

# A MÖSSBAUER STUDY ON GRAY STAINS IN ELECTROGALVANIZED STEEL

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## ABSTRACT

Transmission Mössbauer Spectroscopy (TMS) and Conversion Electron Mössbauer Spectroscopy (CEMS), together with X-ray diffraction (XRD) are applied to identify the origin of stain defects formed on one-side zinc-coated steel used in the automotive industry. The stained sheets were directly exposed to CEMS meanwhile absorbers for TMS were obtained by tape, scrapping, paper and ultrasound bath. Measurements, both by TMS and CEMS, show the presence of the  $\alpha$ -Fe signal in all the cases. CEMS measurements also indicate that a Mössbauer inactive coating covers the stained areas. Fe<sub>3</sub>C and Fe-C signals, as minor ones, appear only when the absorber is prepared by paper. Results show that the stains are not due to a corrosion process and therefore the

corrosion performance of the steel should not be affected by the presence of the stains over the non plated side. An incomplete cleaning of the oil used to protect the steel before entering the electrogalvanizing line would have produced the stains.

Keywords: Mössbauer Spectroscopy applied to surface (stains) studies in zinc coated steel, cleaning in electrogalvanized steel.

## INTRODUCTION

Electrogalvanized steel is being used increasingly for the manufacture of automobiles, domestic appliances, buildings and other products. Many technologies have been developed to improve the quality and cost of zinc coated sheets while trying to fulfill the stringent and diversified quality requirements from users.

The substrates can be generically described as cold rolled, low carbon sheet steel. Both one-side and two side electrogalvanized coatings are being produced. The one-side coated product is particularly desirable in applications that require superior protection on the inside of the low C steel panel, where structural corrosion usually starts. The steel also contains a high quality steel surface on the exterior that can be developed, joined and painted in the usual way. Such parts, needing a good superficial finish, require an uncoated surface with properties as close to that of cold rolled sheet as possible.

One-side electrogalvanized sheet is produced either by plating only one side (in single anode cells) or turning off the plating current to the anodes facing the side that remains uncoated (in double anode cells). In both cases, as the steel strip travels through the plating section, the uncoated side is attacked by the acid electrolyte. This pickling action leads to a highly active surface where sometimes gray- stains appear.

The degree of stain formation depends upon many variables such as prior history and grade of steel, pretreatment practices and plating process conditions. The stains affect the appearance of the uncoated side, this being undesirable. Thus, it is of economical value to know the origin of these defects and its incidence on the final performance and esthetics of the material.

With the aim of identifying the origin of the stain defects, we present results of studies performed on one-side zinc-coated steel surfaces using Mössbauer Spectroscopy and XRD.

## EXPERIMENTAL PROCEDURES

Sheets from one-side 7-9 microns zinc-coated steel used in the automotive industry were collected at the end of the electrogalvanizing line. The sheets showed two kinds of stained areas, clear gray and dark gray ones. When both areas were present, sometimes an interface zone appeared which under a magnifying lens looked as dark gray-clear gray intermixed bands.

The different sheets chosen were named S1, S2 and S3<sub>a</sub>, all of them

corresponding to clear gray zones and S3<sub>b</sub> to a dark gray zone. Different zones of each sheet, without any previous treatment, were analyzed by XRD to check composition and homogeneity.

XRD patterns were taken at room temperature (RT) with a Philips PW 3710 diffractometer with Cu monochromatized radiation ( $\lambda=0.15418\text{nm}$ ) using a curved graphite monochromator, and a  $1/2^\circ$  scattering slit using a  $0.02^\circ$   $2\theta$  step in a  $10^\circ$ - $60^\circ$   $2\theta$  range. A counting time of 25 sec by step was used to increase the resolution and to improve statistics. PC-Identify program (PW-1876) was used for phase identification.

Mössbauer spectra of the sheets were recorded by TMS and by CEMS. TMS spectra were collected at RT and at 15K using a 25 mCi Co<sup>57</sup> in Rh matrix source. Analysis of the spectra was done using the NORMOS program for sites and distributions of hyperfine fields. The CEMS spectra were recorded at RT with a gas flow proportional counter [1] using 5%He/Methane gas, and a 25 mCi Co<sup>57</sup> in Rh source. The spectra were fitted with multiple Lorentzian lines using RECOIL software. IS values found are referred to that of  $\alpha$ -Fe.

