A Method for Assessment of Rust Preventive Oil on Galvanized Steel

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Abstract— ***This paper proposes a new method for the assessment of performance of protective oil on galvanized and skin passed sheets. 11 different protective oil products were applied (1 g/m²) to hot dip galvanized and skin passed 66 sheet samples and subjected to Neutral Salt Spray Fog Testing (NSSFT) with 5% NaCl solution. Amount of white rust on the samples has been determined at 2, 6, 9 and 24 hours. Test results showed that application of NSSF test for 9 hours gives best deterministic results.***

Keywords— **Carbon steel, Zinc, White Rust, Atmospheric corrosion, RPO, Rust Preventive Oil**

I. INTRODUCTION

Protecting galvanized sheets from corrosion is very important in all usage areas of them, whether used as bare or painted [1]. Continuous layer of zinc forms a barrier against the effects of the atmosphere and catholically protects the steel phase. However, usually white rust forms on continuous layer of zinc and causes deformations. It advances with time and formation of red rust begins on the surface after a while.

It is known that corrosion resistance of galvanized sheet changes, depend on the chemical composition of the coating layer. A galvanized coating including 5% Al and 0.1% Mg which increases corrosion resistance significantly have been developed by Yasuhide et al. They have demonstrated that corrosion resistance increased when Al percentage increased in the coating [2]. Prosek et al. have ranged corrosion resistance of some coating composition as; HDG (Zn-0.25% Al) < Zn-Al-Mg < Zn-Al-Mg-Si < Galfan (Zn-Al%5) < Zn-Mg [3].

Chemical composition of galvanized sheets depends mostly on the chemical composition of the liquid zinc in the zinc pot that, the sheet is dipped into. In Zinc-Iron alloy coated sheet (ZF) manufacturing, strip comes out of the zinc pot with a coating of 99% zinc content and subsequent annealing increases iron content to 8 % - 12 % in the coating. By this process the percentage of iron in the coating might increase to a total of 8 to 12% through Fe-Zn phases. While percentage of Al is approximately 5% in the layers of Zinc-Aluminium alloy coated sheets (ZA), Al is 55% and Si is 1.6% in the ones with Aluminium-Zinc alloy coated sheets (AZ) and Al is around 8% and Si is around 11% in the ones with Aluminium-Silicium alloy coated sheets (AS) [4]. In addition to aluminium and Silicium, copper, tin, lead and nickel are the other widely used elements in coating alloys [5].

If galvanized sheet was designed to be painted, surface is roughened between 0.6 and 1.3 μm (Ra) by means of skin pass procedure in order to improve adhesion of paint coat to the galvanized sheet surface. After the sheet dipped into liquid zinc, it is taken out of the bath, excess zinc on the sheet's surface is scraped into the pot with air knives immediately and cooled in the cooling tower at a certain speed. This procedure creates a continuous coat of solid zinc with homogenous characteristics on the surface of the sheet. Then the sheet passed through skin pass rolls with roughened surfaces under pressure. This procedure spoils the smoothness of the surface of the coating, increases surface area to increase adhesion of paint, but it decreases the corrosion resistance of the zinc coating [6].

White rust forms easily on skin passed sheet due to increased surface area and its deformation. It forms a loose intermediate layer between the paint film and galvanized surface and this loose layer causes paint not to adhere to the sheets. Moreover, white rust on galvanized surface under paint film may cause some other problems such as cracking, roughening, and peeling off the paint film during shaping of the painted sheet [7].

During storage and shipment process, surface of the skin passed sheet is coated with corrosion protective oil up to 1 g/m2 in order to prevent the white rust formation. Electrostatic lubricants are usually used for this process. These specially designed oils are hydrophobic materials which can form a perfect bound with zinc. They are easy cleanable in alkali cleaning units.

There are several protective oils to protect galvanised sheets available in the market. Therefore, it is imperative for the galvanized sheet manufacturers to decide the most suitable oil for their application in order to avoid customer complaints regarding white rust formation.

