“Improving Productivity and Quality In the Hot Dip Galvanizing Process”

By Mike Ainsley
International Zinc Association (IZA)
TOPICS

- Brief introduction to zinc production
- Galvanizing Process
- Galvanizing bath composition
- Galvanizing residues (dross and ash)
- Zinc ingots
- Steel factors
- Galvanized product quality problems
Zinc production

Most Zn is obtained from mining operations. The mines produce zinc "ore" which is around 5 -15% Zn content.
Zinc ore is then processed to a “concentrate” of about 50% Zn content
Zinc concentrate → Metal extraction process → Zinc ingot (99.995%)
The final process is Quality Control. Zinc samples are routinely sent to the laboratory for chemical analysis.
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Galvanizing Process

Topics
1. Steel pre-treatment
2. Zinc bath and operating factors
3. Cooling
4. Passivation
Pre-treatment

1. Degrease
2. Water
3. Acid
4. Water
5. Flux
6. Drying
Degreasing

Sodium hydroxide (caustic soda – NaOH) is still the most widely used in Asia

Commonly used degreaser formulations

<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAUSTIC SODA SOLUTION</td>
<td>* Cheap</td>
</tr>
<tr>
<td>Sodium Hydroxide - NaOH (60-100 g/L)</td>
<td>* Moderate cleaning ability</td>
</tr>
<tr>
<td>Use at 80°C</td>
<td></td>
</tr>
<tr>
<td>CAUSTIC SODA (75 g/L)</td>
<td>* Moderately cheap</td>
</tr>
<tr>
<td>Sodium Metasilicate (200 g/L)</td>
<td>* Good cleaning ability</td>
</tr>
<tr>
<td>Wetting Agent (5 g/L)</td>
<td></td>
</tr>
<tr>
<td>Use at 80°C</td>
<td></td>
</tr>
<tr>
<td>CAUSTIC SODA (60 g/L)</td>
<td>* More expensive</td>
</tr>
<tr>
<td>Sodium Phosphate (35 g/L)</td>
<td>* Very Good cleaning ability</td>
</tr>
<tr>
<td>Wetting Agent (5 g/L)</td>
<td></td>
</tr>
<tr>
<td>Use at 80°C</td>
<td></td>
</tr>
</tbody>
</table>

- All solutions must be heated (approximately 80°C) for optimum performance.
Degreasing

- **Caustic Soda solutions**
  - Must be heated to approx 80°C for best efficiency
  - Steam heating is used but modern plants now use gas/oil fired immersion pipes. The technology is simple and maintenance is reduced

- **Acid degreasing solutions**
  - New development
  - The main benefit is some cost saving as no water rinsing is required before the acid pickle and no heating is required
Pre-treatment

Water rinsing after degreasing

Purpose is to remove residual degreasing solution

Is it necessary? Yes

Why?

- Because degreasing solution will consume acid if it is not removed
- Rinsing also ensures no grease/oil is carried across into the acid tank
Water rinsing after degreasing

- Single tank rinse is satisfactory but two rinse tanks are preferable.

- If the water is static (stationary) then best rinsing requires the steel to be moved up and down.
If using a single rinse tank it is better to use recirculating water and to introduce a “weir” to make the water flow more evenly across the surface of the tank.
A further improvement is to introduce a grease/oil trap.
Acid Pickling

Purpose

- To remove rust and oxidized scale without causing significant attack of the steel surface

Acid types:

- Hydrochloric acid (HCl). Most galvanizers in Asia use HCl
- Sulphuric acid (H$_2$SO$_4$)
Since pickling is the slowest stage of the galvanizing process, the acid pickling conditions should be optimized. Optimum conditions are:

1. Acid concentration should be kept in the range 10% - 15%
2. Acid should be agitated (stirred). This accelerates pickling because it keeps fresh acid at the surface of the steel.

- Most effective agitation is by “sparging” with compressed air through a rubber hose.
- If sparging is not done, then the steel should be moved up and down sometimes.
Since pickling is the slowest stage of the galvanizing process, the acid pickling conditions should be optimized.