Different procedures were used to remove the powders from the stained zones for Mössbauer Spectroscopy studies. In the case of the S1 sheets, both tape and 600 grade Al<sub>2</sub>O<sub>3</sub> paper were used, in the case of the S2 sheet the powders were obtained only by scrapping and in the case of S3 (S3<sub>a</sub> and S3<sub>b</sub>) sheets an ultrasound bath (US) was performed. In the US mode, the material is submerged in an ethanol bath and ultrasound bathed for 60 min, with the liquid carefully evaporated. All of the samples were examined by TMS and similar

areas of the S3<sub>a</sub> and S3<sub>b</sub> samples were also examined by CEMS.

## RESULTS

XRD patterns of different zones of the S1 and S3 sheets show the typical  $2\theta = 44.80^\circ$  peak of  $\alpha$ -Fe. No evidence of any Zn, S, Ca secondary phases was detected. S1 and S3<sub>a</sub> patterns also show three small peaks at  $2\theta = 29.58^\circ$ ,  $40.36^\circ$  and  $42.88^\circ$ . It is possible to ascertain the presence of Fe carbide and Cl carbide considering the ICDD cards 35-772, 6-686 and 11-123. The  $2\theta = 26.65^\circ$  peak seen in one of the S3<sub>a</sub> patterns suggested a Cl-substituted goethite. In the case of the S3<sub>b</sub> sample, only the  $\alpha$ -Fe peaks were observed. A further study was performed using a grazing incidence of  $2\theta = 3^\circ$  in an attempt to increase the resolution of a possible second phase. The results obtained were similar; only the Fe peak was observed over an amorphous background. Some of the previously mentioned patterns are shown in Fig.1.

Please insert figure 1

S1 Mössbauer spectra (by TMS) corresponding to the absorber obtained by tape show a prominent  $\alpha$ -Fe sextet at both temperatures and a small doublet, due to Fe-C contribution. The S2 spectra also show a prominent  $\alpha$ -Fe signal and an almost 5% magnetite contribution. In the case of the S1 absorber obtained by paper, spectra looked clearly different from the previous ones and were fitted with 3 sextets and one doublet. The signals were assigned to  $\alpha$ -Fe, Fe<sub>3</sub>C,  $\alpha$ -FeOOH

and Fe-C respectively. The parameters obtained for all the samples are shown in Table 1. The RT fitted spectrum of the S1 absorber obtained by paper is shown in Fig. 2. Assignments are included in the last column of Table 1.

SAMPLE	T		Sextet 1	Sextet 2	Sextet 3	Doublet 1	Doublet 2	Assign.
S1 tape	RT	IS	0.2	—	—	0.17	—	$\alpha$ -Fe[2] Fe-C[3]
		QS	0.00	—	—	0.45	—	
		H	32.8	—	—	—	—	
	15 K	IS	0.09	—	—	0.16	—	$\alpha$ -Fe Fe-C
		QS	0.00	—	—	0.44	—	
		H	33.6	—	—	—	—	
S1 paper	RT	IS	0.00	0.19	0.28	0.22	—	$\alpha$ -Fe Fe <sub>3</sub> C[3] $\alpha$ -FeOOH[4] Fe-C
		QS	0.00	0.00	-0.25	0.54	—	
		H	33.0	22.0	36.4	—	—	
S2	RT	IS	0.00	—	—	—	—	$\alpha$ -Fe
		QS	0.00	—	—	—	—	
		H	32.98	—	—	—	—	
	15 K	IS	0.13	0.54	—	—	—	$\alpha$ -Fe Fe <sub>3</sub> O <sub>4</sub> [5]
		QS	0.00	0.22	—	—	—	
		H	32.97	52.37	—	—	—	
S3b	RT	IS	0.00	—	—	0.17	0.29	$\alpha$ -Fe Fe-C $\alpha$ -FeOOH
		QS	0.00	—	—	0.54	1.08	
		H	33.01	—	—	—	—	

Table1: Mössbauer parameters for all the samples. IS and QS are in mm/s and H in T.

