4}-SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-Na\textsubscript{2}SiO\textsubscript{3} water slurry and an outer coating of special masking agent of low wettablility by molten metal. The former stop-off agent is used for galvanizing and the latter for aluminizing.

The method (3)-(i) is called the meniscus concept\textsuperscript{52} and has been developed and commercially applied by Armco Inc. of U.S.A. The process is schematically illustrated in Fig. 23.

The method (3)-(ii) uses an electromagnetic pump, molten metal pump or ultrasonic vibrator as the source of power. In either case, injection nozzle shape is designed to supply molten metal to the side to be coated uniformly over the width and length of strip even as changes occur in line speed, strip width and other variables and to deposit no molten metal on the other side. The jet flow pump process\textsuperscript{53} is schematically illustrated in Fig. 24.

The method (3)-(iii) is an improvement on the conventional roll coating process for prepainted galvanized sheet etc. and is schematically shown in Fig. 25.\textsuperscript{6} This process has ingenuity exercised in the selection of coating roll material and in the prevention of transfer of scum and dross from the pot molten metal surface to the strip.

For each of the processes mentioned in (3) above, the atmosphere of the one-side galvanizing section must be carefully controlled and a pickling unit is required to remove the oxide film of the uncoated side. Since these processes basically differ from two-side galvanizing in the principle of coating, conversion between one-side and two-side coating operations must be easily made in a short time if the line is a combination one-side and two-side galvanizing line.

2. Electrogalvanizing Process

1. Progress of Measurement and Control Systems

Unlike conventional single-metal plating, single-and two-layer zinc alloy-coated sheet steel manufacturing processes called for new techniques, such as for establishing plating solution conditions and controlling coating composition. Accurate control of these processes has been made possible by the development of sensors and the advancement of controllers.

The operating factors that affect the composition of the electrodeposited coating include the temperature and pH of electrolyte, concentration and ratio of metal ions, current density, and line speed. A strict control of these factors can minimize variations in alloy coating weight and composition. A zinc alloy electroplating operation control system is schematically illustrated in Fig. 26.\textsuperscript{54}

2. Efficient Electrolytic Process

Representative of a new family of electrolytic processes is the Carousel (consumable anode radial one-side electrolytic) process U.S. Steel Corp. developed for the electrogalvanizing of one side of strip. The Carousel process features electric power savings by reduction in interelectrode distance, no throw around to the side not to be coated and large electrolytic capacity, among other things.

Electroplating with a small number of cells in a short time calls for a high current density. In such
a case, the interelectrode distance must be shortened to suppress the resultant voltage rise (increase in power cost), and the diffusion layer must be reduced to improve the metal iron supply speed.

To increase the limiting current density, increasing the electrolyte flow velocity is effective. New plating cells of the jet type that force the electrolyte against the strip are developed in place of conventional electroplating methods under which the electrolyte is relatively stationary like conventional vertical cells. Figure 27\(^5\) shows a high speed cell (jet cell) that throws the electrolyte in a counter-flow manner against horizontally traveling strip. The cell is capable of a high current density of 150 A/dm\(^2\) in electrogalvanizing. In the cell of Fig. 28,\(^6\) the use of a dummy anode permits the uniform distribution of electrolyte flow velocity between the anode and strip and helps to achieve the same current density of 150 A/dm\(^2\). In the anode center injection cell of Fig. 29,\(^7\) the electrolyte is injected through the center of the anode against the strip and a current density of 240 A/dm\(^2\) and a power savings of about 30 % are accomplished. These plating cells not only enable high-current density operation, but also contribute greatly to the composition control of single- and two-layer zinc alloy coatings by uniform electrolyte flow velocity. Also under study is an electrolytic cell\(^8\) capable of preventing strip vibration by static pressure from electrolyte injection and keeping the interelectrode distance constant and minimum.

**VI. Conclusion**

Automotive precoated sheet steels have been classified into groups of body corrosion-resistant steel, fuel tank steel and heat-resistant steel, and sheet steels representative of each group or expected to grow in the future have been described in this report. Selection of body corrosion-resistant steel sheets greatly varies among countries or automakers, although ultimate targets are virtually the same. In Japan, measures for protecting automobile bodies from corrosion came to be earnestly taken only a few years ago and the time has now arrived for making a first-round evaluation of such automobiles on the market. Along with the elucidation of corrosion mechanisms involved and the establishment of evaluation methods, the development of a corrosion protection system based on such findings and composed of body design, precoated steel, and painting and pretreatment is necessary. In this respect, closer joint work with automakers is considered to assume greater importance. Faced with a stiff challenge from competitive materials like plastics, steelmakers intend to spare no effort to develop steel products that meet needs while making the best use of excellent properties of steel sheets.

The quality stabilization of terneplate, a chief material for automotive fuel tanks, has been described. A future problem would be the development of material resistant to alcohol fuel. This development work has just begun and should be observed in expectation of successful results.

Of precoated sheet steel manufacturing processes, recent advances in hot-dip galvanizing and electrogalvanizing processes have been taken up. Thanks to the development of sensors and control techniques, these processes have radically changed from conventional coating concepts and have come to be able to meet more exacting quality requirements from users.
How to comply with a diversification of product types while maintaining high efficiency would be a problem. Prepainted sheet steels and their manufacturing processes have not been touched upon here. Given the potential labor and energy savings achievable by users, this field is expected to expand as automotive steel sheets.

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Review