RUSTING OF COLD ROLLED STEEL SHEET COILS DURING TRANSIT AND STORAGE A CASE STUDY

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Rusting of steel sheet coils imported from other countries to India for the production of tin plate has been studied in detail. The cause of rusting and the effect of vapour phase inhibitor impregnated in the packaging paper for the prevention of rust have been discussed in the paper.

Cold drawn steel sheet in coils are imported to this country from Japan, West Germany, United Kingdom and various other countries. These coils are transported in packed condition by the host countries and the transhipment time normally takes 2-4 months, somtimes even six months, before the consignment reaches the destination. On unpacking the consignment, many of the coils are observed to have rusted especially on overlapping surfaces. The rusting becomes more acute between March and August in India. As reported, the problem of rusting of the coils is not experienced in other countries. So, the host countries are not very much keen to introduce special protective devices other than their usual packaging procedure especially for customers in India.

In view of the importance of the problem, the National Metallurgical Laboratory, Jamshedpur undertook the investigation. The present paper, presents the analysis of rusting of the coils with particular reference to its causes and suitable preventive measures.

EXPERIMENTAL

Visual Observations

A physical inspection of both the packed and unpacked coils was made at the plant site located at Jamshedpur. A package outwardly free from any damage was randomly chosen and unpacked in our presence. It was observed that the package consisted of successive coverages of water proof paper, polythene sheet and finally a steel sheet seathing for protection against physical damage. The steel coil was seen free from rust on the peripheral and vertical faces. However, on uncoiling the roll, several elongated rust patches extending from both sides and distributed althrough the length of the strip were noted (Fig.1). Another package damaged at one place, was also opened and inspected. It was found that the coil was in badly rusted condtion and the packaging materials were sufficiently wet.

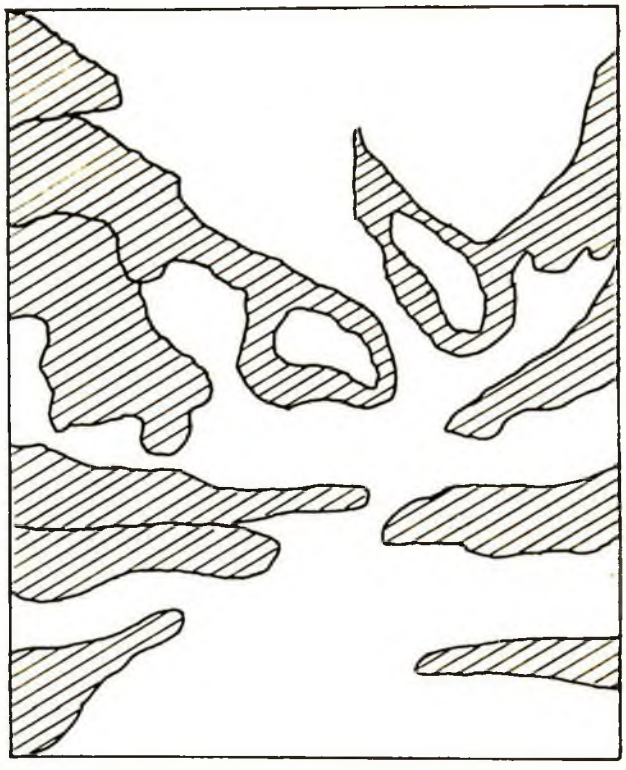


Fig. 1 Schematic presentation of patch marks on steel strips.

Two numbers of cut piece samples of 50 x 40 cm size, were collected for the study from the batch Nos. WG-2175, HWG-2850 and NKK-2420. These are unalloyed cold rolled steels containing 0.1% carbon. It was observed that the sample Nos. HWG-2850 and WG-2175 (Fig.2 and 3) were the worst affected and completely covered with blackish brown rust. At many places, deep pits were found. The extent of attack on the sample No. NKK-2420 was compartatively less (Fig. 4). The pattern of corrosion observed on the surface indicated the fluid flow. Samples of pakaging materials from both freshly opened package and the damaged

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The paper was presented at the International conference on Corrosion Science & Technology held at Calcutta on 21st-23rd Feb. 1985



Fig. 2 Shows the steel sample No. HWG-2850 in as received condition. Marked amount of rust on the surface can be seen.



Fig. 4 Shows the steel sample No. NKK-2420 in as received condition. Comparatively, less amount of rust on the surface can be seen.



Fig. 3 Shows the steel sample No. WG-2175 in as received condition. Marked amount of rust on the surface can be seen.



Fig. 5 Rust spots on the nylon-reinforced packaging paper in as received condition.

package were collected for the study. The imprints of rust spots on the wrapping paper at contact areas are shown in Fig. 5

Chemical Analysis of the Rust and the Packaging Paper.