Please insert figure 2

Please insert figure 3

In the case of the S3<sub>a</sub> sample, we obtained very little amount of powder by US bath and no spectra were run. On the contrary, in the case of the S3<sub>b</sub> sample it was possible to prepare an absorber. Its RT spectrum (Fig.3) shows the  $\alpha$ -Fe spectrum superimposed to a prominent central doublet, containing the Fe-C and  $\alpha$ -FeOOH contributions; the last one being confirmed by the spectrum at low T. The reasons for this spectrum not being of entirely satisfactory quality will be clear during the discussion.

CEMS spectra of S3<sub>a</sub> and S3<sub>b</sub> areas were very similar and correspond mainly to  $\alpha$ -Fe. The spectra have a very low signal to noise ratio especially the last one (S3<sub>b</sub>)(see Fig 4). Backgrounds were about 37.4 million counts and ~1.5% of effect on the 2-5 lines for the S3<sub>a</sub> spectrum and about 61 million counts and ~0.65% effect for the S3<sub>b</sub> spectrum.

Please insert figure 4

## DISCUSSION

On comparing the TMS results, different information is obtained. In all the cases but the one using the US procedure, the Fe signal is the prominent. Other Fe-compounds are seen by scrapping but as very low signals. Fe<sub>3</sub>C and Fe-C, coming probably from the low C steel, are noticeable when using the paper procedure. By the US procedure, a very small quantity of powder was obtained

from the S3<sub>a</sub> sample meanwhile a little bit more was obtained from the S3<sub>b</sub>. The Fe carbides and some contribution of  $\alpha$ -Fe are observed; also the expected  $\alpha$ -FeOOH (characteristic atmospheric corrosion product) appeared. XRD results agree with these findings.

CEMS results indicate that a Mössbauer inactive coating is covering the stained zones, being thicker in the dark areas. There is a lack of any Fe in the first few hundred angstrom and much likely thicker. Then the Mössbauer signal from other than  $\alpha$ -Fe is very low showing that below the inert layer, there is not much other iron compound, only those detected by TMS. In coincidence, a green-yellowed substrate appeared in the S3<sub>b</sub> sample, dark gray area, when applying the US procedure in an amount greater than in the case of S3<sub>a</sub> sample, clear gray area. Besides, grazing XR revealed the presence of non-crystalline compounds in the dark area.

The small amount of magnetite found in one of the clear gray areas is probably due to some slight oxidation in some points during the electrolytic alkaline cleaning of the steel. The goethite found is most likely due to atmospheric corrosion during the dryness in the line and/or during absorbers preparation. Fayalite was not detected, so the stains cannot be attributed to the previous hot rolled process.

Results obtained allow suggesting that the stains were not due to a corrosion process. The presence of magnetite and goethite, also detected in non-stained areas, is a consequence of a slight oxidation process that passivates the sheet surface. Both the clear and dark gray stains would have been produced by

an incomplete cleaning of the oil used to protect the steel before entering to the electrogalvanizing line.

Then, it is possible to assess that the corrosion performance of the steel should not be affected by the presence of the stains over the non plated side, only the esthetic should be affected.

## ACKNOWLEDGMENTS

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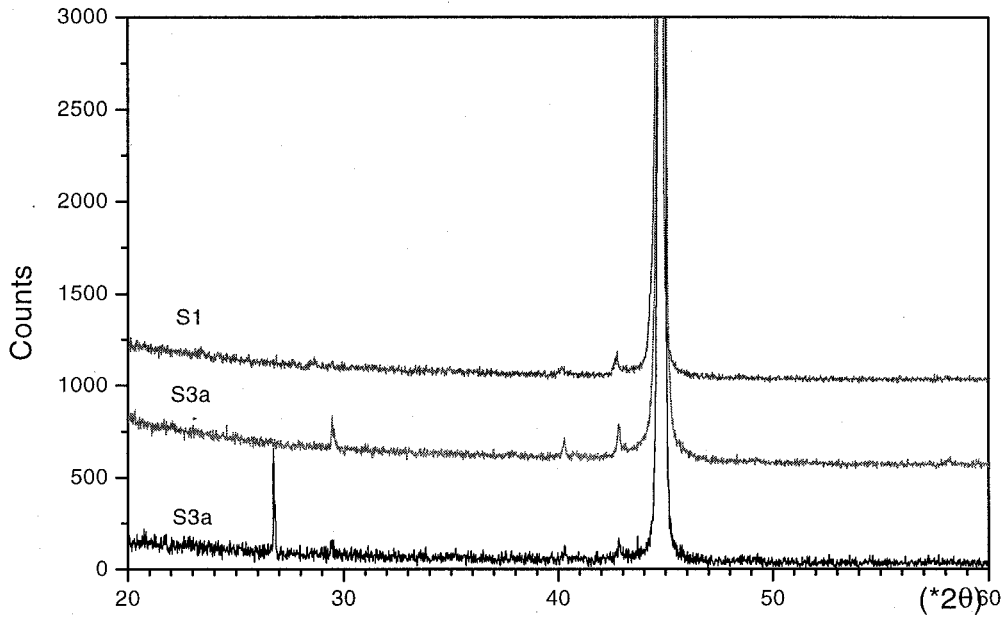