3. The iron (Fe) content in the acid tank should not exceed 120 grams per litre.

   The higher the Fe content the slower is the pickling rate.

   At an Fe content of 120gm/litre the acid cannot absorb any more Fe. Therefore pickling stops.

   ![Graph](image_url)

   Max Fe solubility = 120 g/L
**Pre-treatment**

**Hydrochloric acid pickling**

**Optimum acid tank control**

- **Acid Concentration (%):**
  - Time
  - Fresh Acid Addition
  - Fe Content

- **Iron Content g/L:**
  - 120 g/L
  - No further acid additions
Pre-treatment

Optimum HCl acid tank control

- Never do zinc stripping in a working pickling tank because the zinc contamination in the acid will significantly slow the acid’s pickling speed.
Additives to acid tanks

1. **Inhibitors.** These chemicals ensure the acid only removes the rust or oxide scale on the steel surface. The acid is prevented from attacking the steel surface.

2. **Fume control chemicals:** These form a layer of “froth” on the surface of the acid which prevents acid fume escape.

Chemical suppliers to the galvanizing industry and steel manufacturing industry can supply these additives.
Pre-treatment

Water rinsing after acid pickling

- Single tank rinse is satisfactory but two rinse tanks are preferable. Good rinsing is important to reduce acid (+Fe) contamination of the flux.

- If the water is static (stationary) then best rinsing requires the steel to be moved up and down.
Fluxing

Sometimes called preflux

**Purpose**

To assist the molten zinc to react with the steel surface to form the galvanized coating.

**Flux composition**

Zinc ammonium chloride (ZnCl$_2$.3NH$_4$Cl) in water

- can be purchased already made
- or can be made by mixing zinc chloride (ZnCl$_2$) and ammonium chloride (NH$_4$Cl) according to the ratio

$$\text{ZnCl}_2 : \text{NH}_4\text{Cl} = 1 : 1.13 \text{ by weight}$$
Optimum flux conditions

1. Flux concentration

- 200-300 g/L. (grams/litre)

- Below 200 g/L there is a risk of “black-spots” on the galvanized steel where the coating has not formed.

- Controlling the flux concentration can be done using
  - monthly chemical analysis by a laboratory
  - simple Specific Gravity (SG) measurement then referring to the SG vs concentration graph.
ZAC = Zinc Ammonium Chloride flux solution

SG measured when flux is cool
Optimum flux conditions

2. Flux temperature

- Flux should be hot (60 – 80°C) to assist later drying.

- Galvanizers now using gas/oil fired immersion tube burners. More cost effective than steam heating.
Optimum flux conditions

3. Control the iron (Fe) contamination

Acid + Fe Carryover

Fe carryover to zinc bath

Flux

Pre-treatment
Optimum flux conditions

3. Control the Iron (Fe) concentration

Understanding the type of iron contamination in the flux

- Fe is present in the flux as:

1. **Soluble Fe** (cannot see it). This Fe contaminates the flux layer and therefore is carried into the molten zinc where it forms dross

2. **Insoluble Fe**. This is the brown coloured particles in the flux. This Fe settles to the bottom as a “mud”. It does not significantly contaminate the flux layer on the steel
Control the soluble Fe concentration

- Should be <5 g/L (maximum 10 g/L)

- Achieve by:
  - Good acid rinsing practice to minimise iron carryover.
  - Regular flux chemical treatment using small quantities of hydrogen peroxide (H$_2$O$_2$). This instantly converts soluble Fe to insoluble Fe.
  - Correct pH control.
Control the insoluble iron concentration

- This is not as important as controlling the soluble Fe content but it is still good practice

- Achieve by:
  - Removing the bottom “mud” when it becomes too thick
  - Filter the flux
Flux Filter Equipment
4. Control the pH value \((\text{pH} = \text{acidity content})\)

- Requires \(\text{pH} = 4.0 - 5.0\)
  - To increase pH above 4.0 add ammonia solution \(\text{NH}_4\text{OH}\) (also called ammonium hydroxide)
  - To reduce pH below 5.0 add hydrochloric acid

- If pH is low this causes more soluble Fe
- If pH is too high \((> 5.5)\) the zinc chloride in the flux can decompose and become non-effective
Fe converts from insoluble Fe to soluble Fe as the pH becomes lower.