Although Neutral Salt Spray Fog Testing (NSSFT) method is weak for the simulation of natural corrosion due to the complexity and dynamic conditions of nature compared to NSSFT conditions [8], it is one of the most preferred methods due to providing fast results, monitoring development of corrosion visually and offering standard data. On the other hand, any study to provide a method for choosing corrosion protective oil for the best protection of galvanized sheet from rust formation has not been detected during literature survey.

This study examines the formation of white rust on surface of galvanized sheets when forced into corrosion with Neutral Salt Spray Fog (NSSF) and the effects of protective oil on corrosion resistance. In addition, this study proposes an evaluating method for choosing the correct protective oil for galvanized sheets.

II. EXPERIMENTAL STUDIES

A. *Materials*

Tests were conducted on samples cut from DX51D+Z grade steel sheet galvanized by hot dip method. Chemical compositions of used sheet, zinc pot and zinc coating are given in Table 1 to 3 respectively. Zinc coting thickness of the samples used in the study was 100 g/m2.

Table 1

CHEMICAL COMPOSITION OF THE STEEL SHEET IN WEIGHT (%)

C	0.045
Si	0.024
Mc	0.234
P	0.011
S	0.005

Table 2

CHEMICAL COMPOSITION OF ZINC COATING IN WEIGHT (%)

Al	0.52153
Cd	0.00009
Sb	0.00004
Pb	0.00153

Table 3

CHEMICAL COMPOSITION OF ZINC POT IN WEIGHT (%)

Al	0.21135
Fe	0.01634
Cd	0.00009
Sb	0.00004
Pb	0.00151

Performance of 11 different mineral based protective oil samples from 6 different manufacturers were assessed in this study. Each oil product contains corrosion inhibitors and oil additives which the type and quantities of these agents are not declared by the companies. Considering the principles of secrecy, manufacturing companies of oils were coded with capital letters and the protective oils, manufactured by these companies were coded with numbers. Data regarding these oil products are presented in Table 4.

Table 4

PROPERTIES OF OIL PRODUCTS USED IN THE STUDY

Manufacturing Company Code	Product Code	Density @20 °C (g/ml)	Flashpoint (°C)	Kinematic Viscosity @40 °C (mm^2/s)
A	A1	0,89	165	19,5
	A2	0,89	165	19,5
B	B1	0,86	198	42
C	C1	0,88	201	34
	C2	0,88	198	36
D	D1	0,91	196	60
	D2	0,89	214	36
E	E1	0,87	190	24
	E2	0,87	180	26

B. *Devices and Equipment*

Chemical analysis of the galvanized sheets was performed with Thermo Fisher brand optical emission spectrometer and composition of the zinc coating was analysed with Varian brand ICP-OES 710-ES axial spectrometer. Hommel Wave Werke System was used to measure the roughness of the surfaces of the sheets. Corrosion conditions for the study were provided by Sheen brand, FMC 1000 FogMaster model Cyclic Corrosion Cabinet. DJH MonoZoom Optical Microscope x50 was used for capturing images. Photographs were taken using Sony brand DSC-W530 model digital camera

C. *Chemicals*

In order to create the NSSFT medium in the corrosion cabin, 5% neutral brine solution was prepared with NaCl with analytic purity (Merck katalog No. 1.06404.9050) and ultra-pure water with a conductivity less than 0.1 µS/cm. HCl with analytic purity (Merck katalog No. 1.00317.2501) was used for dissolving zinc coating and some other tests.

D. *Test and Assessment Method*

Tests were performed on 11 different protective oil products, manufactured by 6 different manufacturers. These 11 products comprise approximately 95% of the total protective oil brands used for galvanized sheet sector. Totally 66 sheet samples are used considering the general applications and optimum application amount of electrostatic oilers. Amount of oiling was determined as 1 g/m2.

Protective oil applied on panels manually and amount of oil on samples was determined by weighting precisely. Average oil amount for all panels held in 8% positive deviation because it is impossible to get perfect amount. Realized oil amounts on each sample are presented on Table 5.

