# Advanced Coated Steel Sheets with Excellent Functions to Satisfy Ecological Requirements

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*A range of new coated steel sheets has been developed in response to customer demand for superior performance. This paper describes a number of these new, coated steel sheets developed by NKK, designed specifically for automobile bodies, electrical appliances, construction, and can-making. Chromium-free coated steel sheets aimed at satisfying ecological requirements are also introduced.*

## 1. Introduction

The history of NKK's coated steel sheet production begins with the commissioning in 1961, of the No.1 CGL (Continuous Galvanizing Line) at the Mizue area of the Keihin Works. In 1967, an ETL (Electrolytic Tinning Line) was commissioned. Since then and up to the early 1990's, CGL Nos.2, 3, and 4 as well as CCL (Coil Coating Lines) Nos.1, 2, and 3 have been gradually constructed in the Mizue area. In the Fukuyama Works, the first coated steel production line was No.1 EGL (Electrolytic Galvanizing Line) constructed in 1966. This was followed by the commissioning of ETL No.1 and CGL No.1 in 1971. Since then EGL Nos.2, 3, 4, and 5, CGL Nos.2 and 3, and TFS (Tin-Free Steel) lines Nos.1 and 2 have also been constructed there. The Fukuyama Works is now NKK's main coated steel sheet production plant.

NKK's steel sheets are mainly used in industrial applications such as automobiles, electrical appliances, construction, and can-making. In response to increasing customer demand in these sectors for corrosion-resistant, high-quality steel sheets that can perform various functions at high levels, NKK has developed and marketed a wide variety of coated steel sheets. This paper reports on various coated steel sheets developed and marketed by NKK to meet the diversified requirements of customers producing automobiles, electrical appliances, construction materials, and steel cans. The paper also outlines the technological advances made by NKK in producing environmentally friendly coated steel sheets.

## 2. Coated steel sheet research and development

### 2.1 Coated steel sheets for automobiles

In the 1960's, automobile body corrosion resulting from de-icing salt, used increasingly to secure winter road traffic, became a serious social problem in the heavy snowfall regions of North America and Northern Europe. The Canadian government issued anti-corrosion standards for automobiles in 1976. As a result, automobile manufacturers have started providing anti-corrosion guarantees on the automobiles.

The guarantee period was extended year by year in response to increasingly severe anti-corrosion codes and targets (see **Fig.1**). In recent years, European and some other automobile manufacturers began offering 12-year guarantees in order to promote the recycling of used vehicles[1].

Road de-icing salt use in Japan is also increasing each year. In addition, new car sales tend to be strongly affected by the market value of used cars. As a result, Japanese automobile manufacturers have started providing automobiles for the domestic market with anti-corrosion specifications similar to those cars intended for export.

In light of the increasing social demand for corrosion resistant auto bodies, NKK has developed and marketed unique coated steel sheets for automobiles. This section of the paper introduces the new world-leading products developed by NKK as well as the technologies utilized in the production of these products.

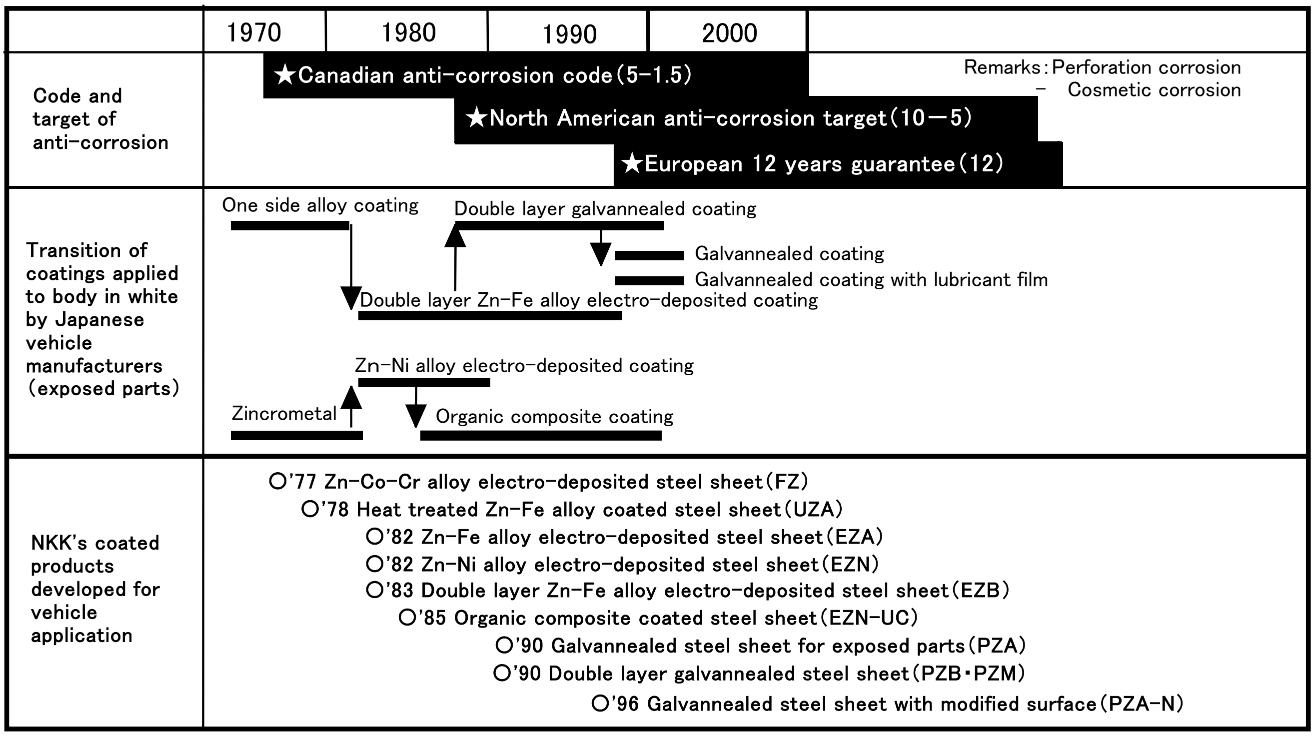


**Fig.1 NKK's coated products for vehicle application**

### 2.1.1 Electroplated zinc-coated steel sheets: NKFZ, UZA, EZA, EZB

In the second half of the 1970's, NKK developed and marketed two world-first types of electroplated zinc coated steel sheets for use in automobile manufacture. These were named NKFZ and UZA. NKFZ is a Zn-Co-Cr alloy electroplated steel sheet, which has a Zn coating layer that contains co-deposited Co and Cr, and exhibits markedly increased corrosion resistance without painting[2]. UZA is a Zn-Fe alloy-coated steel sheet obtained by heat-treating the electroplated steel sheet UZ. This product has excellent paintability and has increased levels of corrosion resistance after painting.

These products are superior in terms of being formed in presses and welded particularly when compared with hot-dip galvanized steel sheets that were being widely used in Europe and North America around the time when NKFZ and UZA were first put on the market. These new products were designed to meet the needs of domestic automobile manufacturers in particular, with their emphasis on the need for efficiency in automobile production. These new products also have a large significance in that they triggered the development of next-generation Zn-Fe and Zn-Ni based automotive Zn-coated steel sheets, products that prospered in the 1980's.

Following the successful development of UZA in which a Zn-Fe alloy layer was obtained by heat-treating the electroplated steel sheet UZ, the development target was set on a technology that allowed the direct production of a Zn-Fe alloy layer in the EGL process. As a result, EZA[3] and EZB were developed. EZA is an electroplated steel sheet with a Zn-Fe alloy coating layer in which Fe is contained at 15-25%. This product exhibits corrosion resistance equivalent to UZA after painting.

Initially, main application of these corrosion resistant Zn-coated steel sheets was as auto panels in positions not visible to the consumer, and one-side-coated steel sheets, which had a Zn coating only on the unpainted surface, were used as exposed panels. The reason for this is because the Zn-coated surface tended to cause a particular painting defect (ED cratering) when a primer was applied by cationic electro-deposition. EZB is a double-layer-coated steel sheet produced by adding a high Fe-content Zn-Fe alloy layer as an upper coating layer to EZA. It is characterized by excellent wet adhesion of primers during the cationic electro-deposition process and thus has an excellent anti-ED cratering property as well as high corrosion resistance (**Fig.2**)[4]. It is noteworthy that the revolutionary concept[5] of applying double-coating layers on a steel sheet, each layer fulfilling a different role, had a substantial effect on the future direction of automotive coated steel sheet development. The commercialization of the double-layered EZB coincided with the period when automobile manufacturers were converting from conventional one-side-coated steel sheets to double-side-coated steel sheets in order to comply with the increasingly strict anti-corrosion standards. The excellent anti-ED cratering property achieved by EZB made the double-side-coated steel sheets suitable as exposed panels of automobiles.

