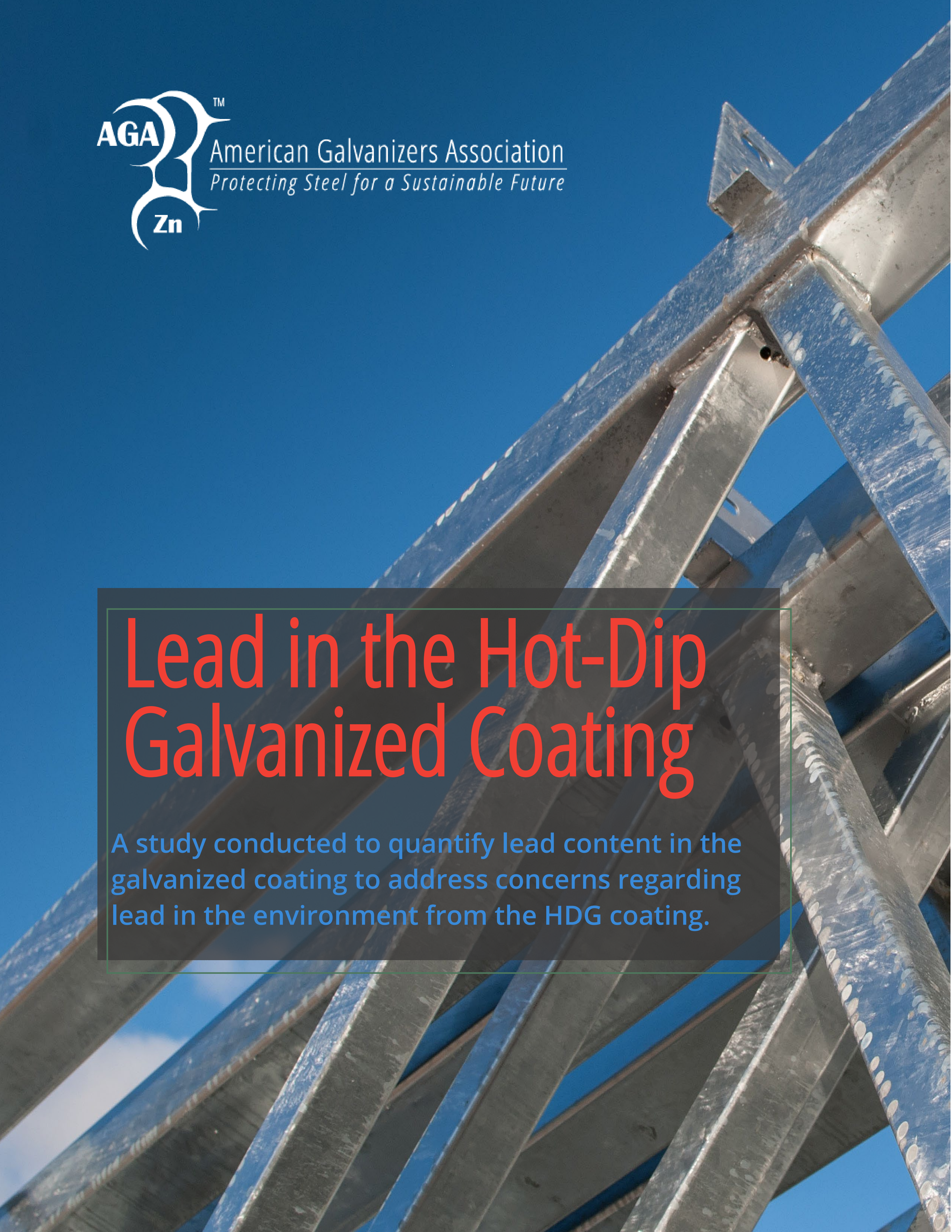
American Galvanizers Association

Protecting Steel for a Sustainable Future



Lead in the Hot-Dip Galvanized Coating

A study conducted to quantify lead content in the galvanized coating to address concerns regarding lead in the environment from the HDG coating.