Table 5

AMOUNT OF WHITE RUST ON 1 G/M^2 PROTECTIVE OIL APPLIED GALVANIZED SHEETS

Test No	Protective Oil		Realized Amount RPO (g/m^2)	White Rust Amount (%)			
	Company code	Product Code		at 2 Hours	at 6 Hours	at 9 Hours	at 24 Hours
1	A	A1	1.06	3	20	30	100
2	A	A1	1.50	5	40	70	100
3	A	A1	1.36	0	15	50	100
4	A	A1	1.43	3	28	60	100
5	A	A1	1.06	3	20	30	100
6	A	A1	1.16	5	15	30	100
7	A	A1	1.16	5	30	70	100
8	A	A1	1.05	0	55	65	100
9	A	A1	0.95	0	65	85	100
10	A	A1	1.03	0	60	95	100
11	A	A1	0.96	0	70	95	100
12	A	A2	0.99	0	20	50	100
13	A	A2	1.10	0	25	40	100
14	A	A2	0.91	0	20	60	100
15	A	A2	1.01	0	15	50	100
16	B	B1	0.98	0	0	10	60
17	B	B1	1.36	2	5	15	100
18	B	B1	1.06	0	3	15	100
19	B	B1	1.20	0	4	10	100
20	B	B1	1.00	5	20	60	100
21	B	B1	1.13	0	4	13	100
22	B	B1	1.36	2	5	15	100
23	B	B1	1.13	0	4	13	100
24	C	C1	1.10	32	48	82	98
25	C	C2	1.20	28	50	83	100
26	D	D1	0.89	0	0	11	100
27	D	D1	1.20	4	15	20	100
28	D	D1	1.36	1	8	15	100
29	D	D1	1.31	0	3	10	100
30	D	D1	1.10	1	6	13	100
31	D	D1	1.20	4	15	20	100
32	D	D1	1.21	1	6	13	100
33	D	D1	0.96	5	9	18	100
34	D	D2	1.02	0	5	16	80
35	D	D2	0.90	0	1	5	100
36	D	D2	1.06	1	5	10	100
37	D	D2	1.13	1	5	20	100
38	D	D2	1.10	1	5	15	100
39	D	D2	0.90	0	1	5	100
40	D	D2	1.10	1	5	15	100
41	D	D2	1.03	0	3	8	100
42	E	E1	1.31	1	4	10	95
43	E	E1	1.13	0	5	20	100
44	E	E1	1.10	0	15	40	100
45	E	E1	1.12	0	10	30	100
46	E	E1	1.25	1	4	10	95
47	E	E1	1.12	0	10	30	100
48	E	E1	1.06	0	35	85	100
49	E	E2	1.12	2	58	95	100
50	E	E2	0.98	3	75	100	100
51	F	F1	1.02	0	1	6	90
52	F	F1	1.06	1	5	13	90
53	F	F1	1.06	1	3	10	100
54	F	F1	1.13	0	1	7	100
55	F	F1	1.10	1	2	8	100
56	F	F1	1.06	1	5	10	90
57	F	F1	1.10	1	2	11	100
58	F	F1	0.96	0	3	12	100
59	F	F2	1.00	7	15	53	100
60	F	F2	1.20	25	30	35	100
61	F	F2	1.00	10	15	15	100
62	F	F2	0.83	15	35	80	100
63	F	F2	0.92	13	25	48	100
64	F	F2	1.20	25	30	35	100
65	F	F2	0.92	13	25	48	100
66	F	F2	1.06	25	65	85	100

1: Preparation of the Test Panels and Conditions of Neutral Salt Spray Fog Test (NSSFT) Cabin: Test samples with 150 mm x 200 mm dimensions were prepared and their surfaces were examined. Sample surfaces were controlled and the samples having surface defect were weeded out in order to eliminate the effect caused by improper samples.

Edges of the cut samples would be subjected to faster corrosion because of anodic reaction in neutral salt spray fog conditions. Therefore, edges of the samples were taped to isolate them. After applying the protective oil, the samples were placed in the cabin with an angle of 15° to vertical axis during all tests. Neutral brine solution with a 5% saturation was prepared with NaCl with analytic purity and ultra-pure water (conductivity <0.1 µS/cm).