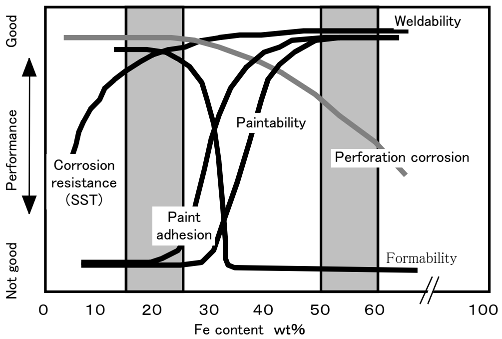


**Fig.2 Relationship between performance and iron content in Zn-Fe coatings**

### 2.1.2 Thin organic composite-coated steel sheet: EZN-UC

Zincrometal, produced by applying a Zn-rich paint to a chromate-treated cold rolled steel sheet, was first adopted in the 1970's as a steel sheet for use in automobiles. Due to its excellent corrosion resistance before painting, Zincrometal was expected to be advantageous when fabricating components that have enclosed structures and are difficult to make corrosion resistant by electro-painting. However, various problems surfaced with the use of Zincrometal such as paint exfoliation at press forming and the resultant degradation of corrosion resistance, as well as difficulty with welding.

NKK intended solving these problems and further enhancing corrosion resistance. Applying a completely new concept, NKK became the first in the industry to successfully develop a thin organic-silicate composite-coated steel sheet. The newly developed product was marketed in 1985 under the trade name, EZN-UC[6]. As shown in **Fig.3**, it is characterized by a high level of corrosion resistance, which was achieved at the same time as a dramatic improvement in press formability and ease of welding. These improvements were achieved by applying a thin organic layer of about 1μm thick. In developing this product, three aspects were combined: (1) the organic-silicate composite coating acting as a barrier; (2) the chromate coating forming a passivation layer; and (3) the corrosion prevention effect of the Zn-Ni electro-plated film. This product later led to the development of EZN-UC-II that allows low temperature curing and has further enhanced corrosion resistance.

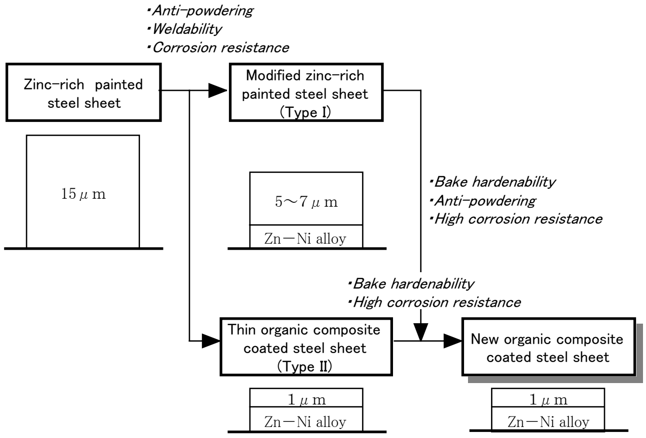


**Fig.3 Flow diagram for the development of new organic composite-coated steel sheets**

### 2.1.3 Galvannealed steel sheets: PZA, PZB, PZM

In the late 1980's, Japanese automobile manufacturers, in line with the "Big 3' 10-5-2-1 anti-corrosion target" guaranteeing no perforation for 10 years, no cosmetic corrosion for 5 years, no engine room rust for 2 years, and no undercarriage rust for 1 year, established a guideline for further enhancing corrosion resistance. Automobile manufacturers who had previously been using Zn-Fe electroplated steel sheets with a coating weight of 20 g/m$^2$ (2.8μm in coating thickness) began converting their material to galvannealed steel sheets, whose coating weight could easily be increased. These automobile manufactures typically adopted the galvannealed steel sheets with a coating weight of 60 g/m$^2$ (8.4μm in coating thickness). On the other hand, automobile manufacturers who had been using thin organic composite-coated steel sheets with a coating weight of 20 g/m$^2$ (2.8μm in coating thickness) responded to this move by increasing the coating weight of Zn-Ni alloy electroplated steel sheets to 30 g/m$^2$ (4.2μm in coating thickness).

NKK's galvannealed steel sheet, PZA, is produced by CGL using the following process. The substrate steel sheet is first reduction-annealed, and then cooled to a galvanizing temperature in the reducing atmosphere, immersed in molten zinc, and finally subjected to a heat treatment called galvannealing. The double-layer galvannealed steel sheets (PZB, PZM) are products that have a high Fe-content Fe-Zn electroplated coating layer added on PZA.

Initially, PZA posed some problems when used as exposed panels in automobiles. In order to solve surface quality problems, NKK constructed a state-of-the-art CGL (Fukuyama No.2 CGL). Various improvements in equipment and strict quality control applied throughout the operation made it possible to consistently produce products that would satisfy the surface quality requirements when used as exposed panels[7]. These technologies were also applied to Fukuyama No.3 CGL and Keihin No.4 CGL. These lines started production in 1992 and 1993 respectively. Customers in various fields hold the product from these lines in high regard.

Increased coating weight brought another problem in terms of the quality of the coating layer, which readily exfoliated and powdered at the press forming stage. It was also found that the sliding property, also at this stage, was degraded due to the structure of the coating layer.

NKK carried out basic research on the Fe-Zn alloying reaction that takes place during the process of forming the coating layer in the CGL[8]. Also, when constructing the Fukuyama No.2 CGL, various improvements were made on the equipment in order to achieve effective control of the coating microstructure and steady production. As a result, industry-leading technologies were established for producing products that consistently met the customers' requirements for quality.

The Iron and Steel Institute of Japan recognized the scientific value of this basic research, and awarded NKK the Tawara Prize.

For the purpose of further improving the press formability of PZA, NKK added a Ni-based inorganic lubricating film, and marketed it as PZA-N. Its high quality (**Fig.4**) won a high reputation from its customers. Details of PZA-N are described in Section **3**.

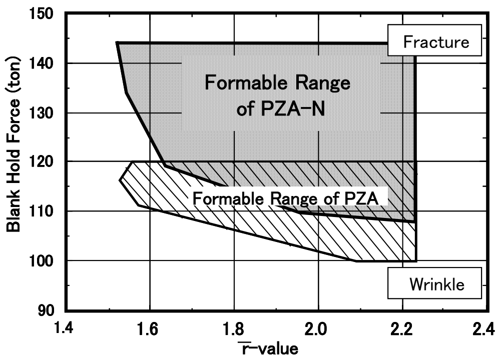


**Fig.4 Comparison of formable ranges of PZA and PZA-N**

NKK has led the industry in developing production technologies that secure a stable supply of products that precisely meet the increasingly sophisticated needs of the customers. Typical new technologies applied in the production of coated steel sheets are: iridium-oxide-coated anodes for electro-deposition; direct-fired furnaces, and high-frequency induction heating furnaces for hot-dip galvanizing. These new technologies have enabled the production of a variety of unique products.

NKK's technology of evaluating and analyzing corrosion progress by disassembling actual vehicles is playing an important role in the development of advanced coated steel sheets for automobile production, and is highly regarded by NKK's customers.

### 2.2 Coated steel sheets for electrical appliances

NKK have, in response to the need to improve corrosion resistance in electrical appliances and make them more functional, been actively developing highly functional chemical-treated steel sheets in which an extremely thin organic or inorganic coating is applied to the Zn-coated steel surface. This process is mainly intended to eliminate the need for painting the internal parts of these appliances. NKK has also been actively developing prepainted Zn-coated steel sheets. These are intended to eliminate the need for post-painting external parts.

#### 2.2.1 Highly functional chemical-treated steel sheets

Conventional chemical-treated steel sheets are produced by forming an inorganic chemical-treatment coating on the surface of Zn-coated steel sheets by phosphate or chromate treatment. In response to the need for making electrical appliances more functional, a new variety of chemical-treated steel sheets have been put onto the market. They are now available as steel sheets with improved corrosion resistance, paint adhesion, fingerprint resistance properties as well as enhanced lubricity, and color. These properties are obtained by forming an organic or inorganic coating (1 to 2 $\mu$m) on the surface of Zn-coated steel sheets[9].

