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Approaching zero discharge: in plant evaluation of zinc thermal diffusion coating technology, phase I

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Abstract There are different zinc coating technologies for corrosion protection of metal surfaces. The most widespread methods are hot dip galvanizing (zincing by dipping items into melted zinc) and electrolytic method by zinc deposition from the electrolytic solution (electroplating). The process of thermo-diffusion of a zinc coating is a newer process that forms a zinc alloy with the substrate. The US EPA conducted a detailed inspection of a manufacturing facility using the zinc thermal diffusion manufacturing process and evaluated the potential for emissions. The internal air at the plant was also monitored. The sampled air within the plant was well within the limitations set forth by OSHA Method ID-121 for zinc and zinc compounds. There are no water emissions from the plant and no drains in the plant. All sludge which contains the used zinc powder (waste) from the rinse and passivation tanks is recycled. There were minimal emissions from the pretreatment and degreasing operations which are seldom used because the process is friendly to “dirty parts,” i.e., parts with light oils and light rust and therefore pretreatment is not necessary for most of the parts entering the plant. It appears that the process does approach zero discharge. The corrosion resistance of the technology will be evaluated by EPA in a phase II study.

items into melted zinc) and electrolytic method by zinc deposition from the electrolytic solution (electroplating). The process of thermo-diffusion of a zinc coating is a newer process that forms a zinc alloy with the substrate. This process is similar to a process known as Sherardizing (European Standard EN 13811 2003) or mechanical plating which have some of the same benefits. The process is designed to coat fasteners as well as small and medium-sized items, including threaded items, made of steel and cast iron, with a required thickness of coating above 15 μm . The technology uses a proprietary zinc powder that is baked into the product in a sealed oven. The unused powder is then recycled back into the proprietary powder. The technology claims (1) that the coating will adhere to lightly rusted (oxidized) parts with light oils without pretreatment, (2) that the corrosion protection is two to four times higher as compared to competitive processes such as hot dip galvanizing and electro-galvanizing as measured by salt spray corrosion (ASTM B117), (3) that the process is environmentally friendly being a near zero discharge process, and (4) that the process is more cost effective than conventional coating methods. This assessment did not attempt to determine the cost efficiency of the process. This phase I paper will evaluate pollution discharge from the manufacturing process by inspection of the manufacturing company known as “DiSTeK Africa (Pty) Ltd” which is located in Johannesburg, South Africa. A phase II (future) paper will evaluate the corrosion protection of the coating with parts obtained from the plant and other parts that are zinc coated with other methods. The plant in Johannesburg has the capacity to coat 12 t/day.

Introduction

There are different zinc coating technologies for corrosion protection of metal surfaces. The most widespread methods are hot dip galvanizing (zincing by dipping

Evaluation of the technology

The US EPA conducted a detailed inspection of the DiSTeK manufacturing facility located in Johannesburg, South Africa. This inspection included recording information about each aspect of the zinc thermal diffusion manufacturing process and evaluated potential

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for emissions. The internal air at the plant was monitored using sampling procedures as detailed in Section 5 (specifically Method 5.4) of OSHA Method ID-121. Product samples were obtained for phase II corrosion testing. The step by step process is described as follows.

Step 1: pretreatment

This step does not apply to most of the fasteners and parts that enter the plant. Most of the parts come to the plant "clean." The clean parts can be lightly oxidized and contain a light oil that burns off before the zinc diffusion takes place. With zinc electroplating or hot dip galvanizing these same parts would have to be cleaner for proper adhesion and corrosion resistance. Parts that are heavily oxidized are shot blasted before the process. Parts that contain heavy oil or grease or parts with a geometry that traps oils must be degreased in an alkaline cleaner. For the plant in Johannesburg, this amounted to only a small amount of parts that require alkaline cleaning. The degreasing step does have emissions associated with it, however, the emissions from this step are minimized by the fact that most of the parts are only lightly oiled or lightly oxidized and do not require pretreatment. The degreasing operation was not in use during the EPA evaluation. The shot blast machine was used during the evaluation.

Step 2: loading of parts and zinc powder

The parts along with the proprietary zinc powder are loaded into a container that is sealed before placing it in the oven. There is dust that is visible during the loading process. There are no outside vents or stacks in this step.

Steps 3 and 4: oven curing and cooling

The sealed container with the parts and the zinc powder are placed into the oven for approximately 3–4 h at 450°C and then cooled at room temperature for 3–4 h. There are no outside vents or stacks in these steps.

Step 5: unloading

The container is opened and the parts are dumped on a vibratory conveyer belt. Excess dust is captured by means of a vacuum with filter and saved for recycle. This step does involve an outside vent from the dust filtering process. The filtering system used in the plant is rated to take out 100% of 0.5 um and larger particles. The zinc powder based on information provided by the company consists of particle size as follows: 78% > 30 um, 22% > 50 um. The particle size was not measured by EPA and environmental release through the exhaust system was not measured. No visible dust was seen.