- pH 4.0 Soluble Fe
- pH 5.0 Insoluble Fe

pH should not exceed 5.5 as this can cause problem with decomposition of zinc chloride.
5. Additives to flux

- Liquid “detergent” (soap). This results in less flux solution on the steel as it comes out of the flux tank. Drying is therefore quicker and less splashing/bubbling during dipping in molten zinc. This reduces ash formation.

- Hang 3 or 4 pieces of zinc ingot from the side of the flux tank. This will help neutralize acid carryover. The zinc slowly reacts with the acid to produce zinc chloride which is required in flux.
Steel should be dried as much as possible before entering the bath

Why?

- for safety (less zinc splashing)
- reduces as formation on the zinc bath surface
- enables faster dipping speeds which saves time and for some items reduces the risk of steel distortion
Zinc bath and operating factors
Zinc “diffuses” into the steel surface and combines with the iron component. This results in the formation of a Zinc–Iron alloy layer.
When the steel reaches 450°C the formation of the Zn-Fe alloy layer occurs very rapidly (under 1 minute).

The reaction then slows down and dipping for longer will not further increase the alloy layer thickness.
How does the coating form?

As the steel emerges from the molten metal, a layer of pure zinc metal solidifies on top of the zinc-iron alloy layer.
Cross-section through an actual galvanized coating at high magnification

**How does the coating form?**

**Zinc bath**

- Zn layer
- Zn-Fe alloy layer
- Steel base

50 µm
Zinc bath

Operational factors
1. Zinc temperature

- 445 – 455°C is satisfactory. 448 – 452°C usually considered best

- << 445°C risk of non-smooth coatings because of low zinc fluidity

- >> 460°C risk of short kettle life due rapid attack by molten zinc
2. Zinc temperature stability

Temperature should be as stable as possible

- +/- 2ºC is acceptable
- more than +/- 2ºC causes extra dross
3. Speed of withdrawal from bath

- 1 metre/minute is regarded as the best speed and 1.5 metres/minute as the maximum speed.

- Slow speed allows excess molten zinc to drain back into the bath. If speed is too fast, the zinc layer in the coating is too thick (wasting zinc).

- Dual speed crane is best. High speed for steel entry, low speed for steel withdraw.
Speed of withdrawal from bath

- **Slow speed**
  - Zinc Layer
  - Zinc-Iron Alloy Layer
  - Steel Base

- **Fast speed**
  - Zinc Layer
  - Zinc-Iron Alloy Layer
  - Steel Base
4. Skimming technique
Some companies consider the skimmer to be the most important person because he controls the appearance of the galvanized steel!!!

Skimming should be done just in front of the steel as it emerges from the zinc (instead of skimming the whole bath surface before the steel emerges).

Skimming operation should be slow and gradual. Avoid “paddling” with the skimming tool as this creates more ash and produces ash-marks occur on the coating.
Cooling

Operational factors
Cooling

- Water cooling (quenching) is the normal method.

Water cooling should NOT be used if there is a risk it will cause distortion of the steel. In this situation the steel should be allowed to cool slowly to 200 - 250°C before water cooling.
Passivation

Operational factors
Passivation

- Most galvanizers add a “passivation” chemical to the cooling water.

- This is to prevent or minimize white rusting of the galvanized coating during storage.

- Passivator chemicals
  - Chromate (traditional method)
  - Soluble polymer (new method)
Chromate Passivation

- Normally 0.1% - 0.15% sodium dichromate content. Higher content can cause green-yellow colour on the coating, especially on thick steel items.

- Keep chromate water temperature preferably below 70°C. This will prevent excessive green-yellow colour on the coating. An external heat-exchanger may be required to control temperature.
Chromate passivation

If using one cooling tank, the chromate water will become contaminated with chloride (from ash/flux carryover on the steel).

- Chloride contamination in the water destroys chromate passivation.
- To avoid this problem, many galvanizers use two water cooling tanks.
  
  1\textsuperscript{st} tank: Water only. This absorbs the chloride and prevents the chromate tank from overheating.
  