Fog density was determined by placing a volumetric measure with a funnel with 80 cm2 surface area in the cabin. The air pressure is set for a fog density to get accumulation of 1-2 ml solution per hour on average and this pressure value was used for all tests. Thus, a standard corrosive medium was created by homogenising the fog density for all samples. The cabin was kept at constant 35 °C temperature and 100% relative humidity during all tests.

2: Assessment of Neutral Salt Spray Fog Test: (NSSFT) samples by using the template method: In order to assess the amount of corrosion, images of sample surfaces were taken from 20 cm distance by means of a high resolution digital camera. Then a grid with 100 equal boxes is placed on each image on computer. The number of boxes containing corrosion yields percentage of corrosion. Whether a box was full of corrosion or only a small part of it had corrosion, the box was considered as corroded. Results are disclosed as % white rust and % red rust. Considering that red rust forms after white rust, boxes with red rust (even if there was not any white rust seen) were counted as boxes with white rust. However, only the boxes with red rust are counted to get percentage of red rust. Thus, percentage of red rust cannot be more than white rust in template method. Fig. 1 to 3 show some samples, forced into corrosion in NSSFT cabin and assessed by the template method.

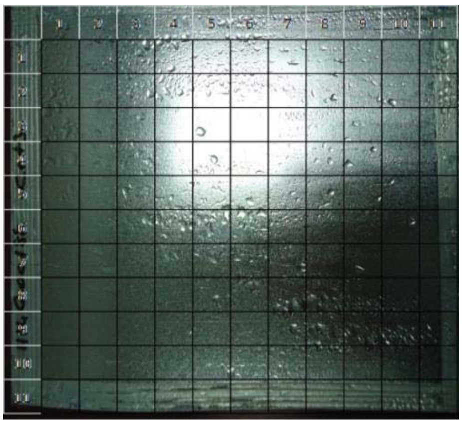


Fig. 6 White Rust = 0%, Red Rust = 0%

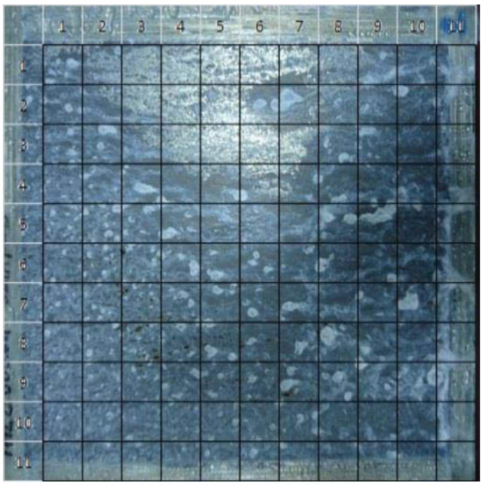


Fig. 7 White Rust = 100%, Red Rust = 0%

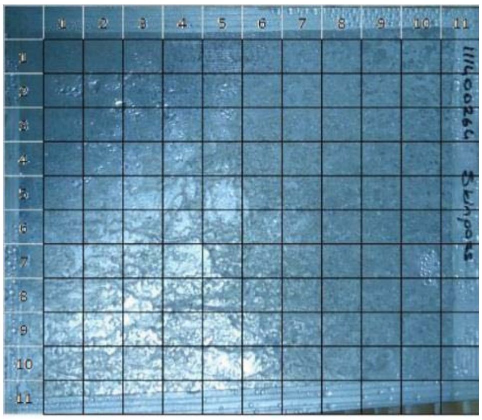


Fig. 3 White Rust = %100, Red Rust = 14%

III. RESULTS

E. *Corrosion status of sheets, on which protective oil was not used*

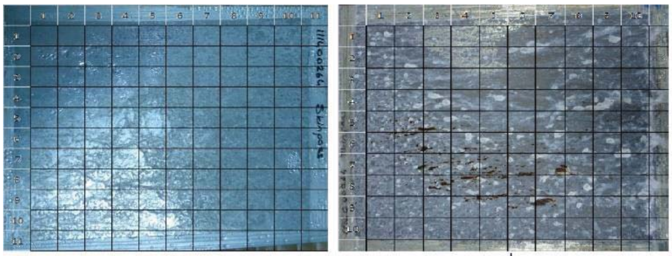
In order to determine the status of specimens without protective oil samples with skin pass without oil (blind) were forced into corrosion in the NSSFT cabin up to 24 hours. As seen in Fig. 4, observed white rust amount is 100% at 2 hours and red rust amount is 34% at 24 hours on blind panels.