(1) Development of highly functional chemical-treated steel sheets (**Fig.5**)

UZ-NX, a highly corrosion resistant steel sheet, is produced by applying the reaction-in-place chromate treatment on the surface of an electroplated Zn-coated steel sheet and forming a thin organic composite coating (acryl-epoxy-silica-based)[10]. In 1982, NKK became the first in the world to market this type of coated steel sheet[11]. UZ-NX is highly corrosion resistant and has excellent paint adhesive properties and was first used as a painting substrate in the fabrication of the outdoor components of air conditioners. Its current applications include: painting substrates for external parts of refrigerators, washing machines, and vending machines. It is also used in the fabrication of the unpainted internal parts of these appliances. UZ-NX was awarded the Ichimura Prize in 1982.

An anti-fingerprint steel, marketed in 1984, effectively suppresses the adhesion of assembly workers' fingerprints to VTRs and other AV products that would otherwise lower the market value of these products. UZ-C2 was first used in the fabrication of VTR and stereo unit rear panels. These items require an anti-fingerprint property since any fingerprints on them will be readily visible to the user. In addition, UZ-C2 is characterized by increased adhesion of silk-screen printing ink, a substance widely used on these panels. It also has a corrosion resistance equivalent to SST 100 hours (medium corrosion resistance). The dry-in-place chromate-coated steel sheet, UZ-MC, developed in 1987, has good electrical grounding properties, adequate anti-fingerprint properties, and medium corrosion resistance. It is used without painting in the fabrication of chassis and other internal parts of AV and OA products[12].

UZ-L2 is a thin, highly lubricating, organic composite-coated steel sheet developed in 1984. It is used in the fabrication of cartridge fuel tanks for kerosene room heaters and other applications that are subjected to severe press forming and must look good even after forming[13]. UZ-SL was developed in 1993 in response to the environmental degradation caused by oiling work, and the tightening up of regulations on the use of specific CFCs once widely used for degreasing (**Fig.6**)[14),15]. UZ-SL is also a thin, organic composite-coated steel sheet with excellent lubricity

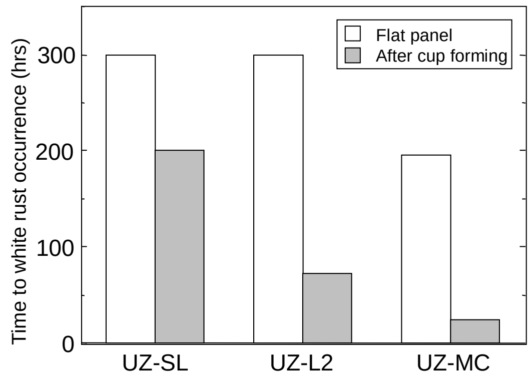


**Fig.6 Corrosion resistance of various coated steel sheets in SST**

that can be press-formed without applying lubricating oil and presents good appearance after forming. Its excellent properties are highly valued in the associated industries and UZ-SL was presented with the 1994 Technology Award of the Surface Finishing Society of Japan.

Lubricating steel sheets are characterized by high lubricity; anti-fingerprint steel sheets by excellent paint adhesion properties. Generally, these two aspects conflict with each other. Therefore, these two types of steel sheets were used separately in different applications[9]. In 1996, NKK successfully developed UZ-C3, a new organic composite-coated steel sheet that is highly lubricating while at the same time having excellent paint adhesion.

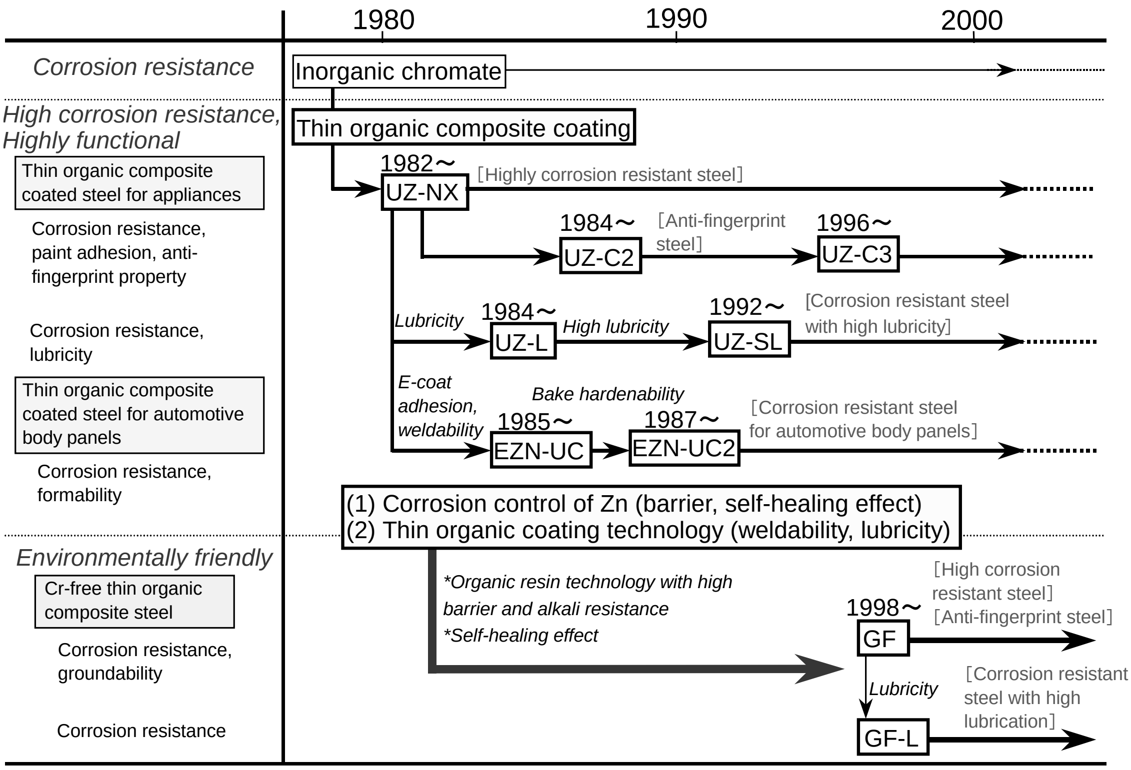


**Fig.5 History and trend shown by thin organic composite-coated steel sheets**

This means that this product can be used in a wide variety of applications[16]. This unique property was achieved by applying a special denatured ethylene resin that can increase the surface density of the polar group, thus significantly improving paint adhesion, which had previously been lowered by the lubricating agent contained in the surface layer of the conventional lubricating steel sheet[16]. UZ-C3 won the 1997 New Technology Development Award (Machinery Material & Material Processing Section) of the Japan Society of Mechanical Engineers.

(2) Corrosion control mechanism using silica

In parallel with the development of these new products, NKK carried out basic research in the field of chemically treating steel sheets. In order to improve corrosion resistance, ultra-fine silica (colloidal silica), fumed silica, or silica sol was added to the upper layer of organic resin coating of anti-fingerprint coated steel sheets and highly corrosion resistant steel sheets. Silica exhibits a corrosion resisting effect in a corrosive environment where chloride ions are present. Its corrosion resisting effect is particularly significant in a corrosive environment where dry and wet conditions are repeated cyclically[17]. This effect is considered to be attributable mainly to the phenomenon that silica promotes the generation of zinc hydroxide chloride, a substance that effectively suppresses corrosion[18]. In addition, a small amount of silica dissolves in a corrosive environment as orthosilicate, forming silicate ions and $Zn^{2+}$ ion, the latter dissolves out of the Zn-coating layer, into an insoluble salt. This acts as a barrier that contributes to the suppression of corrosion[18].

### 2.2.2 Prepainted steel sheets

Prepainted steel sheets, when used in electrical appliance manufacture, eliminate the painting process for appliance manufacturers. Its significance is also increasing in terms of environmental protection. In 1988, NKK constructed a new CCL dedicated to the production of prepainted steel sheets for electrical appliances. NKK also began marketing a high quality prepainted steel sheet for electrical appliances, NKK Excel Coat. In 1998, NKK marketed another new prepainted steel sheet, Geo-Flex. This product has a new coating that combines adequate hardness with excellent formability. The new coating was achieved by introducing a special liquid crystal compound into polyester resin. This was a world-first in combining the two conflicting properties of excellent formability and surface scratch resistance at the same time[19]. Geo-Flex was awarded the 1999 Technology Award by the Japan Coating Technology Association. NKK further successfully marketed a number of new types of prepainted steel sheets, each having a unique function. Lubi-Coat, for example, is highly heat resistant while at the same time having a non-adhesive surface. Another is the anti-bacterial prepainted steel sheet.

