Sherardizing as applied to stampings from light gauge metals

Matthew Patrick Brazill

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SHERARDIZING AS APPLIED TO STAMPINGS
FROM LIGHT GUAGE METALS

by
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A
THESIS
submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY
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in partial fulfillment of the work required for the
DEGREE OF
ENGINEER OF MINES

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1935

Approved by
Professor of Mining
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THE HISTORY OF GALVANIZING

(From Flander's Galvanizing & Tinning—1916)

Sherardizing, or dry galvanizing as it is sometimes called, is a process whereby articles of iron or steel are rendered rust proof by applying a coating of zinc. The coating produced by this process is first an alloy with the underlying metal. After this alloying action is completed the outer layer of zinc is deposited. Briefly stated, this coating is not a pure layer of zinc, but a zinc iron alloy.

Dry Galvanizing in Pre-historic Times

A process practically identical to this was known in prehistoric times, although used for another purpose. At that time it was known that if certain copper tools and vessels were placed in the ground in certain localities and kept hot for a time by building a fire over the place, then, upon removal, it was seen that the copper had assumed a light yellow color and had become harder and more durable. They practically secured dry galvanizing, although it was not known that another metal had become alloyed with the copper.

Also, in Greek History, according to Aristotle the "Bleaching of Copper" was done by the same method.
The modern process of Sherardizing as we know it, was discovered by accident. In the early part of this Century, Commander H. V. Simpson, of the British Navy, was detailed to work out a method of case hardening armor plate for battleships that would not infringe on the Harvey patents, which were being used by nearly all Governments for rendering armor plate shell proof. These experiments were being tried out in the laboratory of Sherard Cowper-Cowles, of London, a noted English Metallurgist. A package of zinc dust had been forwarded to Mr. Cowper-Cowles to determine whether it could be used in making an electrolyte for zinc plating. In the course of their experiments they placed a piece of steel in this zinc dust in a case hardening oven and heated it up to see if it would have any hardening effect on metal. When taken out it was covered with a silvery coating of zinc and upon examination under the microscope they found it had penetrated and alloyed the zinc with the body of the metal. They had carried out the case hardening operation at a temperature below 788° F, or the melting point of zinc.

This was something entirely new, i.e. a piece of metal taking a zinc coat at a temperature below the melting point of zinc.

After thorough and exhaustive tests, it was found that the coating gave the underlying metal better protection from corrosion than either the well known hot or electro-galvanizing processes, and patents were taken out in the principal Countries of the World.
Sherardizing was introduced to the United States by Sherard Cowper-Cowles, after whom it was named, in 1908.

It consisted in heating iron, steel or other metals in contact with a form of zinc, commonly called Blue Powder, in a closed container at a temperature ranging from 300° to 420° C, which is the approximate melting point of zinc, until a sufficient coating of zinc has been applied to make the metal rust proof, or at least highly resistant to rust. This had been very successful with nuts, bolts, screws, nails, pipe fittings, small tubes and other small intricate patterns and castings which had not been treated very successfully by the galvanizing process.

Its chief advantage on any article having threads was that it was unnecessary to recut the threads after sherardizing.

This is a process of cementation, according to Hofman. Flanders in his "Metallurgy of Zinc" said it was a process of sublimation, occlusion and adhesion. The fact is that in the process the zinc passes from the solid to the gaseous state and from the gaseous state direct to the solid state, in both cases stepping over the liquid state; I am inclined to favor Flanders theory.

Microphotographs show the following layers, reading from the inside out: Iron, Iron Zinc alloy, Zinc Iron alloy, Zinc. The Iron-Zinc alloy resembles FeZn3 while the Zinc-Iron alloy resembles FeZn7.

(Hofmans Metallurgy of Zinc).
In 1920 the differential in price between Galvanized sheets, and black Iron sheets became such that the Kant-Leek-Kleat Company, a subsidiary of the Johns-Manville Corp., decided to try making their product from Black Iron sheets of 28 gauge, and then Sherardizing the finished product, which prior to this time had always been made from Galvanized Sheets. There was no particular problem to making the cleats from Black Iron, but the Sherardizing of the product was a very serious one. The product was a roofing cleat for the purpose of holding paper, felt, slate coat or asbestos roofing firmly to the roof or any surface it was applied to, in such a way as to prevent leaks due to gaps in the joints of the roofing.