Figure 1: XRD pattern of S1 and S3 sheets

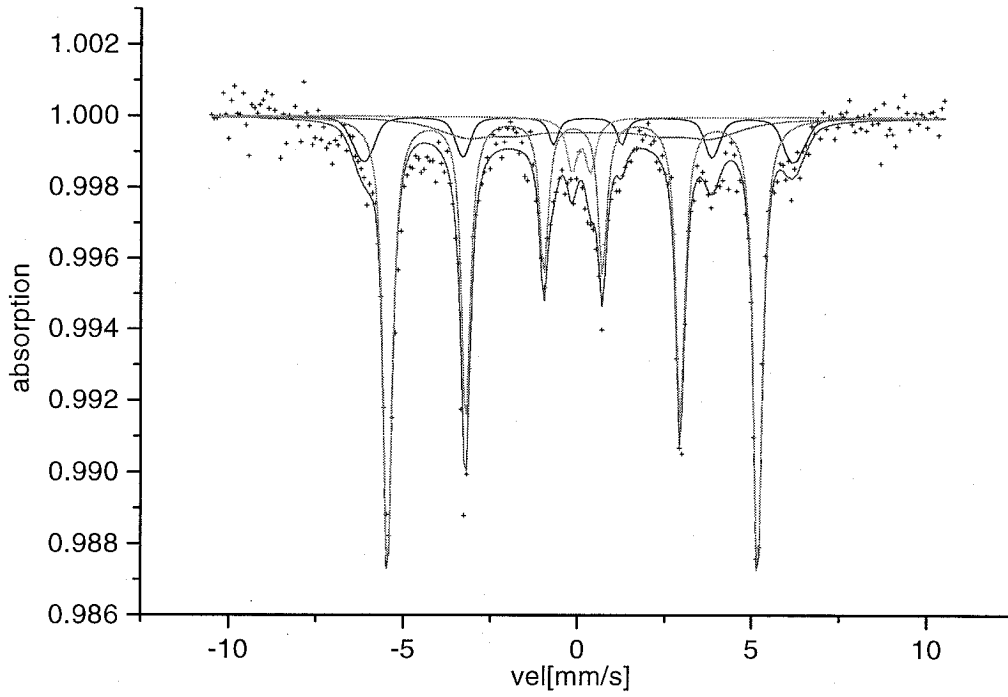


Figure2: S1 (paper) spectrum at room temperature