Contents

Disclaimer

Introduction

Five grades of zinc metal are used for galvanizing. They are London Metal Exchange Grade (LME), 99.995% zinc, Special High Grade (SHG), minimum 99.99% zinc, High Grade (HG), minimum 99.95% zinc, Intermediate Grade (IG), 99.5% zinc, and Prime Western (PW), minimum 98.5% zinc. The main difference between the grades of zinc is the amount of impurities, notably lead, present. *Table 1* shows the chemical requirements for the zinc grades. Each of these zinc grades contain a small amount of lead, because lead is found in most natural deposits of zinc. *Table 1* is taken from the specification ASTM B-6 for zinc metal.

Table 1: Chemical Requirements for Zinc

Grade	Composition, %							
	Lead Max	Iron Max	Cadmium Max	Aluminum Max	Copper Max	Tin Max	Total Non-Zinc Max	Zinc, Min by Difference
LME Grade (LME)	0.003	0.002	0.003	0.001	0.001	0.001	0.005	99.995
Special High Grade (SHG)	0.003	0.003	0.003	0.002	0.002	0.001	0.010	99.990
High Grade (HG)	0.03	0.02	0.01	0.01	0.002	0.001	0.05	99.95
Intermediate Grade (IG)	0.45	0.05	0.01	0.01	0.20	...	0.5	99.5
Prime Western Grade (PWG)	0.5-1.4	0.05	0.20	0.01	0.10	...	1.5	98.5

A standard galvanized coating, shown in *Figure 1*, consists of two portions, a series of alloy layers of zinc and iron in contact with the base steel and an outer layer of unalloyed zinc metal. The alloy layers are made up of three phases of varying iron and zinc content. The phases in order of decreasing iron content are called gamma (**Γ**), delta (**δ**) and zeta (**ζ**).