  2\textsuperscript{nd} tank: Water + chromate.

Water from 1\textsuperscript{st} tank can be used for the acid pickling tanks.
Passivation using water soluble polymer

- Chromate is under environmental pressure to be banned due to its very toxic nature.

- Galvanizers have now started to change to (non toxic) water soluble polymers. The polymer film is invisible.

- 2 tank process **MUST** be used. 1st tank is water. 2nd tank is water + soluble polymer. This is because the steel must be partially cooled before entering the polymer tank.
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Zinc bath

Galvanizing bath composition
Bath additives are:

- Lead (Pb)
- Aluminium (Al)
- Nickel (Ni)
Zinc bath

Lead (Pb)

Most galvanizers operate with a 100mm molten Pb layer on the bottom of the bath. This has two purposes:

- Helps in drossing operations because the dross floats on the Pb, making it easier to lift out.
- Gives protection to the bath (kettle) bottom corner welds. Zinc in contact with these welds is considered to be a risk due to rapid zinc attack. True or false??
Zinc bath

Lead (Pb)

- Some Pb from the bottom layer is absorbed into the molten zinc. The Pb content in the zinc will usually stabilize around 0.6 - 0.8% Pb content.

- Pb is progressively “lost” from the bottom layer and must be replaced from time to time. This loss is due to:
  a) absorption into the molten zinc
  b) unavoidable removal of some Pb during the drossing operation

- The thickness of the Pb layer must be regularly checked. An L shape metal bar can be used to do this.
Measuring Pb layer thickness

Zinc bath
Zinc bath

Lead (Pb)

“Pb - free” galvanizing

- Some baths operate Pb-free for environmental reasons. Certain project specifications may require Pb-free coatings, or export customers may request it.

- Changing to Pb - free galvanizing means:
  - Pumping out the bath and Pb layer and replacing with pure zinc. Just pumping out the Pb layer will not result in Pb-free due to the Pb already absorbed into the zinc.

  - Modifying the furnace chamber so that the lower 150mm of the bath is insulated. This prevents the dross layer from becoming “hardened” and difficult to remove.
Aluminium (Al)

- Al is added to make the coating “shine”
- Optimum Al content is 0.002 – 0.005%
- Al content > 0.01% can cause “black spots” on the coating where the coating has not formed. This is because Al reacts with flux on the steel surface and reduces flux effectiveness
- Simple method to establish if Al content is satisfactory (discussed later)
Aluminium (Al)

Method of adding aluminium to the bath

1. Adding pieces of pure Al or scrap Al (wire)
   - Advantage: cheap to purchase
   - Disadvantage: Poor control of Al content in the bath, because: -

   a) Aluminium does not melt into the zinc. The molten zinc only “absorbs” the Al very slowly. It is not possible to control this speed of this.

   b) The Al floats on the bath surface. Absorption of Al by the zinc is confined to the bath surface. Most of the absorbed zinc in then “lost” due to oxidation.
Method of adding aluminium to the bath

2. Using Zn-Al pre-alloy (e.g., Padaeng DA3 alloy).

Advantage:
- Does not float and it melts rapidly. The Al is therefore uniformly distributed within the bath and this occurs rapidly.
- Easy to control the Al content in the bath. For example, one ingot of DA3 alloy with each one tonne of zinc added will achieve the desired Al% in the bath (after allowing for Al consumption during galvanizing).
Zn-Al pre-alloy (eg, Padaeng DA3 alloy)

Advantage:
More economic to use than pure Al pieces because ....

- **100%** of the Al in DA3 alloy is absorbed into the zinc bath.
- purchasing pure Al may appear cheaper BUT most of the aluminium is “lost” to oxidation at the bath surface.
Comparing Al dispersion efficiency

Pure Al

Molten Zinc

Zn-Al alloy
Nickel (Ni)

- Nickel is increasingly being used by galvanizers in Europe, North America and Asia.