Generally, hexavalent chromium compound is used in primer chemical treatment and primer paint coating for prepainted steel sheets in order to increase corrosion resistance. Recently however, requests for prepainted steel sheets produced without using chromate are increasing, and chromium-free products have been marketed for applications where the corrosion resistance levels are not especially high. By applying unique chromium-free coating design, NKK developed the Chromium-free Excel Coat. This product is excellent in terms of formability and corrosion resistance. Both are required of prepainted steel sheets used in electrical appliances. This product is marketed as one of NKK's environmentally friendly steel products.

### 2.2.3 Future of coated steel sheets for electrical appliances

Due to increased concern over the global environment, makers of electrical appliances have recently begun to establish their own green procurement standards for materials used in their products. This is part of their policy of actively promoting resource recycling, energy saving, and environmental protection[20]. Some of these green procurement standards refer to hexavalent chromium and its compounds as being a harmful substance, whose use should be reduced. In response to these moves, NKK has actively developed organic-inorganic composite-treated steel sheets that are chromate-free. In 1998 NKK successfully marketed Geo-Frontier Coat, a product that has excellent corrosion resistance properties while at the same time providing high electrical conductivity. Geo-Frontier Coat is described later in Section **4**. In order to completely replace conventional chemical-treated steel sheets with chromium-free coated steel sheets, both the general purpose and high-corrosion resistant types, a difficulty needs to be solved. This is, how to achieve corrosion resistance that is equivalent, both in terms of cost and performance, to that achieved by the excellent self-healing effects of hexavalent chromium. New coating materials that have the function of supplementing the self-healing effect or provide a high barrier against corrosion need to be developed by evaluating corrosion resistance under conditions that realistically reflect the environment in which electrical appliances are actually used.

### 2.3 Coated steel sheets for construction

Materials that have longer service life are increasingly required in the construction industry in order to conserve resources and reduce maintenance work. As a result, in the field of Zn-coated steel sheets used for construction, the demand is shifting from conventional hot-dip galvanized steel sheets to more corrosion resistant Zn-Al alloy-coated steel sheets. In particular, the production of 55%Al-Zn alloy-coated sheets with or without prepainting is increasing due to excellent corrosion resistance. In partnership with NKK Steel Sheet & Strip Corporation (N3S), NKK has been developing various coated steel sheets for construction based on 55%Al-Zn alloy-coated sheets[21].

#### 2.3.1 Highly corrosion resistant 55%Al-Zn alloy-coated sheets

A highly corrosion resistant steel sheet is produced by applying a thin organic coating of 1-2 $\mu$m to a 55%Al-Zn alloy-coated sheet. This is characterized by suppressed peeling and scoring of the metal coating layer during forming and excellent corrosion resistance. The corrosion resisting effect of the thin organic coating depends on the passivation layer covering the metal coating surface and how the protection it provides is maintained in a corrosive environment. A new steel sheet, Genius, was developed by NKK. This is a 55%Al-Zn alloy-coated steel sheet with an organic-inorganic hybrid coating that exhibits improved performance over conventional organic coatings. It has won a high reputation in the marketplace due to enhanced corrosion resistance and formability[22]. A new chromium-free corrosion inhibitor was developed by NKK and incorporated into the hybrid coating originally developed for Genius. Degradation of corrosion resistance at a formed area, a shortcoming of conventional 55%Al-Zn alloy-coated sheets, improved markedly when the new coating was applied. The 55%Al-Zn alloy-coated sheet to which this new coating was applied, was marketed as Super Genius[23]. The new corrosion inhibitor used in Super Genius has an excellent self-healing capacity. In a corrosive environment, Super Genius helps corrosion resistant layers form over cracks generated in the metal coating layer during a sheet forming process, thus effectively suppressing the progress of corrosion (**Photo 1**). Corrosion resistance, improved by the chromium-free corrosion inhibitor, makes a significant contribution to enhancing the environmental compatibility of steel products. Super Genius also has excellent formability (anti-scoring property during forming) owing to the improved organic component in the coating. Since Super Genius production started in Autumn 2000, its superior properties have been widely recognized by customers and it is gaining a position as a new industry standard for 55%Al-Zn alloy-coated construction sheets.

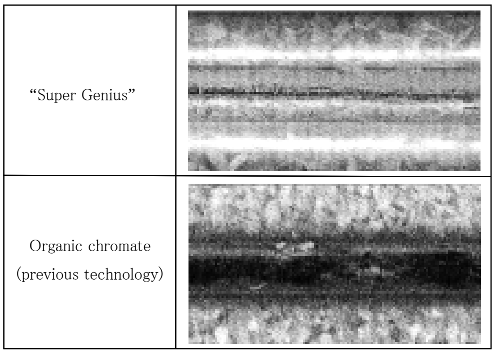


**Photo 1 Appearance of formed areas (3T bend)**

#### 2.3.2 Highly formable prepainted 55%Al-Zn alloy-coated steel sheets

Prepainted steel sheets using 55%Al-Zn alloy-coated sheets as substrates are highly resistant to corrosion, and their use in applications such as roofing and siding, is rapidly expanding. However, their metal coating layers are rather hard and tend to crack when bent. These cracks appear in upper paint coating layers as well and downgrade appearance. Also, since corrosion progresses from these cracks, it is difficult to use these steel sheets in applications where they are subjected to severe forming. NKK and NK3S planned to expand the sales of prepainted 55%Al-Zn alloy-coated sheets in the construction industry by improving its formability, and has been successful in giving high formability to the metal coating layer as well as the paint coating layer. The prepainted 55%Al-Zn alloy-coated sheet, Galflex-Color, was the first in the world to offer excellent properties in terms of both formability and corrosion resistance at the same time[24]. Its alloy-coating layer was softened to the level of a conventional Zn-coating layer by a unique structural control technology. Its paint-coating layer was also a new development and has excellent ductility and high adhesion. Thus, Galflex-Color is highly formable while maintaining corrosion resistance inherent in a 55%Al-Zn alloy-coated steel sheet (**Photo 2**). Because of its excellent formability and corrosion resistance properties, it can be formed into many versatile shapes while at the same time prolonging the useful life of construction materials. NKK has also developed other unique products based on 55%Al-Zn alloy-coated sheets that are high in quality and functionality. Among them are Skeleton-Color and Taimax. The former is characterized by beautiful patterned surfaces, the latter by excellent resistance to wear, a property in demand by users of roofing materials.

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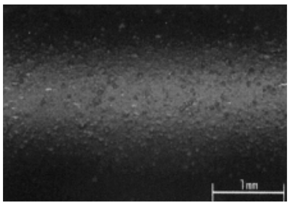
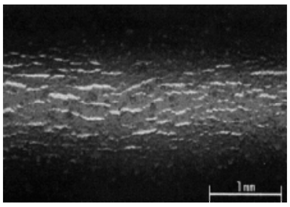
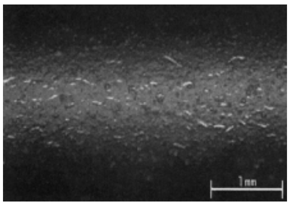
| "Galflex-Color" (New orepainted 55%Al-Zn alloy coated steel sheet) |  |
| Prepainted 55% Al-Zn alloy coated steel sheet (previous technology) |  |
| Prepainted 5% Zn-Al alloy coated steel sheet (previous technology) |  |

**Photo 2 Appearance of formed areas (3T bend)**

### 2.4 Coated steel sheets for can-making

Food and beverage cans made of tinplate and TFS (Tin-Free Steel) sheets have been widely used all over the world. These materials are now experiencing fierce competition from containers made of other materials such as aluminum, paper, and PET. Bisphenol-A (BPA) contained in paint is considered to be an endocrine disrupter, and its elimination is required by society. Under these circumstances, there is a strong demand to develop cost-competitive and environmentally friendly steel sheets for can-making. An increasing trend among steel cans over recent years is the promulgation of welded cans and plastic film laminated cans. NKK has been developing new can-making steel sheets in response to these social demands.

#### 2.4.1 Steel sheets for welded cans

Since the lap-seam welding method using copper wire, called the Soudronic welding method was developed, welded cans have been widely used. Tinplate has high speed weldability owing to the tin's properties of softness and high electrical conductivity. In order to reduce the cost of this material, NKK has been developing a surface coating technology for producing steel sheets for welded cans. Two alternative approaches were taken: one is to make the tin coating layer thinner, the other is to modify the quality of TFS.