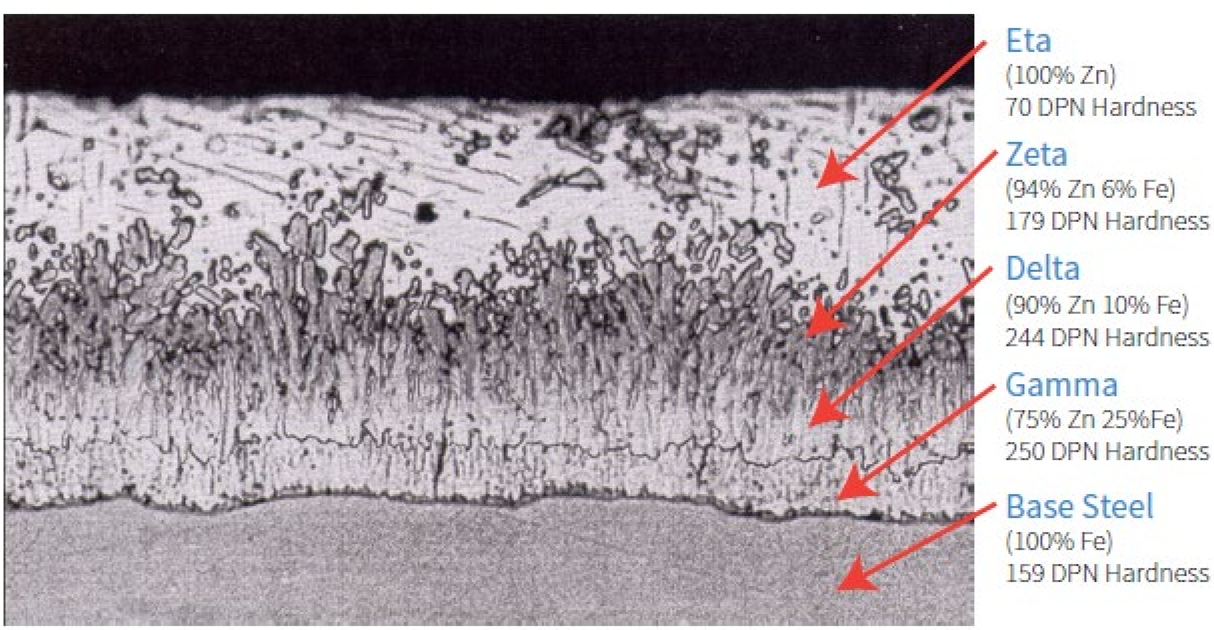


Figure 1: Alloy Layers of a Typical Galvanized Coating

The outer layer of unalloyed zinc metal has essentially the same composition as the molten metal in the galvanizing bath. Both layers contribute to the corrosion resistance of the galvanized steel and are consumed during the life of the coating. Since zinc used for galvanizing contains up to 1% lead, and the galvanized coating sacrificially corrodes to protect the base steel, there is a concern that lead in the coating may be released into the environment. In order to determine if there could be a significant impact on the environment, a study was conducted in order to quantify how much lead is in the galvanized coating and where in the coating lead resides.

Lead Content Measurements

A test program was conducted to determine how much of the available lead from the galvanizing bath was incorporated into the zinc coating. Two separate compositions of steel plates were used as the sample material. One of the compositions had a low silicon content (0.03%) and the other had a relatively high silicon content (0.27%). The variation in silicon content is intended to produce some coatings that are composed primarily of iron-zinc intermetallic layers with little or no free zinc layer. There were five different zinc bath compositions selected to give different amounts of lead and nickel in the final coating. Different zinc bath compositions were chosen to see if lower levels of lead are incorporated more fully into the final coating. The repeatability of the testing was verified by selecting two galvanizers for each type of bath composition. The test matrix is shown in *Table 2*.

Table 2: Test Matrix for Content Study

ZINC BATH COMPOSITION	STEEL COMPOSITION LOW SILICON	STEEL COMPOSITION HIGH SILICON
Prime Western	***	***
Prime Western + Nickel	***	***
Mixed (PW + HG)	***	***
High Grade	***	***
High Grade + Nickel	***	***

The steel samples were 4” x 6” plates, ¼” thick, with a hole punched in one comer to provide a support point for holding the part throughout the galvanizing process. A total of forty test samples were galvanized. The galvanizing conditions were similar for all of the samples in order to eliminate any potential differences due to process variables other than the zinc bath composition. The plates were cut into sections of suitable size for coating composition analysis and Scanning Electron Microscope (SEM) examination.

Three separate laboratories, Zinc Corporation of America, Cominco Product Technology Centre, and Noranda Technology Centre performed the sample analysis for the lead content and the coating examinations. The samples were labelled with alphanumeric designations so the composition of the bath was not known by the laboratory when they performed the analysis. Samples were split and cross-checked by different combinations of the three laboratories. The results of the analysis on the lead content in the coating are listed in *Table 3* and *Table 4*.

Table 3: Lead Content in Various Zinc Coatings in Low Silicon Steel

ZINC BATH COMPOSITION	LAB 1: LEAD CONTENT (%)	LAB 2: LEAD CONTENT (%)	LAB 3: LEAD CONTENT (%)	LEAD IN ZINC BATH (%)
Prime Western	0.51	***	0.572	0.88
Prime Western	0.53	0.617	***	1.14
Prime Western	0.58	0.624	***	1.14
Prime Western + Nickel	***	0.61	0.596	1.12
Prime Western + Nickel	0.32	0.36	***	0.886
Prime Western + High Grade	***	0.309	0.323	0.46
Prime Western + High Grade	0.15	***	0.141	0.324
High Grade	0.017	0.01	***	0.022
High Grade	0.11	***	0.101	0.189

Table 4: Lead Content in Various Zinc Coatings in High Silicon Steel

ZINC BATH COMPOSITION	LAB 1: LEAD CONTENT (%)	LAB 2: LEAD CONTENT (%)	LAB 3: LEAD CONTENT (%)	LEAD IN ZINC BATH (%)
Prime Western	0.61	***	0.631	0.88
Prime Western + Nickel	***	0.518	0.559	1.12
Prime Western + Nickel	0.32	0.268	***	0.886
Prime Western + High Grade	***	0.277	0.281	0.46
Prime Western + High Grade	0.10	***	0.083	0.324

Each of the laboratories used a different technique to measure the lead content in the galvanized coating. They all stripped the coating from the steel substrate and then examined the coating material. The coating thicknesses were measured by three different methods: magnetic thickness gauge, stripping and weighing, and metallographic examination. Bath compositions were reported by the individual galvanizers.