- An advantage of using nickel is improved molten zinc fluidity. This contributes to:
  - reduced zinc consumption of 5 -15%
  - more smoother coatings
Another advantage of using nickel is to modify the galvanizing reaction between zinc and steel resulting in a coating structure that:

- Is more uniform in coating appearance (less grey colour). This applies especially to coatings on thicker steel sections and steels with higher silicon and phosphorous content.

- Gives less problems with coating cracking or loss of adhesion (flaking) on thicker steels or steels with higher silicon or phosphorous content.
Zinc bath

Nickel (Ni)

➢ Optimum Ni content in the bath is 0.05 - 0.06%

➢ Ni is added to the bath using Zn-Ni pre-alloys. Padaeng produces two pre-alloys as follows:

❖ ZnNi0.15 alloy (0.15%Ni content)
   Using only this alloy for bath additions will result in an 0.05 - 0.06% stabilized Ni content in the bath

❖ ZnNi0.5 alloy (0.5%Ni content)
   Used in the addition ratio of 1 tonne alloy with 2 tonnes pure zinc to achieve the stabilized 0.05 – 0.06% Ni content in the bath.
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Galvanizing Residues

- Bottom dross
- Top Ash
Steel
"kettle"

Top ash layer

Molten Zn

Bottom dross layer (Zn-Fe compound)

Pb layer
Galvanizers “bottom dross”
Dross

- It forms as a result of a chemical reaction between molten Zn and Fe impurity.

- During galvanizing, some Fe is constantly transferring into the molten Zn.

- Molten zinc can only dissolve a small amount of Fe (about 0.04% maximum). As more Fe transfers into the molten zinc, the “surplus” Fe combines with zinc to form very tiny dross particles. The reaction is

\[
\text{Fe} + 13 \text{Zn} \rightarrow \text{FeZn}_{13}
\]
Dross

Close-up view of dross

Needle-like dross crystals can be seen
The dross particles are slightly denser than molten zinc and so gradually settle to the bottom of the bath as a layer.

In this bottom layer the dross particles mix with molten zinc. Dross particles form 50% of the layer and molten zinc forms 50%.

Therefore since dross particles have the ratio Fe:Zn = 1:13, then in the dross layer the ratio is Fe : Zn = 1 : 26.

The composition of the dross layer is therefore about 4%Fe + 96% Zn.
Dross formation is therefore extremely sensitive to the amount of Fe dissolving into the molten zinc.

One part by weight of iron combines with nearly 26 times its weight of zinc to form dross.

Since dross is a waste product, it is therefore extremely costly in terms of zinc loss.
Cross section of bottom dross layer viewed in microscope
Dross formation is approx 7-11% of zinc consumption

Dross has a very high zinc content but it is not possible for galvanizers to recycle their dross to recover some of the zinc

Dross is purchased by recyclers. Dross sells at 65-75% of zinc price

Recycled dross is used to make pure zinc oxide
How can dross be reduced?

- Use pure zinc which has a very low Fe content (SHG 99.995% Zn)

- 90% of all dross is produced from Fe absorption mostly from the steel products being galvanized. Lower zinc temperatures mean less absorption of Fe from steel.

- Maintain bath temperature at 445 - 455°C. Do not exceed 465°C
How can dross be reduced?

- Temperature should be as stable as possible
  - +/- 2°C is acceptable
  - more than +/- 2°C causes extra dross
How can dross be reduced?

- Maintain a very low Fe content in the flux since Fe from the flux is carried across into the zinc bath.

  Upto 10% extra dross can be produced due to Fe in the flux.
Dross needs to be removed regularly.

Why is it important to regularly remove dross?

Answer: Unless regularly removed the dross layer will thicken. Since dross is a poor conductor of heat a “hot-spot” can develop at the kettle wall next to the dross. This hot spot can result in a hole in the kettle wall.
Drossing procedure

- Maintain Pb layer at about 100mm deep. Depth of Pb layer can easily be measured using an L shape steel bar.

- Best drossing temperature is 450°C - 455°C. If < 445°C the molten zinc becomes less “fluid” so more molten zinc remains in the dross as it comes out of the bath. This is wasted zinc.

- If using a dross shovel do not always remove the dross using the same direction. This prevents dross accumulating at one end of the kettle.

