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High Durability Clear Painted Stainless Steel Sheets

Hiromasa NOMURA*1 Yoshio KIMATA*1
Kohei UEDA*1 Hiroshi KANAI*1
Yoshiyuki YOKOTA*2 Masaya YOSHIDA*2

Abstract

Highly durabile, clear-painted stainless steel sheets Hals-hybrid clear painted stainless steel sheets for buildings have been developed. The deterioration mechanism of polymer outdoors is known as an auto oxidation which is caused by radical chain reaction. Hindered amine light stabilizers (hereafter HALS) have been introduced to capture the radical, and cyclohexyl metacrylate (hereafter CHMA) has been introduced to improve the light stability and hydrophobicity. Hals-hybrid resin is an acrylic polyol resin composed of HALS copolymerized CHMA. The newly developed Hals-hybrid clear painted stainless steel sheet showed good weatherability in outdoor exposure tests.

1. Introduction

Because of its excellent corrosion resistance and beautiful appearance, a stainless steel sheet has been widely used in the fields of construction materials, kitchen equipment, home electric appliances and in vehicles. In most cases, it has been used unpainted to take advantage of its appearance, although its kind and surface finish have been selected according to its application and the environment where it issued. With the need for highly-added value growing in recent years, however, a high-performance clear painted stainless steel sheet with newly added functions has been developed while making the most of its beautiful appearance by applying clear paint (transparent organic paint) thereto. As **Table 1** shows, Nippon Steel has commercialized a high-performance clear painted stainless steel sheet by giving it processability, microbial resistance, pollution controllability, and weatherability[1]. This paper introduces the technical concept and performance of "Hals-hybrid clear painted stainless steel sheets," a highly durable clear painted stainless steel sheet newly developed for use as an outdoor construction material.

2. Guideline on the design of highly durable clear painted stainless steel sheets

Various studies have been made relative to the mechanism in the deterioration of organic polymer compounds outdoors. It is known that deterioration is chiefly attributable to the mechanism of auto oxidation in which radicals and oxygen, generated by UV rays and heat, are involved[2]. **Fig. 1** shows the mechanism involved in auto oxidation. The radicals (R ·) generated with the initiation of reaction as shown in Fig. 1 (1) lead to reactions (2) to (5), with the radicals generated in (3) and (5) leading to (2) thereby causing a radical chain reaction. Besides UV rays and heat, water also has an influence that must not be ignored. Water plays a critical role chemically, not only in primary-bonding hydrolysis as in ester bonding, but also in separating the secondary bonding as in hydrogen bonding. In addition, water absorbed by paint film physically leads to swelling, plasticization, blistering, peeling and cracking, and further to the corrosion of a substrate steel sheet.

The resins used so far for painted stainless steel sheets for outdoor use are chiefly fluorocarbon resin and silicon modified polyester resin. They introduced C-F bonding or Si-O bonding, high in bond dissociation energy, to the paint film thus to stabilize the film-forming polymer[3,4]. The bond dissociation energy of the C-F bonding contained in fluorocarbon resin, for example, is as large as 450 kJ/mol, an energy strong enough not to be cut with a light energy of about 400 kJ/mol, equivalent to the shortest wavelength (about 300 nm) of the sunlight[3]. Moreover, it is generally well known that fluorocarbon resin is highly hydrophobic. This hydrophobicity inhibits the entry of water to serve as the deterrent force of chemical and

*1 Technical Development Bureau

*2 NIPPON SYOKUBAI CO., LTD.

Table 1 Typical high-performance clear painted stainless steel sheets[1)]

Name	HALS-hybrid	NS-COAT	NS-COAT-D	NS-COAT-DX	NS-COAT-DB
Characteristics	Weatherability	High transparency	Processibility (highly lubricant)	Microbial resistance	Pollution controllability
Clarity	○	◎	○	○	○
Film hardness	○	◎	○	○	○
Pollution controllability	○	○	○	○	◎
Processibility	○	–	◎	○	○
Microbial resistance	–	–	–	◎	–
Weatherability	◎	–	–	–	–
Application examples	Outdoor building material		Rice cooker cover (Various processed parts)	Refrigerator for business use (Ice machine)	Dish washer

$$\begin{aligned}
&\xrightarrow{h\nu} \\
RH &\rightarrow R\cdot + H\cdot && (1)\\
R\cdot + O_2 &\rightarrow ROO\cdot && (2)\\
ROO\cdot + RH &\rightarrow ROOH + R\cdot && (3)\\
ROOH &\rightarrow RO\cdot + \cdot OH && (4)\\
RO\cdot + RH &\rightarrow ROH + R\cdot && (5)
\end{aligned}$$

Fig. 1 Mechanism of auto oxidation of organic polymer compounds

physical deterioration as above-described.