For the low silicon steel, the lead contained in the coating as a percentage of bath composition is an average of 54%. The lowest percentage of incorporated lead was 36% and the highest was 77%. For the high silicon steel, the lead that is contained in the coating as a percentage of bath composition is an average of 48%. The lowest percentage of incorporated lead was 26% and the highest was 72%. The lower incorporation of lead for the high silicon steel is most likely due to the higher proportion of iron/zinc intermetallics in the high silicon steel coatings.

The High-Grade samples did not show a higher proportion of incorporated lead than the Prime Western samples, and the Prime Western samples with nickel also did not show higher levels of lead incorporation. The High Grade plus nickel samples were not examined after reviewing the results from the High-Grade samples as well as the Prime Western samples that included nickel. For both high and low silicon steel samples, the lead exists mainly in the free zinc layer and in the free zinc trapped between intermetallic crystals in the coating.

Coating Thickness Measurements

Table 5: Coating Thickness Measurements for Low Silicon Steel

ZINC BATH COMPOSITION	LAB 1: HDG (mils)	LAB 2: HDG (mils)	LAB 3: HDG (mils)	AGA
Prime Western	2.4	***	2.9	2.88
Prime Western	2.3	2.9	***	2.82
Prime Western	2.7	2.7	***	2.56
Prime Western + Nickel	2.0	2.4	3.0	2.3
Prime Western + Nickel	2.6	2.9	***	2.81
Prime Western + High Grade	2.3	1.9	2.2	1.9
Prime Western + High Grade	2.6	***	2.3	2.2
High Grade	3.7	3.4	***	2.93
High Grade	2.9	***	3.4	3.09

The thickness of each of the samples was measured by the laboratories and by the AGA. *Table 5* lists the results of the thickness measurements.

The thickness measurements varied as much as 1.0 mil between different techniques and labs. There was not a great deal of difference between the samples with nickel added to the bath and without nickel; although this is a small population on which to draw any definite conclusions.

The coating thickness measurements for the high silicon steel are listed in *Table 6*. The higher silicon steel was expected to generate thicker coatings because of the higher reactivity.

Table 6: Coating Thickness Measurements for High Silicon Steel

ZINC BATH COMPOSITION	LAB 1: HDG (mils)	LAB 2: HDG (mils)	LAB 3: HDG (mils)	AGA
Prime Western	2.8	***	2.9	2.95
Prime Western + Nickel	4.6	4.8	5.1	5.04
Prime Western + Nickel	9.4	8.4	***	8.84
Prime Western + High Grade	3.0	2.2	2.3	2.2
Prime Western + High Grade	7.8	***	7.9	7.83

There was a wide range in the coating thicknesses of the samples containing high silicon levels possibly due to processing differences at the galvanizing facilities. There were two samples with coating thicknesses in the same range, 2 to 3 mils, as the low silicon steel. These samples had distinct free zinc layers and the lead in the final coating as a percentage of the bath was over 50%. On the other hand, there were three samples in the range of 5 to 9 mils.

These coating thicknesses are typical for high silicon steels. The coating is mainly iron/zinc intermetallics with little or no free zinc layer. There is free zinc from the bath trapped between the iron/zinc intermetallic crystals which form as tall columns. This trapped free zinc is the source of the lead in these thicker coatings. The percentage of lead that is incorporated into the final coating is below 50% for these thicker coated high silicon steels samples.

Looking at the percentage of lead in the high silicon samples, it is noticeable that the thicker coatings have a lower percentage of lead due to the greater amount of intermetallic layers. The lead exists mainly in the free zinc layer, so those coatings with a very thin free zinc layer have a lower percentage of lead in the coating.

Coating Microstructure

The micrograph in *Figure 2* shows the typical galvanized coating microstructure with about 50% of the coating containing free zinc. The micrograph shown in *Figure 2* is from a kettle containing Prime Western Zinc with a lead level of 1.12% in the zinc bath.