The qualitative spectrographic and the quantitative chemical analysis of the rust samples collected from the coils and the packaging paper are given in Table-1.

Phase Analysis of the Corrosion Product

The rust samples were analysed by X-ray Debye-Scherror powder pattern in 11.46 cm dia camera using Co Kα radiation in Philips X-ray diffractometer PW-1130. Table-2 shows the 'd'values and the presence of possible phases.

Total Immersion Test

Samples of 2.5 x 2.5 x 0.15 cm size were cut from the steel sheet, polished with '400' emery paper

TABLE 1

SPECTROGRAPHIC AND CHEMICAL ANALYSIS OF RUST COLLECTED FROM THE STEEL STRIPS AND THE PACKAGING PAPER

Sl. No.	Sample	Cl^-	SO_4^{--}	NH_4^+	Mg^{++}	Cl^- in packaging paper %
		per 100 cm of rusted area in mgs				
1.	WG-2175	5.67	1.0	Nil	- trace	0.78
2.	HWG-2850	3.34	0.6	Nil	-do-	0.28
3.	NKK-2420	0.30	Trace	Nil	Trace	0.28

TABLE 2

X-RAY ANALYSIS OF RUSTS COLLECTED FROM STEEL STRIPS

Radiation = Co $K\alpha$
Ratings = 35 KV, 20 mA
Philips X-ray diffractometer PW 1130
Camera : 11.46 cms dia

Sample	Sl. No.	Intensity	Values A'	Identification
HWG-2850	1	S	3.248	Fe_2O_3
	2	S	2.498	Fe_3O_4 , Fe_2O_3
	3	F	2.245	Fe_3O_4 , Fe_2O_3
	4	M	2.072	Fe_3O_4 ,
	5	M	1.937	Fe_3O_4 ,
	6	VF	1.738	Fe_3O_4 , Fe_2O_3
	7	VF	1.541	Fe_3O_4 , Fe_2O_3
	8	VF	1.470	Fe_3O_4
NKK-2420	1	F	3.100	Fe_2O_3 ,
	2	MS	2.895	Fe_3O_4 , Fe_2O_3
	3	S	2.493	Fe_3O_4 , Fe_2O_3
	4	VS	2.006	Fe_3O_4 , Fe
	5	V	1.675	Fe_3O_4
	6	MF	1.609	Fe_3O_4
	7	MF	1.474	Fe_3O_4 , Fe_2O_3
	8	S	1.422	Fe
	9	VF	1.236	Fe_3O_4 , Fe_2O_3
	10	VS	1.167	Fe_2O_3 ,
	11	F	1.094	Fe_3O_4 ,
	12	VS	1.014	Fe
	13	VF	0.9696	Fe_2O_3 ,
	14	D & S	0.0088	Fe, Fe_2O_3

cleaned with MgO paste, rinsed with distilled water and finally degreased with acetone, dried and weighed. These were kept immersed in an un-aerated 500 ml of 3% NaCl solution for 168 hours at room temperature (30 ± 1°C). The samples were than taken out and the corrosion product on the samples was removed in an inhibited HCl solution. The samples were, then, re-weighed to determine the loss in weight during the test. The corrosion rate in terms of m.d.d are set forth in Table-3.

TABLE 3

CORROSION RATE AND POLARIZATION DATA OF THE STEEL STRIPS IN 3% NaCl SOLUTION AT ROOM TEMPERATURE

Sl. No.	Sample Number	Corrosion rate mdd	Steady open circuit potentials, vs SCE mV	Corrosion current from polarization curves, mA/cm^2
1	HWG-2850	50.79	460	0.63
2	WG-2175	70.08	470	1.59
3	NKK-2420	42.33	450	0.60

Polarization Studies

Potentiostatic polarization studies were conducted by exposing an area of 1 cm^2 of the sample in an un-aerated chloride solution at room temperature. Potential of the steels w.r. to saturated calomel electrode was measured in the chloride solution using philips VTVM. Platinum was used as an auxiliary electrode in potentiodynamic measurements. Results are shown in Table-3.

Testing of Inhibitive Properties of the Nylon-reinforced Packaging Paper

A few samples of the nylon-reinforced packaging paper were collected during inspection for examining their inhibitive properties under constant condensation test involving high humidity and high temperature [2]. For the test the dimension and the preparation of the sample No.NKK-2420 were the same as mentioned above. The weighed samples after wrapping with a nylon-reinforced packaging paper, in as received condition or with the nylon-reinforced packaging paper impregnated with dicyclohexylamine nitrite (DICHAN,2 gm/ft^2) were exposed to the test conditions for 7 days. For comparison, an uninhibited packaging paper of an Indian origin was used in the test. The corrosion rate in terms of m.d.d and the performance of different packaging papers used in the study are set forth in Table-4. Imprints of rust spots appeared on different packaging papers after the test are shown in Fig.7.