As is clear from the foregoing, fluorocarbon resin-painted or silicon modified polyester resin-painted stainless steel sheets are excellent in physicochemical properties. However, they pose a problem in industry in terms of high cost. With acrylic resin, cheaper than fluorocarbon resin, in mind, the authors studied how to improve its durability. The following three points are the concrete guideline on design:

(1) Instead of introducing C-F bonding, high in bonding energy, to the molecular chain, inhibit auto oxidation by capturing radicals with hindered amine light stabilizers[5)], hereinafter abbreviated to HALS. **Fig. 2** gives the structure of HALS (Hindered amine light stabilizers) employed.

(2) With the exception of aromatic monomers which readily generate radicals after absorbing sunlight, apply cyclohexyl methacrylate, hydrophobic and high in glass transition temperature, hereinafter abbreviated to CHMA, as the basic structure of acrylic resin. Fig. 2 gives CHMA's structure.

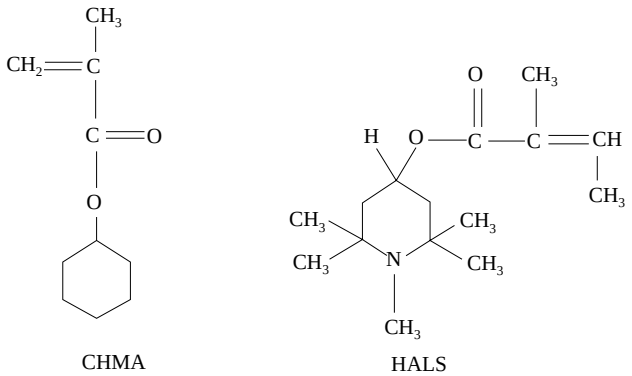


Fig. 2 Structures of resins applied to highly durable clear painted stainless steel sheets

(3) The flow of HALS out of the painted film is considered responsible for a decrease in durability. HALS-hybrid resins therefore applied, in which HALS is copolymerized with CHMA, so that a long-term durability can be retained by preventing the outflow of HALS.

3. Durability of HALS-hybrid clear painted stainless steel sheets

3.1 Weathering tests

Fig. 3 shows the results of evaluation by the Sunshine Weatherometer test in which the weatherability of the HALS-hybrid resin was compared with that of general polyester resin, silicon modified polyester resin, and fluorocarbon resin (polyvinylidene fluoride resin). This test was carried out to compare the weatherability of resins using the film painted white with white titanium pigment instead of clear painted film. The y axis shows a ratio of gloss retention, which shows a ratio of 60-degree gloss value before and after the Sunshine Weatherometer test. A value close to 100% stands for an excellent weatherability. A comparison of the 3,000-h test results shows that the ratios of gloss retention of general polyester resin and silicon modified polyester resin are below 50%, while that of the HALS-hybrid resin is about 80%, a high ratio equal to that of fluorocarbon resin.

The above results reveal that the weatherability of the HALS-hybrid resin is far excellent than that of general polyester resin and silicon modified polyester resin, and almost equal to that of fluoro-