(1) Lightly coated steel sheet: Litewel-N

By reducing the tin coating weight to approximately 1.0 g/m$^2$, LTS (Lightly Tin-coated Steel) sheet was developed[25]. However, it had problems with reduced weldability and post-painting corrosion resistance. New technologies were developed to overcome these problems. Weldability degrades when metallic tin of the amount of more than 0.1 g/m$^2$ is not maintained on the surface of the steel sheet[26]. When making a can from tinplate, paint is applied on one side or both sides of the sheet, baked, and then welded. Throughout this process, the Fe-Sn alloy layer grows, reducing the metallic tin amount accordingly. When a minute amount of Ni coating (less than 30 mg/m$^2$) is applied before tin coating, the tin-coating layer becomes 'island-like' by flow melting and the growth of the Fe-Sn alloy layer is suppressed[27]. By applying this technology, metallic tin of the amount required for high speed welding is retained on the surface even when only a small amount of tin coating is applied. The products thus produced are generally called TNS (Tin-Nickel-coated Steel)[28]. NKK developed a process for producing TNS, in which both the Ni coating and tin coating are deposited on a steel sheet in the tinning line, and marketed as Litewel-N (LTW-N)[29]. Its cross section is shown schematically in **Fig.7**. **Photo 3** illustrates the SEM (Scanning Electron Micrograph) view. In order to improve paint adhesion after painted[30] and also to improve resistance against underfilm corrosion and filiform corrosion, chromate chemical treatment was employed. Metallic chromium, about 10 mg/m$^2$, and hydrated chromic oxide of the same amount, are deposited on the surface. The presence of island-like tin is effective at increasing the resistance against filiform corrosion. The chromate-treated layer is effective at increasing the resistance against underfilm corrosion since it increases oxygen over-potential on the metal surface under the paint-coating layer, and suppresses the reducing reaction (cathodic reaction) of oxygen[29].

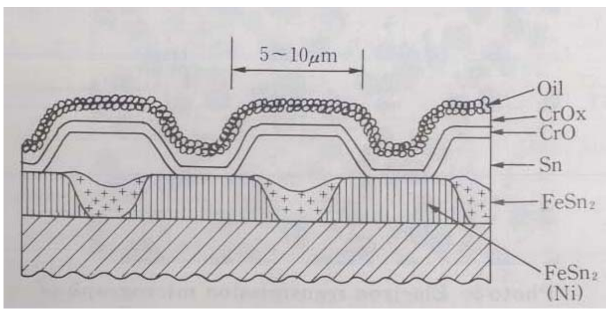



**Fig.7 Schematic cross-section diagram of Litewel-N**

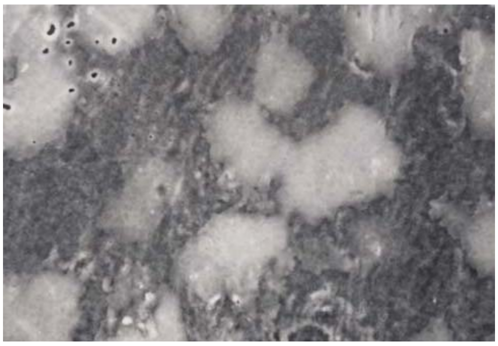


**Photo 3 Scanning electron micrograph of Litewel-N**

(2) TFS for welded cans: Britewel

A new TFS product for welded cans was developed by NKK and is being marketed under the trade name Britewel[31]. The production of this product involves accurate control of the electrolytic condition to deposit metallic chromium on the steel sheet in either granular or plate shapes. This is then covered by a hydrated oxide layer that is extremely thin compared with conventional products. When this TFS[32] product is pressurized during welding, the hydrated oxide top layer can be destroyed easily. Welding current paths are evenly formed inside the pressurized area thus suppressing the generation of whisker-like iron splash that is the cause of dust generally seen when welding a conventional TFS. This new product enabled polish-free welding of TFS for the first time in the world. It has paint adhesion and corrosion resistance levels equal to a conventional TFS, and yet can be produced at a cost lower than LTS and TNS. Its use is expanding in applications such as 18-liter cans widely used in Japan.

### 2.4.2 Plastic film laminated steel sheets

A plastic film laminated TFS was first applied to two-piece beverage cans[33]. In an effort to expand its use, it was next applied to three-piece beverage cans[34),35]. In line with increasing concern about environmental problems, its use is rapidly increasing. NKK has been developing unique laminated steel sheets that can be produced economically, thus expanding this product's use to applications other than beverage cans.

(1) Laminated steel sheet for food cans: Universal Brite

A new BPA-free can-making material that eliminates a painting process, and is applicable within existing can-making facilities, is desirable and should be developed. In response, NKK developed the first new low-cost laminated steel sheet in the world that satisfies the requirements of food cans such as easy access to contents. In terms of cost, it is desirable to apply homo-PET film. However, its extremely high speed of crystallization causes rapid crystal growth during the can-making process, and reduces the formability. As a result, it is not applicable as it is. By providing the amorphous part in the homo-PET film with the quasi-cross-linking structure, the mobility of polymer was lowered, and crystallization suppressed, thereby making DRD (draw-redraw) forming possible. Further, by optimizing the layer structure in the film after lamination, excellent formability was achieved. This was nearly equal to that of co-polymerized PET laminated steel sheets used for beverage cans.

Taking can contents out (content release property) is dependent on the level of stickiness between the content and film, and is mostly governed by the wettability of the film surface (surface energy) as shown in **Fig.8**. The content release property was evaluated by packing meat, eggs, and oatmeal in cans. Steel sheets, experimentally laminated with various types of films were formed into cans by drawing. Each content type was packed in a can, subjected to retort treatment (121℃, 90 min). The content release property was evaluated as well as the amount of content left behind stuck to the inner surface of the can.

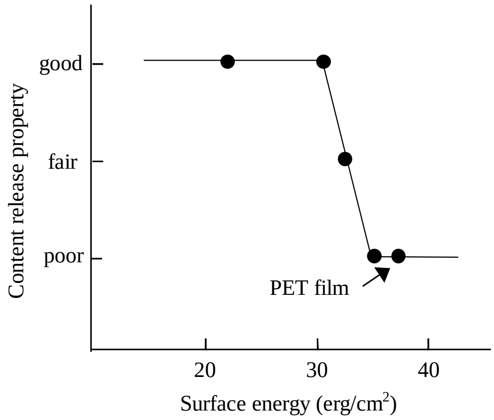



**Fig.8 Effect of surface energy on content release property**

In order to improve the content release property, the wettability between the content and PET film would need to be reduced. In other words the surface energy of the PET film would need lowering. The surface energy can be divided into two components: dispersion part and polar part[36]. The latter is correlated to the effect of the PET film's surface energy on the stickiness[37]. Focusing on the polar part of PET polymer, the film surface was depolarized. An excellent content release property was achieved by adding a minute amount of natural vegetable oil. This oil has the effect of activating the surface of the PET resin, thus affecting the polar part of the PET polymer on the film surface and lowering the surface energy.

The film structure is shown in **Fig.9**. The surface of the PET film in contact with the content has a thin layer that contains a minute amount of vegetable oil. This oil acts as a surfactant. Since this product was first marketed in the U.S., its use is expanding all over the world.

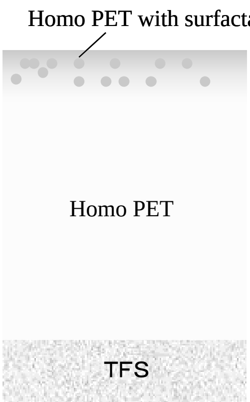



**Fig.9 Schematic cross-section diagram of Universal Brite**

(2) Laminated steel sheet for general-line cans[38)]

In the field of general-line cans, such as 18-liter cans and pail cans, the conversion from conventional painted cans to more environmentally friendly laminated cans is desirable. Various contents with a wide range of pH values, from acidic to alkaline, are packed in general-line cans. A new laminated steel sheet has been developed which applies a chemically stable PP (polypropylene) film (structure shown in **Fig.10**). The substrate is TFS, on which two layers of PP film are laminated by heat adhesion. The upper layer is made of high melting point PP due to the heat resistance necessary in the printing and baking processes.