Step 6: rinsing/polishing/passivation

From the conveyer belt, the parts are dumped to a circular vibratory machine. Here the parts are first spray rinsed with water and at the same time polished with porcelain chips that continuously stay in the machine. The rinse is about 4 min long at room temperature. The rinse water is pumped from a separate tank into and out of the circular vibratory machine. Then, zinc phosphate is pumped into and out of the same machine with the porcelain chips for 7 min at room temperature. This completes the first stage passivation.

Zinc solids are removed daily from these two tanks (water rinse and zinc phosphate) through a centrifugal filtering machine. The damp zinc powder cake is then recycled with the rest of the used powder, back into virgin product. Periodically, these two tanks are pumped to temporary holding tanks and the sludge is cleaned out and saved for recycle as well. The zinc phosphate in the holding tank is pumped back to the original tank and makeup water is used from the rinse water in the other holding tank. The zinc phosphate solution is then strengthened. The balance of the rinse water is pumped back into the rinse tank with fresh water makeup. There are no air stack emissions or water discharges in this step and all sludge is recycled back into virgin product.

Steps 7–10: rinse/dry/second passivation/final dry

- The product is dumped from the circulatory vibrator to a hot rinse basket at 55°C.
- From the hot rinse to air dried basket.
- From air dry to second passivation using a silica solution at 55°C.
- To final heated dry on vibratory conveyer belt.

The second passivation uses a silica solution as opposed to the zinc phosphate in the first passivation. Similar to step 6 there are no air stack emissions or water discharges in this step and all sludge is recycled back into virgin product.

Sample collection: internal air monitoring

The internal air in the plant was sampled for zinc analysis. The sampling procedures as detailed in Section 5 (specifically Method 5.4) of OSHA Method ID-121 were followed. The method uses a small pump and filter cassette that samples the air at a rate of 2 l/min for 8 h. The filters are then analyzed for zinc. The samples were collected at various points along the manufacturing process. The monitors were not placed on the workers in the plant, but instead were located at the various unit processes as follows.

Table 1 Air sampling data: zinc

Date	Sample area/sample ID	Average flow rate (LPM)	Total sample time (min)	Total volume sampled (l)	Total zinc (mg/m ³)	OSHA PEL limit (mg/m ³) for zinc oxide in fume/total dust forms
11/15/05	1/A1	2.064	489	1,009.0	0.032	5/10
11/15/05	2/A2	2.051	486	996.8	0.020	5/10
11/15/05	3/A3	2.049	480	983.5	0.034	5/10
11/15/05	4/A4	2.049	479	981.5	0.018	5/10
11/15/05	5/A5	2.135	479	1,021.5	0.015	5/10
11/16/05	1/B1	2.044	565	1,154.9	0.202	5/10
11/16/05	2/B2	2.061	562	1,158.3	0.031	5/10
11/16/05	3/B3	2.072	560	1,160.3	0.009	5/10
11/16/05	4/B4	2.078	558	1,131.7	0.011	5/10
11/16/05	5/B5	2.026	556	1,126.2	0.023	5/10

Sampling areas

1. At the point of loading the parts and zinc powder into the ovens
2. The oven area
3. At the point of unloading the parts for rinsing
4. At the rinsing/sealant/drying area
5. At the pretreatment (degreasing and shot blast) area
6. Field Blanks were taken twice, one each day.

Samples were collected in each area for approximately 8 h according to method 121 on two consecutive days. Air sampling data from the 2 days of testing along with the maximum zinc OSHA limit in the Method 121 requirements are shown in the Table 1.

The data show that the total zinc concentrations in the plant are well within OSHA limits for zinc oxide in both fume and total dust forms. They are also within limits of all other OSHA regulated zinc compounds (zinc chloride and zinc stearate).¹

Quality assurance/quality control (QA/QC) checks and results

Several QA/QC checks were performed in the field and in the laboratory to ensure the quality of the data generated.

Field QA/QC—air sample collection pumps were calibrated before and after each run. A field blank was collected each day of sampling by opening the filter cassette for 3 s and re-sealing the cassette.

Laboratory QA/QC—filter samples were digested with nitric acid and analyzed for zinc using inductively coupled plasma. Laboratory QA/QC checks included a laboratory reagent blank, a laboratory fortified blank, and matrix spikes. Also, continuing calibration blanks and continuing calibration verification standards were analyzed at the beginning of the run, after eight samples, and at the end of the run. The results of these laboratory

QA/QC checks and the blanks were within the project criteria QA/QC specifications.

Other issues

Finish

The standard finish is a gray flat finish. The finish is not shiny like hot dip galvanizing. It is also available in black, green, and light gray where the color is diffused into the alloy. The product can be dyed, painted, power coated, etc. for more final colored finishes.