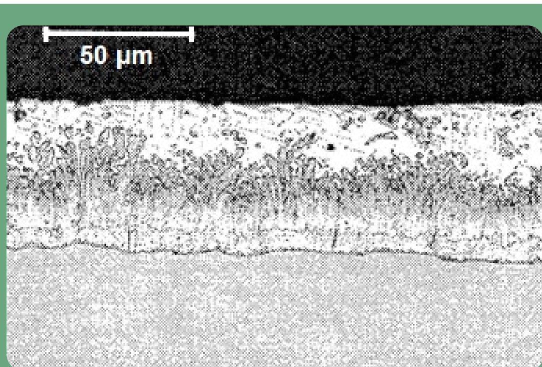


Figure 2: Coating Microstructure of Sample C1 (500X).

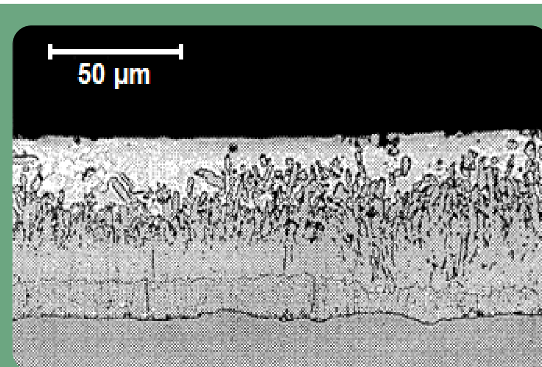


Figure 3: Coating Microstructure of Sample P1 (500X).

Molten zinc may contain lead up to the solubility limit of 1.2% at galvanizing temperatures. When the coating is formed, the intermetallic layers reject the lead and force it back into the zinc bath. The free zinc layer is solidified zinc bath metal, so it should contain the same percentage of lead. If the free zinc layer forms half of the coating, then the lead percentage in the entire coating should be half of the bath lead percentage.

The next micrograph, *Figure 3*, is taken of a coating that was formed in a kettle containing High Grade zinc with a low lead level of 0.022%. This figure shows the free zinc layer is close to 50% of the coating thickness, and also shows some iron/zinc intermetallic particles floating in the free zinc layer.

The lead level in the coating shown in *Figure 3* is again about 50% of the lead level in the bath. Since this happens for both Prime Western and High Grade zinc, the lead content in the coating should depend on two factors, the amount of lead in the kettle and the amount of free zinc in the coating.

The picture becomes much clearer when the coatings for the high silicon steel are examined. *Figure 4* is a micrograph for a thick coating with a large portion of the coating containing iron/zinc intermetallics. This micrograph is at a lower magnification than the previous two figures so the actual coating is much thicker than the two samples with distinct free zinc layers.

In this case, lead was observed in the spaces which contain free zinc between the upright iron/zinc crystals. The lead percentage for this coating is 30% to 35% of the bath lead composition. The lack of a definite free zinc layer and the thick coating both contribute to the lower lead content in this mainly intermetallic coating.

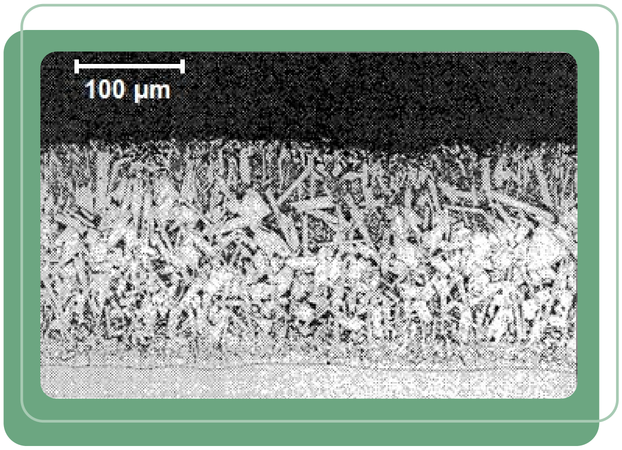


Figure 4: Coating Microstructure of Sample B4 (200X).