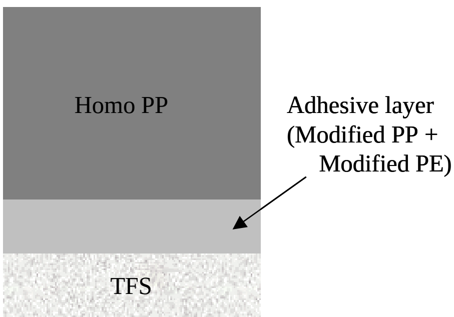



**Fig.10 Schematic cross-section diagram of laminated TFS for general-line cans**

The adhesive layer was positioned between the substrate and the PP because PP generally has poor adhesive qualities. This adhesive layer is a mixture of PP, the adhesion of which is enhanced by acidic modification, and a small amount of modified PE (polyethylene). By mixing with modified PE, the wettability of the melted polymer during heat adhesion is enhanced, thus strengthening the film's adhesion to the substrate TFS. Thus, strong film adhesion was obtained as well as excellent corrosion resistance with regard to the can's contents.

### 2.5 Technology for evaluating corrosion resistance

Accelerated corrosion testing is indispensable when developing a new coated steel sheet. Up until about 1980, the only testing method available for evaluating corrosion resistance of coated steel sheets was SST (Salt Spray Testing). After Zn-coated steel sheets use in automobile manufacturing began in the 1980's, it became known that corrosion resistance evaluated by SST had, in the real world, only a low correlation with corrosion resistance[39)]. Accordingly, each automobile manufacturer developed and standardized its own corrosion resistance test method. These differed from manufacturer to manufacturer, each producing different evaluation results. In 1990, in order to supply coated steel sheets that exhibit excellent corrosion resistance in the actual environment, NKK on its own initiative, started to develop technology for evaluating corrosion resistance by investigating corrosion behavior on real automobiles. In addition to developing the technology that can accurately reproduce corrosion behavior on automobiles in service, NKK carried out research on coated steel sheets that exhibit excellent corrosion resistance in applications such as residential construction and electrical appliances. The following are some of the results from NKK's technological development for evaluating corrosion resistance of steel sheets used in automobiles and construction.

The mode of corrosion that takes place on automotive steel sheets can be classified in two categories: perforation and cosmetic. NKK successfully carried out quantitative analysis of crystalline compositions of iron rust formed on automobiles that had been in service in those North American regions where a lot of deicing salt is applied to roads in winter as well as in coastal regions in Japan, and devised a new ternary diagram of iron rusts, as shown in **Fig.11**[40)]. It was determined that both types of corrosion, perforation and cosmetic, appearing on alloy-coated steel sheets in use in those days were mostly governed by coating weight regardless of coating type[41),42)]. A new model was proposed on corrosion progress of Zn-coated steel sheets, as shown in **Fig.12**. Corrosion progress was divided into four stages[43)]. Stage 1 ( $\tau_1$) is the period when the corrosion progresses in the metal coating layer. In this stage, the metal layer still remains over the whole steel sheet surface. Stage 2 ($\tau_2$) is when part of the substrate steel sheet is exposed and galvanic corrosion progresses due to the contact between two different metals. Stage 3 ($\tau_3$) is when steel corrosion is suppressed by the corrosion product of Zn. Stage 4 ($\tau_4$) is when the corrosion-suppressing effect of the corrosion product of Zn is lost and steel corrosion progresses rapidly, finally resulting in perforation. It was clarified that $\tau_1$ and $\tau_3$ both play an important role in corrosion resistance of automobiles in service.

A concern in the construction field is red rust and underfilm corrosion that develop from cut edges and formed areas of coated steel sheets. The corrosion test method still applied widely in this field is SST (JIS Z2371). It appears to have almost no correlation with performance in the real-life environment. No alternate method has yet been developed. NKK found that design degrading factors of each part of steel-framed houses can be detected by an ACM (Atmospheric Corrosion Monitoring) type corrosion sensor[44]. This method was used for predicting the lifespan of these houses for the first time[45].

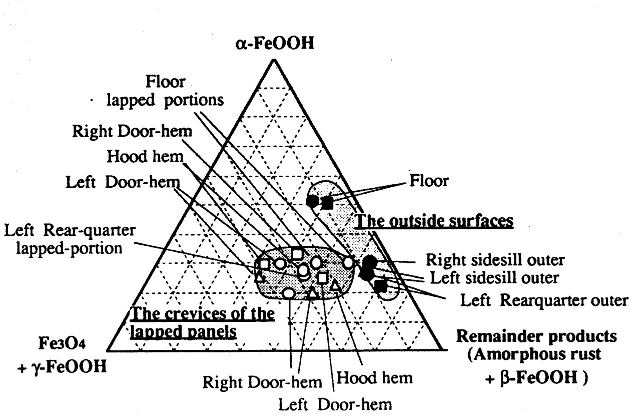



**Fig.11 Ternary diagram for the rust composition in automobiles**

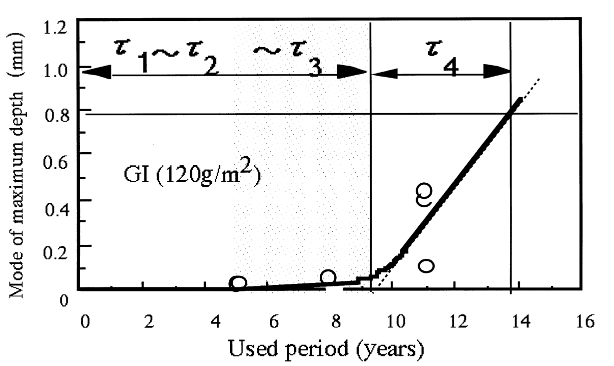



**Fig.12 Schematic progress of corrosion in automobile lapped panel crevices**

The design of a product that enables proper and efficient use of natural resources is increasingly required in recent years as indicated by LCC (Life Cycle Cost) analysis. In partnership with its customers, NKK is developing material evaluation technologies that are also applicable in terms of predicting the useful life of materials.

## 3. Highly lubricating automotive steel sheets: PZA-N

Society's demand for improving corrosion resistance of automobile bodies in the 1990's dramatically increased the use of galvannealed steel sheets. This was due to the fact that the coating weight could be easily increased at comparatively low costs.

However, as mentioned in **2.1.3**, increased coating weight of a galvannealed steel sheet tends to cause powdering and degradation in terms of its sliding property resulting from the coating structure. In particular, when galvannealed steel sheets were applied to large integrally formed panels subjected to severe forming and other parts that are hard to form, various problems were induced such as press-forming fracturing. NKK has continued its R&D with the aim of improving the press formability of galvannealed steel sheets. NKK was the first in Japan to adopt a full high frequency induction furnace within a CGL process and establish a coating microstructure controlling technology. Further efforts have been directed to stabilizing the press formability. As a result, a new surface modified galvannealed steel sheet, that has enhanced lubricity, was developed and marketed as PZA-N.

The commercial production of PZA-N began in 1996. It is used to form various hard-to-form parts such as side panels. It was also found effective at lowering the required grade levels of steel sheets, and press-forming high tensile strength steel sheets that are generally hard to form. These unique properties are making a large contribution toward reducing the material cost for customers, as well as expanding the uses of PZA. Its industrial value was recognized, resulting in the Japan Institute of Metal's Technical Development Award in 2001[47].

The following is an outline of coating design concept applied to PZA-N and its performance in commercial applications.

### 3.1 Coating design concept

Lubrication between two pieces of solid materials is either fluid lubrication, using a fluid film such as an oil film, or boundary lubrication, where the two surfaces contact each other via an adsorbed molecule film. When the contact pressure in press forming is low, lubrication is a mixture of fluid and boundary lubrication with a higher amount of fluid lubrication. With increasing contact pressure, the region of boundary lubrication increases, leading to direct contact between metals. Once micro adhesion results from direct contact between metals, friction resistance increases significantly.

When developing the PZA-N coating design, the following five points were set as objectives:
(1) It shall be a solid lubricant coating little affected by changes in contact pressure and temperature during press forming. It shall consistently provide an excellent level of lubricity.
(2) A strong boundary lubrication layer shall be formed, which has a high affinity with lubricating agents in oil in order to achieve excellent lubricity by using an extremely thin coating.
(3) It shall not cause micro adhesion easily even when the boundary lubrication layer is broken and direct contact between metals is induced.
(4) It shall be easy to produce at low cost.
(5) Other properties shall be more than equal to those of PZA.

PZA-N is a surface modified galvannealed steel sheet the lubricity of which is enhanced by adding an extremely thin Ni-Fe-O-based inorganic lubricating film on the PZA surface. **Fig.13** shows the coating structure and development concept.