- Drossing should be done at least every 2 weeks. Do not allow dross to accumulate for more than 4 weeks as this is dangerous for the kettle.
Where does bottom dross go after it leaves the galvanizing plant?

Answer

- It is used by recyclers who extract the zinc
- Due to the high % of zinc content in dross (approx 96%Zn) and the fact that dross sells at approx 75% of the market price of SHG zinc, it is economically attractive to extract zinc from dross
How is the zinc extracted from the dross?

Answer

- The only practical method to "extract" all the Zn is to melt the dross at 1000°C.

- The Zn is then released as a Zn vapour. The vapour burns in contact with air to produce very pure zinc oxide which is a white powder.
Dross

Furnace using dross to produce Zinc oxide
Zinc oxide powder

Some zinc oxide applications
Zinc ash
What is ash?

Answer

Ash forms due to natural oxidation of zinc in contact with air due to the reaction

\[
\text{Zinc} + \text{oxygen} = \text{Zinc oxide (impure)}
\]

- Ash also contains about 10 - 25% of zinc lumps and some iron oxide, aluminium oxide and flux residues.
Ash (on the surface of the zinc bath)

- Ash formation is normally approx 15 - 20% of Zn consumption.

- Total Zn content in ash is about 70 - 80%. It is therefore important to reduce ash as much as possible during galvanizing.

- Ash is purchased by recyclers. Ash sells for 35% - 45% of zinc price.
How to reduce ash formation

- Dry the steel as best as possible to avoid turbulence or splashing during dipping of the steel item into the molten Zn.

- Avoid using zinc ingots that are wet or damp. It is also desirable to avoid white rusted zinc ingots, therefore zinc should be stored under-roof.

- Skimming tools should be correctly used. Do not “paddle” when using the tool. Slow, steady motion is best.

- Bath aluminium additions should be maintained at the correct level. Aluminium slows down the rate of oxidation of the bath surface.
Caution: Ash should not be allowed to “build-up” on the kettle wall above the zinc surface. This build-up must be removed every few days.

This can cause a “hot-spot” on the kettle wall beneath the ash and rapid localized erosion of the kettle wall (see picture).
Can some of the zinc in ash be recovered at the galvanizing plant?

Answer: Yes.

Various methods are used which give different recoveries.
Ash can be treated by galvanizers to recover some zinc.

Treatment method 1

Accumulate the ash at bath end where it is “chopped”

Zinc recovery is very low (5 -10% recovery)
Treatment method 2: The box method

- An open steel box is located in the bath corner. The box is open at the top and bottom and the lower 1/3 of the box is in the molten zinc.

- The box is then filled with fresh, hot ash.

- Some flux powder is then added and the ash is vigorously stirred with a steel bar.

- This causes the zinc lumps to melt and re-enter the molten zinc bath.

Zinc recovery is 30 - 40%
Treatment method 3: The rotating drum method

- This method uses a sloping cylindrical drum which slowly rotates. The lower part of the drum is perforated with small holes. The inner wall of the drum has “blades” attached.

Hot fresh ash is fed into the upper part.

- As the ash moves down, the blades crush the ash lumps and separate out the zinc lumps. The lumps exit from the bottom of the drum.

- Ash powder passes through the small holes.

Zinc recovery is 50 - 70%
What happens to ash sold to recyclers?

- Ash is crushed and screened to remove the zinc lumps. These are melted and cast as “secondary” zinc ingot which is sold to galvanizers and zinc oxide producers.

- The remainder of the ash is a powder which is ......
  - used to make zinc chemicals (eg, zinc chloride)
  - added to fertilizers to improve crop growth.
Low zinc content soil

Example of better rice plant growth by using zinc
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Zinc composition should conform to the international zinc standard EN (ISO) 1179

Example is Padaeng Zinc (Special High Grade – SHG)

<table>
<thead>
<tr>
<th>CHEMICAL COMPOSITION (%)</th>
<th>PADAENG SHG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>99.995 min.</td>
</tr>
<tr>
<td>Lead</td>
<td>0.003 max.</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.003 max.</td>
</tr>
<tr>
<td>Iron</td>
<td>0.002 max.</td>
</tr>
<tr>
<td>Copper</td>
<td>0.001 max.</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.001 max.</td>
</tr>
<tr>
<td>Tin</td>
<td>0.001 max.</td>
</tr>
</tbody>
</table>
Zinc ingot shape

Zinc slab. 25kgs. 40 slabs per bundle
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Steel factors

- surface condition
- composition
Steel

Surface condition

Sand blasting the steel surface is a method used by galvanizers to achieve extra thick coatings.
Steel composition

- Silicon and Phosphorous contents have a large effect on the appearance of steel.