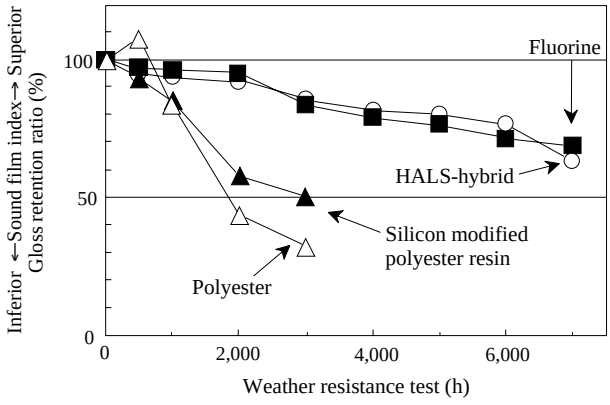


Fig. 3 Weatherability of HALS-hybrid resin

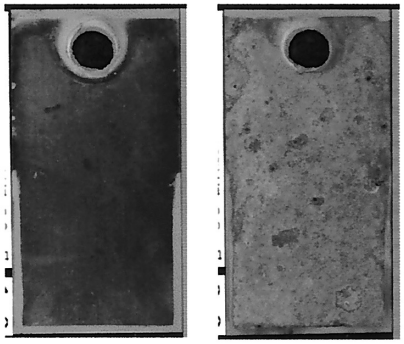
carbon resin.

3.2 Outdoor exposure tests

The HALS-hybrid resin paint (paint film thickness: 2 to 3 μm) and fluorocarbon resin (polyviniyldidene fluoride resin) clear paint (paint film thickness: 10 μm) were applied to stainless steel sheets, SUS 430, respectively for outdoor exposure tests in the seaside area of Okinawa Prefecture. The HALS-hybrid clear paint was applied directly to the stainless steel sheet, degreased and without pretreatment for painting, and then baked. On the other hand, the fluorocarbon resin paint was applied to the stainless steel sheet, degreased and chromate-treated, and then baked.

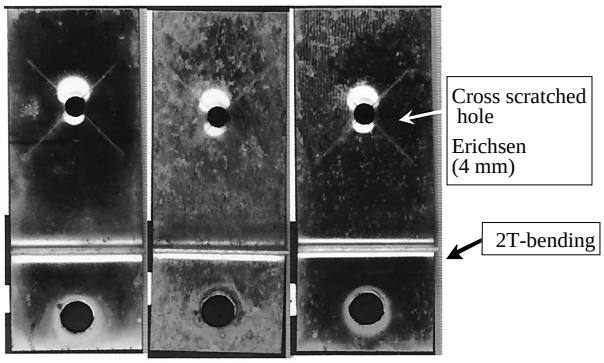
Photos 1 (38 months) and **2** (12 months) show the results of the exposure tests. In Photo 1, a bare (without clear painting) stainless steel sheet was used for comparison. The upper and lower edges and the lower halves of right and left edges of the test piece were painted with sealing material. Photo 1 reveals that, despite 38-month exposure to the severe outdoor corrosive environment, the HALS-hybrid clear paint stainless steel sheet looked fine externally with no film peeled, proofing that rusting was prevented to a greater degree than in the bare stainless steel sheet.

Photo 2 shows a comparison between the bare stainless steel sheet and the fluorocarbon resin clear painted stainless steel sheet. The test pieces were shaped combined with 2T-bending, a hole for checking with a bolt, a cross scratch, and Erichsen processing (4-mm extrusion). Upper, lower, right and left edges were also not painted with a sealant. Photo 2 shows that even the edge parts, cross scratched parts and processed parts are slightly corroded with no paint peeling, and that adhesion and durability (weatherability and corrosion resistance) are maintained in good order even without chromate treatment. It also shows that the HALS-hybrid clear paint stands comparison with fluorocarbon resin clear paint, a paint well known for its high durability.



HALS-hybrid clear painted film 1.5μm thick | No film

Photo 1 Results of 38-month exposure tests of HALS-hybrid clear painted stainless steel sheets at the seaside area of Okinawa[1)]
Substrate: SUS430-28, 0.4 mm thick



HALS-hybrid clear painted film, 1.5 μm thick | No film | Fluorocarbon resin clear paint, 2C2B 10 μm thick

Photo 2 Results of 12-month exposure tests of HALS-hybrid clear painted stainless steel sheets at the seaside area of Okinawa[6)]
Substrate: SUS430-No.4, 0.6 mm thick; No sealant coat at edge parts

4. Conclusion

The "HALS-hybrid clear painted stainless steel sheet," a highly durable clear painted stainless steel sheet developed for outdoor use, can be expected to be used over a wide range because of its durability nearly equal to that of a fluorocarbon resin clear painted stainless steel sheet.

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