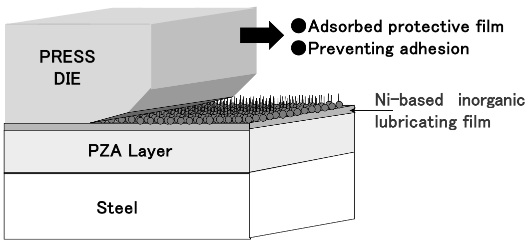



**Fig.13 Structure and benefits of a Ni-based inorganic lubricating film**

### 3.2 Quality

**Fig.14** compares the press formability of PZA-N with that of PZA and the double-layer galvannealed steel sheet PZB, all made from the same materials. In this test, these steel sheets were press-formed into front fender model panels of actual size at a speed of 10SPM using a single-action mechanical press. They were press-formed under varying blank holding forces, and the cracks and wrinkles generated by press forming were evaluated. PZA-N exhibited the press formability equivalent to that of PZB.

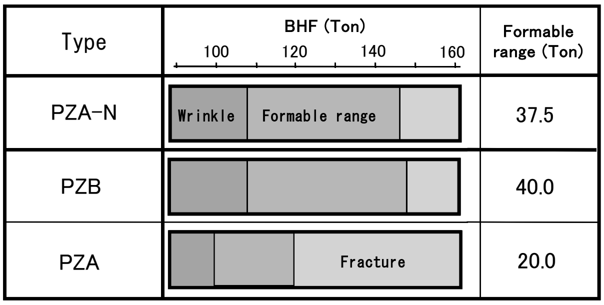



**Fig.14 Formable range of PZA-N, PZA, and PZB**

**Table 1** compares various performances of PZA-N in actual use with those of PZA and PZB. Owing to the excellent lubricity equivalent to PZB that was achieved by using an extremely thin lubricating film, the production cost of PZA-N was markedly reduced when compared with that of PZB. PZA-N also has superior spot weldability and compatibility with adhesives while being corrosion resistant, easy to paint, and with other properties in actual use equal to those of PZA.

**Table 1 Performance of PZA-N, PZA, and PZB**

| Performance | PZA-N | PZA | PZB |
|---|---|---|---|
| Press formability | ◎ | ○ | ◎ |
| Powdering resistance | ○ | ○ | ○ |
| Adhesive compatibility | ○ | ○ | ○ |
| Spot weldability | ◎ | ○ | ○ |
| Phosphatability | ○ | ○ | ○ |
| ED cratering | △ | △ | ◎ |
| Corrosion resistance | ○ | ○ | ○ |

◎:Excellent ○ : Good △ : Worse

## 4. Chromium-free coated steel sheet with excellent properties: Geo-Frontier Coat

NKK developed a chromium-free coated steel sheet with excellent properties. This product is marketed as GF (Geo-Frontier) Coat[48)-50)].

### 4.1 Unique organic composite coating features

Generally, the increase in the organic composite coating thickness leads to improved corrosion resistance, but lowers electrical conductivity and weldability. In order to secure excellent electrical conductivity, the coating thickness needs to be less than 1 to 2 $\mu$ m. In conventional chromium-free steel sheets, however, the coating thickness needs to be more than 3 $\mu$ m to secure corrosion resistance. As a result, electrical grounding was poor.

Geo-Frontier Coat was the first product in the world to achieve excellent electrical grounding and weldability while at the same time showing excellent levels of corrosion resistance by applying a thin layer of a newly developed unique organic composite coating as described below (also see **Fig.15**)[48].

(1) Geo-Frontier Coat uses a special chelate-modified epoxy resin that has an excellent barrier effect.

(2) It uses unique inorganic corrosion inhibitors that result in a self-healing effect.

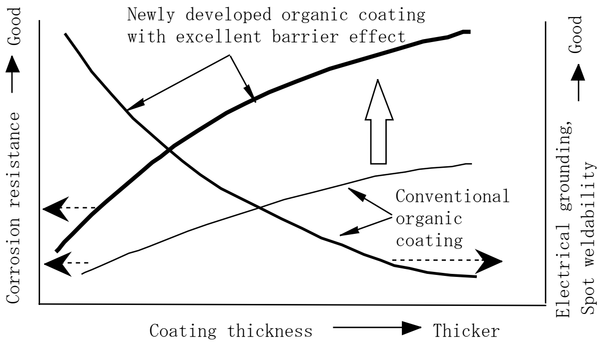



**Fig.15 Basic concept of the new chromium-free organic composite coating[46]**

## 4.2 Features of the new product

**Photo 4** shows the appearance of various coated steel sheets that were exposed to SST for 72 hours and those that were first subjected to alkaline degreasing and then exposed to SST for 72 hours[48]. Geo-Frontier Coat exhibited excellent corrosion resistance equal to that shown by chromate-treated steel sheets. It maintained excellent corrosion resistance even after alkaline degreasing. Its electrical grounding and weldability are far superior owing to its thin coating thickness. Ricoh Corporation, a major copying machine manufacturer, evaluated the spot weldability of chromium-free steel sheets produced by four major Japanese steel companies, and concluded that GF is the best in terms of performance (**Fig.16**)[51]. It also exhibits excellent properties in terms of fingerprint resistance and paintability.

In response to the needs of forming hard-to-form parts without applying lubricating oil, NKK next developed Geo-Frontier Coat Type-L. This product has excellent lubricity.

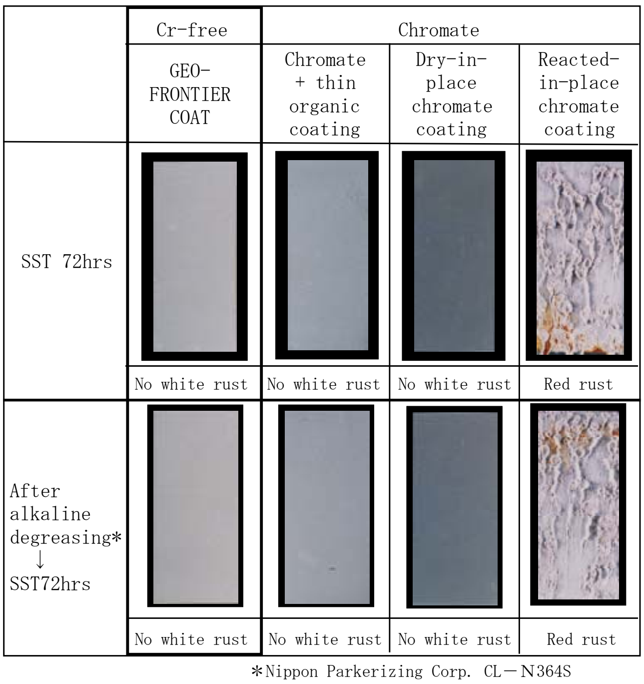



**Photo 4 Appearances of various coated products after exposure to SST for 72 hours**

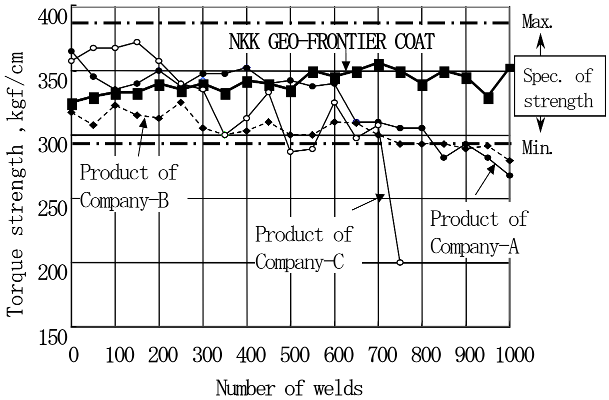



**Fig.16 Weldability of Cr-free coated steel sheets developed by major steel companies[51]**

## 4.3 Marketing

Geo-Frontier Coat was launched onto the market in 1998. It is now widely used for forming various parts such as OA chassis and AV products. This product has won a high reputation among its customers. The Surface Finishing Society of Japan, an organization representing Japan in the field of surface finishing including metal coating, organic or inorganic coating, painting, and dry processes, recognized the innovativeness, uniqueness, and commercial performance of this technology by awarding its Technology Award in 2002[50].

## 5. Conclusion

NKK started producing coated steel sheets in 1961. Annual production reached 2.3 million tons in 1991. This increased production was made possible by various new products successively developed based on NKK's proprietary technologies in response to a changing society and customers' needs. We will continue developing new high-quality coated steel sheets based on customer requirements, while at the same time improving their environmental friendliness.