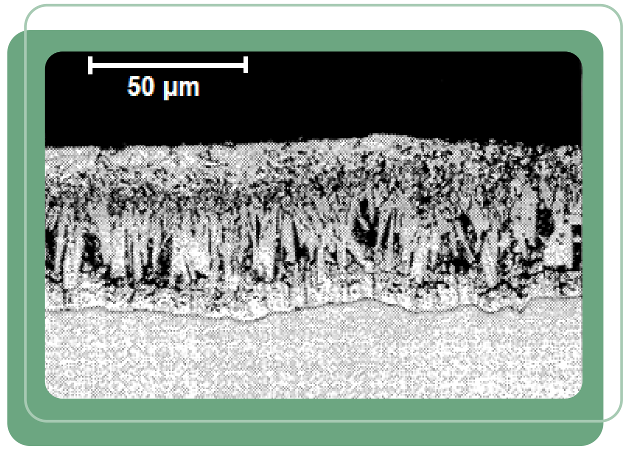


Figure 5: Coating Microstructure of Sample G4 (500X).

A different coating on the same high silicon steel is shown in *Figure 5*. The coating thickness is more standard, similar to that of the low silicon steel coating shown in *Figure 2*.

The coating in *Figure 5* contains a distinct free zinc layer, as well as trapped free zinc between the thick columnar structure of the iron/zinc intermetallics. This causes the lead level to be slightly higher than the average, about 60% of the bath lead level.

Other samples also followed the trend of thinner coatings having a higher percentage of lead from the kettle bath being incorporated into the coating and thicker coatings having a lower percentage of lead in the final coating.

Lead Distribution

Some of the samples were examined using Energy Dispersive X-Ray Spectrometry (EDS) to determine the location of the lead in the final coating. The EDS system is used in conjunction with a Scanning Electron Microscope (SEM) to examine the microstructure of materials. The previous sections in this paper discussed the lead in the coating as being contained in the free zinc since the intermetallic compounds have no lead solubility.

The next set of micrographs highlight the location of the lead in actual coatings on low reactivity steels. *Figure 6* shows the SEM picture of the total coating on one of the Prime Western zinc samples. The coating is clearly seen as four distinct layers with a free zinc layer occupying about 40% of the total coating.

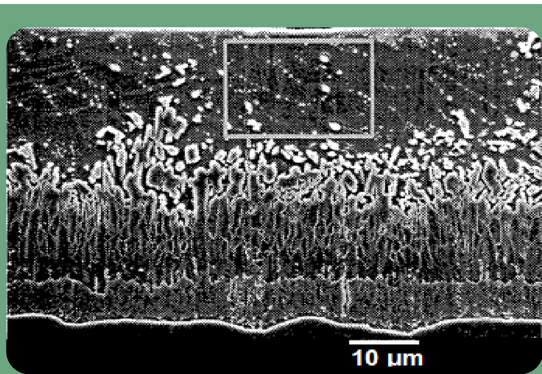


Figure 6: S.E.M. Micrograph of Sample C1.

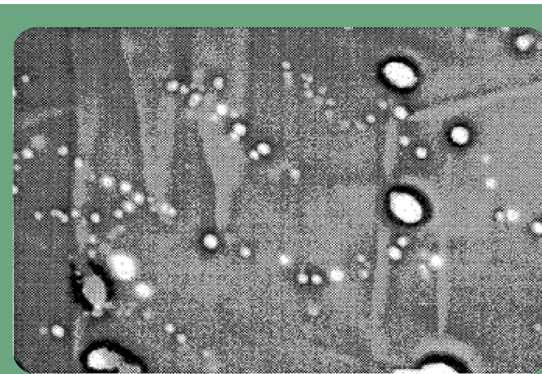


Figure 7: Higher Magnification Image of Highlighted Box from Figure 6.

The area within the box in *Figure 6* is magnified in *Figure 7*. This is a micrograph of the free zinc layer including what look to be small particles of lead included in the free zinc layer. Most of the particles are small and circular in shape.

This area was then examined using EDS to detect the lead atoms in the free zinc layer. *Figure 8* shows the EDS profile.