Coating thickness:
- Shiny
- Partly Shiny
- Grey

Graph: Si + 2.5 x P (%) vs Coating thickness
Steel

Silicon and phosphorous modify the coating structure

- Normal coating with top pure Zn layer present
  - Zn layer
  - Zn – Fe alloy layer
  - Steel
  - Si + 2.5 x P ( < 0.09%)

- Coating is all Zn-Fe alloy layer
  - Zn – Fe alloy layer
  - Steel
  - Si + 2.5 x P (0.09% - 0.2%)
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Galvanized product quality problems
Topics

- Bare areas (black spots)
- Non-smooth coatings.
  - Zinc flow-marks.
  - Ash pickup.
  - Dross pimples.
- Grey coatings.
- Flaking (peeling) coatings.
- White rust.
Bare areas

Surveys show 85+% of galvanizing quality problems relate to bare areas.
Usual causes of bare areas are:

- Poor steel cleaning (degreasing or acid pickling).
- Poor flux condition.
- High aluminium content in the bath.
Bare areas (black spots) caused by a high aluminium content in the bath.

Recommended normal aluminium content in the bath (and near the surface) is 0.002 – 0.005%.

Bare areas often occur when the aluminium content is > 0.01%
Bare areas (black spots) caused by a high aluminium content in the bath.
Simple test for high aluminium content

Clean a small area of the bath surface, then throw a small (1cm) lump of flux onto the cleaned area.

- **BATH SURFACE**
  - Flux lump moves across the zinc surface = safe aluminium content

- **BATH SURFACE**
  - Flux lump remains stationary = too much aluminium content
Bare areas (black spots) caused by a high aluminium content in the bath.

Usual reasons causing the problem are:-

- too much aluminium being added to the bath
- a non-uniform distribution of aluminium in the bath (i.e., bath surface too high in aluminium content)
Bare areas (black spots) caused by a high aluminium content in the bath.

Remedy:

1. Add flux powder to the bath surface. This quickly reduces the aluminium content but does create a lot of fume.

2. Change from adding pure aluminium additions at the bath surface to use of a zinc–aluminium alloy addition (such as Padaeng DA3 alloy added as 1 piece with each tonne zinc added during operations).

3. Aluminium (alloy) additions to the bath should be regular and consistent with each tonne of zinc added to the bath, or at specific set times during operation.
Repair of bare areas
Repair of bare areas
(as specified in ISO and ASTM Standards)

- Paint coating thickness should be 30 microns thicker than the surrounding zinc coating (ISO) and contain > 65% Zn in the liquid paint or > 92 % in the dry paint layer (ASTM)

- Apply final top coat of aluminium paint (sometimes called silver paint) for a good colour match with the galvanized coating.

Important: Do not use aluminium paint as a substitute for zinc-rich paint.
Non smooth coatings

Problem: Zinc flowmarks
Problem: Zinc flowmarks

**Cause:** Galvanizing temperature too low (which reduces zinc fluidity)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Solidification Temperature of Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>450°C</td>
<td>419°C</td>
</tr>
<tr>
<td>440°C</td>
<td></td>
</tr>
</tbody>
</table>

Change of only 10°C in the galvanizing temperature (440°C to 450°C - approx 2%) causes a 33% change in the temperature difference before zinc solidifies.

Optimum galvanizing temperature is 450- 455°C.
Problem: Zinc flowmarks

Cause: Excess zinc due to withdrawal speed from bath being too fast. The excess zinc has no time to flow back into the bath.