Determination of Moisture in the Packaging Paper

The moisture content of the nylon-reinforced

TABLE 4

PERFORMANCE OF DIFFERENT PACKAGING PAPERS WRAPPED ON THE STEEL SAMPLES

Sl. No.	Paper used	Weight loss m.d.d	Observation
1	Packaging paper (Indian craft paper) without vapour corrosion inhibitor (control)	30.10	Very heavy rust on the surface
2	Nylon-reinforced packaging paper (Imported)	76.20	Very heavy rust on the surface
3	Nylon-reinforced packaging paper (Imported impregnated with DICHAN (2 g./ft^2)	No loss 100 % inhibition	Bright surface

packaging paper used by the host countries for wrapping the steel coils was determined by drying the weighed paper at 110°C for two hours. The paper after cooling to room temperature in a desiccator was re-weighed to know the mositure loss. The % moisture content of the paper samples taken from a dry portion was 2.85 whereas the % moisture content of the samples taken from the wet portion was 5.34.

RESULTS AND DISCUSSION

Visual examination of the surfaces of the samples Nos. HWG-2175 and NKK-2420 taken from a sound package and a damaged package showed that there was an ingress of the fluid with subsequent stagnation of the corrosive fluid at different locations (Fig.1&4). This might have resulted from either the condensation of mositure present in the air entrapped in the crevices or the ingress of water from an external source.

Qualitative spectrographic analysis of the rust samples collected from the strip indicated the presence of magnesium as 'more than trace' amount in samples Nos.HWG-2850 and WG-2175 and as 'trace' in sample No.NKK-2420. Chemical analysis of the rust samples and the packaging paper showed appreciable amount of chloride. A good amount of sulphate in the rust samples was also found (Table-1). Also, the packaging paper contained appreciable amount of moisture. The presence of magnesium in the rust is an indicator of ingress of water from an external source. The source of chloride may be an external one or from the packaging paper which contains 0.28% chloride (Table-1).

X-ray diffraction analysis of the rust samples collected from the sample Nos. HWG-2850 and NKK-2420 indicated the predominance of magnetite (Table-2). The formation of magnetite (Fe_3O_4) in the presence of chloride is possible when the supply of oxygen to oxidise is restricted in the crevices. The corrosion reactions expected to take place in the crevices are as below :-

$$Fe \longrightarrow Fe^{2+} + 2e \quad \ldots \quad (1)$$

$$H_2O + 1/2\ O_2 + 2e \longrightarrow 2(OH)^- \quad \ldots \quad (2)$$

adding (1) & (2)

$$Fe + H_2O + 1/2\ O_2 \longrightarrow Fe(OH)_2$$

In presence of excess of oxygen, ferrous hydroxide is converted to ferric hydroxide in accordance with

$$2Fe(OH)_2 + H_2O + 1/2\ O_2 \longrightarrow 2Fe(OH)_3 \text{ or } Fe_2O_3 .3H_2O \quad \ldots\ldots\ldots\ldots (3)$$

X-ray analysis of the rust also shows the presence of Fe_2O_3 which may be in accordance with the equation-3. When access of oxygen is limited because of the restricted convenction, the anodic reaction is balanced by the cathodic reduction of ferric rust ($Fe_2O_3 .3H_2O$) to magnetite under wet condition in accord with

$$4\ Fe_2O_3 + Fe^{2+} + 2e \longrightarrow 3Fe_3O_4 \quad \ldots \quad (4)$$

The predominance of magnetite in the rust shown by the X-ray analysis is considered to be due to the equation-4.

There is often a long incubtion period associated with the crevice corrosion. If the time gap between the packaging of the coils at the manufacturer's end and unpacking of the coils for further processing i.e. tinning at the user's end is kept minimum, say about a month, a crevice corrosion could be avoided.

Sample No. WG-2175 showed maximum corrosion rate whereas the sample No.NKK-2420 corroded least in 3% NaCl solution at room temperature (Table-3). The same trend was also observed in the corrosion current calculated from the polarization curves (Fig.6). Extent of corrosion as evident from visual examination was also more in the case of the sample No.WG-2175 (Fig.3) than on the sample No.HWG-2850 (Fig.2) and NKK-2420 (Fig.4). This is attributed to the compositional difference and heterogeneity of the surface of the steels. The steady state open circuit potentials of the sample in the chloride solution are shown in Table-3. The active potential shown by the sample No.Wg-2175 substantiates its higher corrosion rate as compared to other samples.