The concentration of lead appears to be at the location of the particles indicating that lead is contained in the free zinc layer as distinct particles. There is an overall background low level of lead atoms, but the major concentration of lead is in the small circular particles.

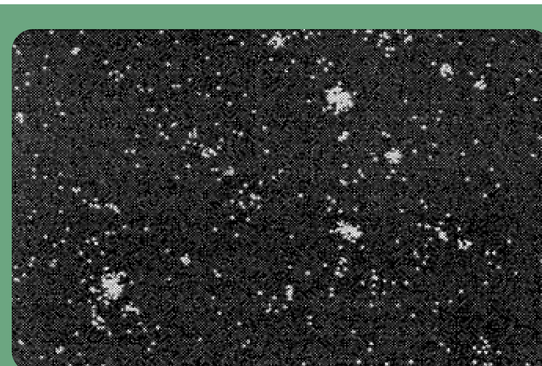


Figure 8: EDX Map of Highlighted Box from Figure 6 for Lead.

Lead in the Environment from HDG

A study[1] was conducted in the early 1990s at the sites of electrical transmission towers in four distinct climate zones to determine the run-off of zinc and lead from these structures. Samples from the soil were collected at varying depths and increasing distances from the galvanized towers in order to determine vertical and horizontal migration of any metal run-off from the structure.

Towers were sorted into three age groups, one to nine years, 10 to 19 years, and over 20 years. The background metal levels were measured at each tower site to determine if the lead measurements were statistically significant. Samples were collected at two depths at each site, 0 to 5 centimeters and 5 to 30 centimeters. The sample pattern for the collection of soil samples was directly at the base of the tower, 3 meters from the base, 6 meters from the base and 9 meters from the base.

The summary of the lead measurements in the soil is presented in *Table 7*. The background levels for lead in the soil ranged from 6 µg/g to 83 µg/g (µg/g is another way to express parts per million or PPM).

Table 7: Average Concentration of Lead (µg/g) at Increasing Distances from the Tower

AGE	DISTANCE	25-100 CM RAIN	ARID CLIMATE	MARINE SPLASH	ACID RAINFALL
1 - 9	Base	13	12	33	20
	3M	12	18	44	31
	6M	11	14	19	23
	9M	12	10	23	29
10 – 19	Base	20	51	***	19
	3M	19	22	***	18
	6M	17	17	***	20
	9M	13	15	***	24
20 - 29	Base	56	79	54	51
	3M	35	38	57	31
	6M	38	27	57	32
	9M	37	50	58	36

There were few samples in which the lead concentration exceeded the background level of lead in the soil, even after 29 years. The lead in the lower depth of soil sample was always close to the background level reading. The only spot in which the lead could be called an elevated level was at the base of the towers.

The lead levels were all lower than 20% of the value which the EPA uses to determine whether a clean-up is necessary, 500 µg/g. There is very little horizontal movement of lead through the soil, regardless of the rain amount in various regions.

The lead does not travel throughout the soil either vertically or horizontally. The lead from the run-off of transmission towers barely exceeds the background levels of lead in the soil even after 29 years of service.

Summary

The lead content and location in the HDG coating were determined by examining a number of galvanized coatings using various combinations for zinc grades in the galvanizing kettles. The lead content varies between 25% and 75% of the lead level in the galvanizing bath. The average lead content in the finished coating is 50% of the lead contained in the zinc bath. Galvanized articles with high silicon steel produce a thicker, mainly intermetallic coating which contains a lower percentage of lead from the zinc bath. Both the lead content and the final coating thickness are very consistent for low silicon steel articles. High silicon steels produce inconsistent coating thicknesses and variable lead contents. Lead is present in the free zinc layers and between the iron/zinc intermetallic crystals and is mainly in the form of small particles.

Acknowledgements

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- Court Galvanizing Ltd. - Vacaville
- Daam Galvanizing, Inc.
- Intermountain Galvanizing, Inc.
- Los Angeles Galvanizing Company
- North American Galvanizing - Denver
- Rogers Brothers Company, Inc.
- Silver City Galvanizing, Inc.
- Young Galvanizing, Inc.

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