Recommended practice: Reduce withdrawal speed to 1.0 - 1.5 metres per minute.
Non smooth coatings

Problem: Ash pick-up on the coating surface

Ash lumps and streaks
Non smooth coatings

Problem : Ash lumps or ash streaks on the coating surface

Remedy:

- Careful, slow and steady skimming technique. Do not “paddle” as this creates waves causing ash streaks

- Skim bath surface just in front of the emerging galvanized steel items.

- Proper design of the ‘skimmer’ tool. Use a floating type skimming tool
HANDLE

SMALL VENT HOLE

HOLLOW STEEL CONDUIT TUBE Sealed AT ENDS

BLADE

CROSS-SECTION
Non smooth coatings

Problem: Dross pimples in the coating

Zinc layer
Steel
Dross particle
Zinc layer
Non smooth coatings

Problem: Dross pimples in the coating

Remedies:

- Do not allow the bottom dross layer to become very thick. Remove dross from the bottom of the galvanizing bath regularly.

- Keep a Pb layer at the bottom of the galvanizing bath at 50 - 100mm deep. The Pb assists in holding the dross at the bottom.
Problem: Dross pimples in the coating

Remedies:

- Keep iron contamination in flux at a low level. This iron will produce extra dross when the steel enters the zinc bath.

- Avoid high aluminium levels in the bath especially at the surface since this can change normal Zn-Fe dross particles into an Al-Zn-Fe dross which float and stick to the coating.

Therefore add aluminium using a zinc-aluminium alloy instead of pure (or scrap) aluminium to avoid the problem of excessive bath surface aluminium content.
Grey coatings

Cause: High silicon and phosphorous content in the steel composition.

Occurs when \( \%Si + 2.5 \times \%P > 0.09\% \)
Grey coatings
Grey coatings
Grey coatings

Steel

Zn layer

Zn – Fe alloy layer

Si + 2.5 x P (< 0.09%)

Steel

Zn – Fe alloy layer

Si + 2.5 x P (0.09% - 0.2%)
Grey coatings

Remedy:

1. If customer rejects the coating, remove the galvanized coating in the acid stripping tank and re-galvanize.

   The 2\textsuperscript{nd} coating is usually “normal”. This is because the first coating removed Si and P from the steel surface.

2. The problem is much less observed in baths with nickel additions because nickel slows the growth of the Zn-Fe layer.
Nickel addition can reduce grey coating problem

Zn-Fe alloy layer thickness

Si + 2.5 x P (%)
Grey coatings

**Cause:** Thick steel sections being galvanized. These remain very hot immediately after exiting from the bath. The Zn-Fe alloy layer then has time to grow and reach the coating surface before the steel is water cooled.
Grey coatings on thick steel

- Probability of grey colour:
  - Low for thin steel
  - High for thick steel

Faster transfer to water cool or Ni in the bath.
Thick and brittle coatings which crack or peel-off
Thick and brittle coatings which crack or peel-off
Thick and brittle coatings which crack or peel-off
Thick and brittle coatings which crack or peel-off

Cause:

- **Always** due to very high silicon and phosphorous content in the steel composition.
- Occurs when $\%Si + 2.5 \times \%P = 0.13 - 0.18\%$ or $>> 0.35\%$
- High Si + P causes the coating structure to be mostly a thick and brittle Zn-Fe alloy layer which is not strongly bonded to the steel surface.
Thick and brittle coatings which crack or peel-off

Remedy

- Remove the coating in the acid stripping tank and re-galvanize. The 2nd coating is usually “normal”. This is because the first coating removed Si and P from the steel surface

- Nickel additions to the bath reduce the probability of thick and brittle coatings
White rust

Cause: Corrosion of the galvanized coating surface due to storage in wet (or humid) conditions where there is poor air circulation
White rust

Remedy:

- Correct storage conditions (store under roof if possible, keep away from galvanizing fumes)

- Good ventilation during storage. Avoid closely contacting galvanized items

- Galvanized coatings should be passivated in chromate solution or with soluble polymer

- Avoid chloride contamination of passivation solution. Therefore it is preferable to use two water cooling tanks. 1st tank is water only and the water should be replaced regularly
Questions and Answers