## References


1) S. Suzuki. "Prolongation of Automobile Life and Corrosion Preventive Technology". The 42nd Shiroishi Memorial Seminar, Tokyo, 2000-06, The Iron and Steel Institute of Japan, pp.75-92.
2) K. Matsudo et al. "Development of Highly Corrosion Resistant Composite Zn Coated Steel Sheet: NKFZ". NKK Giho. No.77, pp.12-19(1978).
3) T. Adaniya et al. "Fe-Zn Alloyed Electrogalvanized Steel Sheet". NKK Giho. No.90, pp.41-49(1981).
4) Steel Sheet & Strip Technology Dept. "Automotive Corrosion Resistant Steel Sheet". NKK Giho. No.105, pp.119-124(1984).
5) K. Matsudo et al. Inventor; NKK, Applicant, "Electrogalvanized Steel Sheet with Excellent Corrosion Resistance with or without Painting". Patent No.1137263, Applied 1978-11-22.
6) M. Yamashita et al. "Corrosion Resistant Coated Steel Sheet for Automobiles Coated by Composite Resin 1038-1043 (1986)". Tetsu-to-Hagane Vol.72, pp.1038-1043(1986).
7) K. Takagi et al. "Equipment and Operation of Fukuyama No.2 CGL". NKK Giho. No.135, pp.34-42(1991).
8) K. Sagiyama et al. "Alloying Behavior and Coating Structure od Hot-dip Galvanized Steel Sheet". NKK Giho. No.135, pp.49-56 (1991).
9) M. Yamashita et al. "The 167-168th Nishiyama Memorial Seminar, Growing Steel Sheets and Coated Steel Sheets". Tokyo, The Iron and Steel Institute of Japan, 1998, p.158.
10) S. Hori et al. "Factors Affecting Anti-fingerprint Property in Coating-type Chromate Treatment". Material & Process. Vol.1, p.1665 (1988).
11) T. Hara et al. "Cr-free Chemical Treatment of Zn Coated Steel Sheet". NKK Giho. No.91, pp.386-392(1981).
12) M. Ogawa et al. "Highly Corrosion Resistant Chromate Treated Steel Sheet: UZ-NX". NKK Giho. No.95, pp.550-553(1982).
13) M. Ohmura et al. "Quality Property of Corrosion Resistant, Lubricating Zn Coated Steel Sheet". Tetsu-to-Hagane. Vol.70, S1123 (1984).
14) T. Miyoshi et al. "Development of Highly Lubricating, Corrosion Resistant Steel Sheet for Electrical Appliances". Collection of Synopses of The 87th National Conference of The Surface Finishing Society Of Japan, pp.251-252(1993).
15) T. Miyoshi et al. "Effects of Base Organic Resin and Additives on Quality Property of Highly Lubricating, Corrosion Resistant Steel Sheet". Tetsu-to-Hagane. Vol.83, pp.145-150(1997).
16) M. Yamashita et al. "Multi-functional Organic Composite Coated Steel Sheet for Electrical Appliances". NKK Giho. No.153, pp.32-35(1996).
17) T. Kubota et al. "Corrosion Protective Mechanism of Silica in Organic Composite Coated Steel Sheet". Material & Process. Vol.4, pp.637-640(1991).
18) T. Kubota et al. "Corrosion Protective Mechanism of Silica in Organic Composite Coated Steel Sheet". Tetsu-to-Hagane. Vol.81, pp.76-81(1995).
19) Nippon Keizai Shinbun. June 5, 1997.
20) K. Yoshida et al. "Development of New Prepainted Steel Sheet for Electrical Appliances". Tosoh-Kougaku. Vol.34, No.11, pp.396-402 (1999).
21) K. Yoshida. "Prepainted Steel Sheet for Construction". Zaityo-to-Kankyo. Vol.50, No.5, pp.210-215(2001).
22) M. Yamashita et al. "Highly Corrosion Resistant 55%Al-Zn Alloy Coated Steel Sheet: NKK Galvalume Steel Sheet (Genius Coat)". NKK Giho. No.167, pp.20-23(1999).
23) M. Yamashita et al. "Highly Corrosion Resistant 55%Al-Zn Alloy Coated Steel Sheet: Super Genius Coat". NKK Giho. No.173, pp.49-33(2001).
24) K. Yoshida et al. "Highly Formable Prepainted 55%Al-Zn Alloy Coated Steel Sheet: Gal-Flex Color". NKK Giho. No.76, pp.102-103(2002).
25) Kuroda, H et al. "Characteristics of Lightly Tin-coated Steel Sheet". Procceedings of The 2nd International Tinplate Conference, 1980, p.124.
26) M. Ono et al. "Seam Weldability of Lightly Tin-coated Steel Sheet". Tetsu-to-Hagane. Vol.68 (1982), S1170.
27) T. Watanabe et al. "Characteristics of Ni-primer-treated & Lightly Tin-coated Steel Sheet". Tetsu-to-Hagane. Vol.71 (1985), S1147.
28) S. Miyazaki et al. "Characteristics of Unevenly Tin-coated Steel Sheet for Welded Cans". Metal Surface Technology. Vol.37, p.701(1986).
29) T. Watanabe et al. "Characteristics of Lightly Tin-coated Steel Sheet". NKK Giho. No.122, p.157(1998).
30) H. Iwasa et al. "Electrolytic Chromate Treatment of Lightly Tin-coated Steel Sheet". Tetsu-to-Hagane. Vol.69 (1983), S1232.
31) H. Iwasa et al. "Electro-deposition Behavior of Granular Metallic Chromium in TFS". Material & Process. Vol.2, p.1708(1989).
32) Iwasa, H et al. "Development of a New Type of Electrolytic Chromium Coated Steel with Granular Metallic Chromium for Welded Cans". Seminar on the Technical and Economic Aspects of the Manufacture and Application of Coated Steel Products, Economic Commission for Europe, United Nations, 1990, Geneva, Italy.
33) K. Imazy. "Stretch Draw Forming of Laminated Sheet". Sosei-to-Kakoh. 38, 432, p.52(1997).
34) S. Miyazaki. Technical Information for Soft Drinks. 112(1995), p.110.
35) H. Yamazaki. Beverage Japan, No.174(1996), p.98.
36) Owens, D. K. et al. J. Applied Polymer, Science, 13, p.1741 (1969).
37) K. Kadotani et al. Journal of The Adhesion Society of Japan, 18, p.345(1982).
38) I. Suzuki et al. "New Laminated Steel Sheet for General-line Cans". NKK Giho. No.175, p.52(2001).
39) F. O. Wood, Corrosion '78, NACE, Houston, TX, NACA (1978), Paper No.7.
40) S. Fujita and H. Kajiyama. "Quantitative Corrosion Control of Aluminum and Steel in Lightweight Automobile Applications". Ed. by N. Soepenberg, NACE International, ISBN 1-877914-88-6 (1995), No.378.
41) S. Fujita, Proc. of 4th Int. Conf. on ZXinc and Zinc Alloy Coated Syeel Sheet, (GALVATECHalvatech '98), ISIJ, Chiba, Tokyo, Japan, (1998), 659.
42) K. Sasai et al. Material & Process. Vol.9, No.3, (1996), p.474.
43) S. Fujita et al. Material & Environment. 50, (2001), p.115.
44) S. Tsujikawa. Proceedings of the 111st Symposium for Corrosion & Corrosion Prevention. JSCE, (1996), p.1.
45) S. Fujita. Surface Finishing Technology, 48, No.9, (1997), 27.
46) T. Sakurai et al. "Highly Lubricating Galvannealed Steel Sheet: PZA-N" NKK Giho. No.162, pp.15-20(1998).

47) T. Sakurai et al. “Development of Highly Lubricating Galvannealed Steel Sheet for Automobiles: PZA-N”. MASTERIA. Vol.40, No.2, pp.190-192(2001).
48) N. Yoshimi et al. “Newly Developed Chromium-free Thin Organic Composite Coated Steel Sheets with Excellent Corrosion Resistance”. GALVATECH-2001, pp.655-662.
49) N. Yoshimi et al. “Chromium-free Chemical Treated Steel Sheet: Geo-Frontier Coat”. NKK Giho. No.170, pp.29-33(2000).
50) M. Yamashita et al. “Development of Environmentally Friendly, Highly Functional, Chromium-free Chemical Treated Steel Sheet”. Collection of Synopses of The 105th National Conference of The Surface Finishing Society Of Japan, Speech for Commemorating the 2002 Technology Award, pp.461-464(2002).
51) Nikkei Mechanical. No.551, pp.33-36(2002).