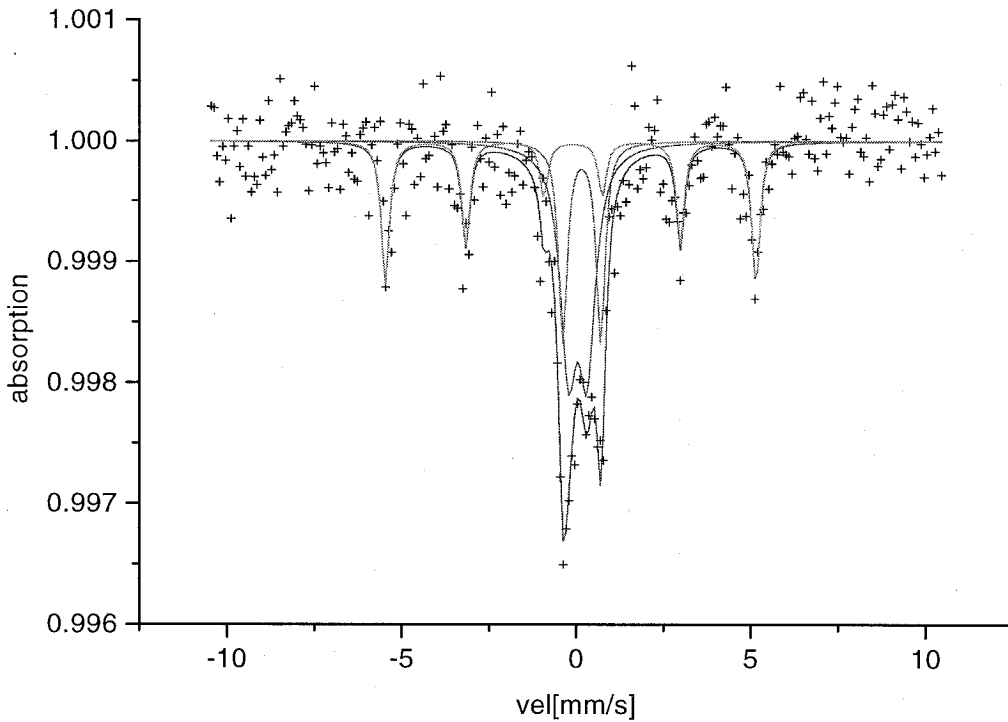


Figure3: S3b spectrum at room temperature

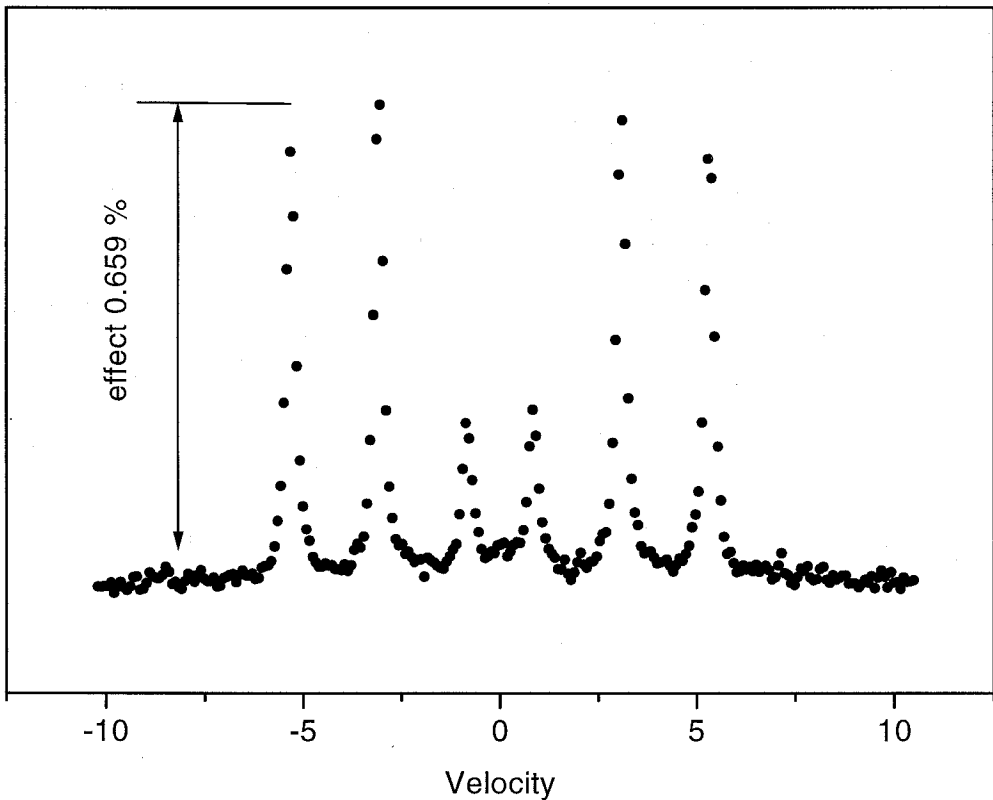


Figure4: CEMS spectrum of S3b sample