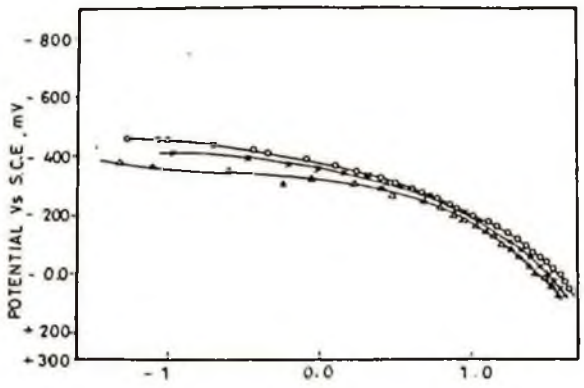


Fig. 6 Potentio dynamic polarization curve for 1. HWG-2850, 2. NKK-2420, 3. WG-2175 in 3.0% NaI

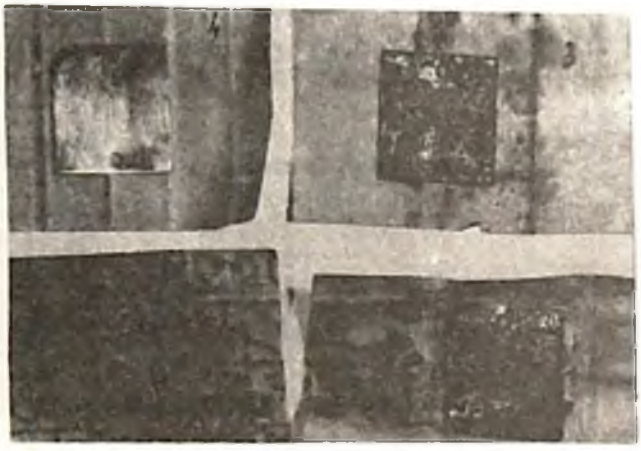


Fig. 7 Surface condition of a sample and imprints of rust spots on the packaging paper after "Constant d condensation test" after 7 days.

No. 1 Imprint of rust spots on nylon reinforced packaging paper developed during transit and storage.

No. 2 NKK-2420 steel cum nylon-reinforced packaging paper after the laboratory test.

No. 3 NKK-2420 steel cum packaging paper (Indian craft paper) after the laboratory test.

No. 4 NKK-2420 steel cum nylon-reinforced packaging paper impregnated with DICHAN after the laboratory test.

The sample No.NKK-2420 wrapped in nylon-reinforced packaging paper in as received condition (0.28% chloride) corroded more in comparison to the sample No.NKK-2420 wrapped in an Indian craft paper (0.12% chloride) under constant condensation conditions (Table-4 & Fig.7). This is attributed to a higher chloride content in the imported paper [4] under similar test conditions. The steel sample, wrapped with the nylon-reinforced wrapping paper impregnated with DICHAN, did not show rust. This indicates that the nylon-reinforced packaging paper containing no vapour phase inhibitor has led to the rusting of the steel coils under the prevailing conditions.

CONCLUSIONS

1. The rusting of steel Nos. HWG-2850, WG-2175 and NKK-2420 has been found to be due to ingress of corrosive fluid in between overlapping steel surface, resulting in crevice corrosion.

2. The presence of magnesium and chloride in the rust suppliments the view of direct contact of metal surfaces with sea or esturary water.

3. The presence of Fe_3O_4 as major constituent in the rust supports the view of crevice corrosion of the coils in the presence of chloride.

4. Condensation of moisture due to diurnal fluctuation of temperature inside the crevice and the gradual build up of chloride in the stagnant liquid with associated corrosion is also possible for the undamaged packages.

5. The studies indicate that the nylon-reinforced packaging paper does not contain vapour phase inhibitor. If the vapour phase inhibitor could have been used in the nylon-reinforced paper, it could have protected the strips completely from corrosion.

ACKNOWLEDGEMENT

The authors record their thanks to Prof. S. Banerjee, Director, National Metallurgical Laboratory, Jamshedpur for his permission to publish the paper and to Mr. B.K. Bhasin, Managing Director, the Tin Plate Company of India limited, Golmuri, Jamshedpur for supplying the samples for this investigation.

REFERENCES

1. K.N.P. Rao and A.K. Lahri, *Corrosion Map of India*, (Corrosion Advisory Bureau, Metals Research Commitee NML, CSIR, Jamshedpur,) (1972), pp. 20 & 23

2. I.S. - 5730 (1970), *Volative Corrosion Inhibitor Powder*

3. L.L. Shreir, *Corrosion Vol.I*, (Newnes Butterworths, London), (1976), pp.12:35

4. H.H. Uhlig, *Corrosion and Corrosion Control*, (John Wiley & Sons Inc. New York), (1971) pp. 113.

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