F. *Determining the protective performances from corrosion of protective oils*

After application of 1 g/m^2 oil on a total of 66 samples, using 11 different protective oils, samples were forced into corrosion in NSSFT cabin. Formations of white rust in 2, 6, 9 and 24 hours were assessed and findings are provided in Table 6.

To get 95% reliability, extreme values belonging to each oil samples, which are highlighted on Table 3, were determined by Q test and eliminated. This has caused C1, C2, and E2 data to be out of table completely. Average and standard deviation values for remaining oil products are listed in Table 6.

When Table 6 is examined, it is seen that standard deviations in average white rust amounts were low at the end of the first 2 hours and therefore 2 hours did not offer optimum data for an assessment. Furthermore, surface of many panels were completely covered with white rust in 24 hours and amount of corrosion reached 100% white rust or became very close to this value at the end of 24 hours. Such as the data at the end of 2 hours, the data at the end of 24 hours are devoid of providing significant differences for a distinctive assessment.



a b

Fig. 4 When blind samples were forced into corrosion in the NSSFT cabin, 100% white rust and 0% red rust was observed in 2 hours (a) and 100% white rust and 34% red rust was observed in 24 hours (b).

Data at 6th and 9th hours yield higher standard deviation in comparison to the data at 2nd and 24th hours and the average white rust formation percentage at 6th and 9th hours comprise more suitable distinctiveness amounts in terms of visual distinctiveness.

It can be seen that 9th hour data offer both higher amount of average white rust data and have relatively higher standard deviations when the most suitable one among 6th and 9th hour data are examined to determine the protective performance of the oil. So, application of NSSFT for 9 hours can be suggested for the most distinctive determination of performance of protective oil products on galvanized and skin passed sheets.

According to Table 6 data, the oil with the highest performance for protection of galvanized sheets against white rust is F1 oil means the 1st oil of the manufacturer F.

Table 6

AVERAGE CORROSION AMOUNTS AND STANDARD DEVIATIONS FOR PROTECTIVE OILS

Product Code	Realized Amount of Oil (g/m²)		White Rust Amount							
			at 2 hours		at 6 hours		at 9 hours		at 24 hours	
	Average	Std Dev.	Average	Std Dev.	Average	Std Dev.	Average	Std Dev.	Average	Std Dev.
A1	1.15	0.22	1.79	2.38	49.64	17.14	77.14	14.39	100.00	0.00
A2	1.00	0.08	0.00	0.00	20.00	4.08	50.00	8.16	100.00	0.00
B1	1.17	0.14	0.57	0.98	3.43	1.69	12.86	2.25	94.29	15
D1	1.17	0.19	0.40	0.42	4.40	3.03	12.20	1.89	100.00	12
D2	1.03	0.09	0.50	0.53	3.75	1.83	11.75	5.55	97.50	7.07
E1	1.17	0.09	0.33	0.52	8.00	4.43	23.33	12.11	98.33	2.58
F1	1.06	0.05	0.50	0.46	2.75	1.58	9.63	2.45	96.25	5.18
F2	1.04	0.13	15.33	0.76	23.33	6.83	38.83	13.77	100.00	0.00

IV. CONCLUSION

Protective oil is used to prevent white rust formation on galvanized sheet. Choosing the protective oil with the highest performance has critical importance for galvanized sheet manufacturers to overcome problems related to white rust formation. A method for comparing corrosion protective oil on galvanized and skin passed sheet suggested as:

1) Approximately 1 g/m² protective oil might be applied on the samples

2) The samples should be kept in NSSFT cabin with 5% brine NaCl solution hold at 35 °C temperature and 100% relative humidity for 9 hours.

3) Formation of white rust might be assessed and compared using template method mentioned in section 2.4.2.

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