Hydrogen embrittlement

The process does not give rise to hydrogen embrittlement (HB; European Standard EN 13811 2003).

No actual testing was conducted, however, HB may not be a problem because there is no acid cleaning and the treatment for HB is a heat treatment that is part of the thermal diffusion process.

Adhesion

No suitable European or International Standards currently exist for testing the adhesion of sherardized coatings on fabricated products. Adhesion between zinc and basis metal generally does not need to be tested as good bonding is characteristic of the Sherardizing process (European Standard EN 13811 2003).

Part shapes

Cracks—if air can get in a crack or crevice, then part can be coated. Parts that would normally “acid bleed” due to fine cracks or crevices have shown to coat in tight places. Coating of internal diameters as well as fine threads are easy to coat with this process (see Fig. 1). Typically the acid tanks used to clean these parts are a

¹OSHA Method ID-121, metal and metalloid particulates in workplace atmospheres.

major source of pollution, and are not necessary for this process.

One of the advantages of this process is the elimination of acid on certain types of work. Certain work pieces (such as hinges) where entrapment of acid aggravates bleed-out during and after other types of plating (brass, copper, zinc, cadmium, and tin; Innes and Toller 1982) do not have this issue with the zinc thermal diffusion process. Pictured in Fig. 1 is a forged steel part with a very tight crack that normally might acid bleed. This part was coated with the zinc thermal diffusion technology and the protective coating managed to get into the crack and coat the part on the surface inside the crack. Table 2 shows the coating thickness on the inside of the part as well as the outside. This was measured after the part was separated with a hacksaw.

From the data above, on this particular work piece, the coating thickness in the “very tight” spaces is reduced by an average of about 20%.



Fig. 1 Part: forged steel with tight crack

Coating thickness

Coating thickness can be applied at approximately 15–100 um at 5 um intervals with this process.

Results and discussion

The process does approach zero discharge. There are no water emissions from the plant and no drains in the plant. All sludge which contains the used zinc powder (waste) from the rinse and passivation tanks is recycled. Hence there are no water emissions from the plant. This paper does not evaluate the recycling process of the zinc powder which is not conducted in the plant. It does not evaluate the emissions or problems associated with the recycling of the used powder/sludge.

There are no stack air emissions from the thermal diffusion process, but during the unloading process the excess or unused zinc powder is captured for recycle by filtering using the 0.5 um filter which is then vented outside. There is a possibility of an environmental release through this exhaust system if the filter was not working properly. This outside vent is the only emission source and was not measured and currently EPA does not regulate this emission. The sampled air within the plant was well within the limitations set forth by OSHA Method ID-121 for zinc and zinc compounds.

The only other emission in the plant would not be from the zinc thermal diffusion process, but would be attributed to the necessary pretreatment. This would be the oily waste from the degreasing unit if used. The plant has indicated about 1 l of oil has skimmed off the degreaser unit in 1 month of production. The alkaline cleaner will ultimately have to be disposed in a proper manner. The process is friendly to “dirty parts,” i.e., parts with light oils and light rust and therefore pretreatment is not necessary

Table 2 Coating thickness

Coating thickness along the outside (exposed side) of the work piece (um)	Coating thickness along the inside (unexposed) of the work piece after separation (um)
45	35
46	48
43	32
47	33
49	39

for most of the parts entering the plant. The corrosion resistance of these dirty parts will be evaluated by EPA in a phase II study.

The process can evenly coat a large variety of part shapes and sizes and is limited by the size of the container and oven. The process claims significantly better corrosion resistance and hardness compared to hot dip galvanizing and electroplating and a phase II testing of the process will be conducted.

Future testing: phase II

Corrosion testing

After obtaining product samples in the form of fasteners (specifically screws and nails) from the DisTek process, similar products will be purchased from competitors that represent hot dip galvanizing and electro galvanizing. Salt spray corrosion testing (ASTM B117) procedures will be followed for the conditions listed below.

Condition A: products by themselves.

Condition B: screw type products used with galvanized sheet metal fastening.

Condition C: screw type products used with ACS lumber.

Condition D: nail type products used with ACS lumber.
Condition E: nail products with various degrees of rust coated with the zinc thermal diffusion process.

The purpose of conditions B–D is to assess real world use where the coating can be scraped or worn from use. The various products will be compared and photographed every 50–250 h of salt spray and observations recorded as part of the phase II evaluations. Condition E will give some indication of the amount of light corrosion that the process can handle.

Other testing may include hydrogen embrittlement and hardness.

References

- European Standard EN 13811:2003 (2003) Sherardizing-zinc diffusion coatings on ferrous products-specification, p 10
Innes AL, Toller WH (1982) Considering recycling and recovery. *Plat Surf Finish*, pp 26–27