It consisted of a narrow metal cleat; called Kleat by them in order to correspond with their Trade name. It was about 6" long, and 1/2" wide, the shape as shown in the accompanying sketch.
Roofing Cleat

Plan View

Cross Section

Elevation

Scale = Actual
CLEANING THE METAL PREPARATORY TO SHERARDIZING

The first step in the process must be the cleaning of the metal to be Sherardized. The grease, oil and other dirt it has acquired during the various stages of its manufacture is first removed by treating with a solution of caustic soda, or other similar chemical, into which it is dipped. This has a strength of about 40# of soda or other chemical of equal strength, to 100 gallons of water, at a temperature of from 60° to 80° C. We finally adopted Oakite as giving us the most economic method for removing grease and oil.

Oxide of Potassium, 50# of the oxide to 500 gallons of water, at a boiling temperature, is now used and recommended by the General Electric Company, for removing grease and oil.

Sand blasting and shot blasting may also be used, but are not as suited for general practice as they are for some special types of articles.

After the grease and oil is removed the metal is then washed in hot water to remove the caustic soda or other cleansing agent.

It is then pickled with Hydro-Fluoric or Sulphuric acid to remove any scale, slag or other foreign particles that might have adhered to it. Sulphuric acid is almost universally used with a solution of 12 parts of water to one of acid.
It is then treated with Milk of Lime to neutralize the acid; about 20# of air slacked lime to 100 gallons of water. It is washed again in hot water and finally dried with either hot air or superheated steam.

The metal is then ready for the Sherardizing process.

NORMAL CHARGE FOR SHERARDIZING

The usual method of Sherardizing nuts, bolts and other similar articles at that time was to pack them either in cylinders with Blue-Powder, and in turn place them in reverberatory furnaces where they could be rolled back and forth - or - to place them in iron containers which were placed in electrically heated drums and kept at a temperature of from 380°C to 420°C for three hours; then allowed to cool to a temperature of 100°C, which took from ten to twenty hours. Then they were dumped over a screen and thus the Sherardized articles were separated from the Blue-Powder. (From General Electric Co. Bulletin on Sherardizing).

Theoretically the thickness of the Sherardized coating need not be in excess of .002" to give complete protection from the oxidizing effect of the air or water, but due to mechanical abrasion it is usually found advisable to increase this deposit from .003 to .005 depending on the service that is expected of the article being treated.
The thickness being increased usually by increasing the time to which the metal was exposed to the zinc powder; but of course it can also be increased by raising the temperature, provided of course that it does not go above 420° C. The normal charge at that time for Sherardizing nuts, bolts and etc. had been 3# to 5# of Blue Powder to 100# of Iron or other metal to be Sherardized. (Flanders Metallurgy of Zinc.)

At this point let me say something about Blue-Powder, which at that time was almost exclusively used as the Sherardizing agent. Blue-Powder is a by-product of the smelting of zinc. All the vapor from a zinc retort does not condense as a liquid, a part passing directly to the solid state to form a finely divided powder of Bluish color. This runs from 5 to 10% of the total spelter produced. This Blue-Powder usually runs from 35% to 45% Metallic Zinc, although there are some high grades that run as high as 80% Metallic Zinc. This Blue-Powder is dried at a temperature of 215° C. before being used as a Sherardizing agent. It must not contain over 10% Zinc oxide; we found 8½ a desirable amount, (Recommended by General Electric Bulletin), and the Metallic content of the Blue-Powder had a direct bearing on the length of time and the temperature necessary to produce the desired coating. The higher the zinc content, the lower the temperature and the shorter the time of exposure necessary.

Not having any precedent to go by we decided to run our first trial with the normal charge, recommended by both Flanders and the Engineering Department of the General Electric Company, used in the Sherardizing of the usual articles most commonly treated by this process.
THE EQUIPMENT.

For cleaning the metal preparatory to Sherardizing we had:

1. Tank for Caustic Soda solution to remove grease, oil, etc.
2. Tank with hot water to remove Caustic Soda.
3. Tank, zinc lined, for Sulphuric Acid solution.
4. Tank of Lime Water to neutralize Acid.
5. Tank of Hot water to remove Lime.
6. Oven for drying metal.

For the Sherardizing we had an electrically heated drum, manufactured by the General Electric Company, (Picture attached.) The inside dimensions were 24" by 24" by 40". The limits of the drums or containers for Sherardizing is from 24" to 30" diametrically, chiefly due to the low conductivity of zinc dust, which would require excessive heat at the periphery of the container before the desired temperature could be reached at the center. The length of the container can be almost any length that is required by the article to be Sherardized. The Mark Manufacturing Company, of Chicago, Ill., has drums 26" in diameter and 23 feet long and are designed for Sherardizing Merchant pipe.

The drum we used revolved at about 2 R.P.M. It was equipped with two current loads; High load to heat drum to desired temperature—Low load to maintain it at desired temperature.
The charge was placed in a steel container which just fitted into the drum. The top of the container was held in place with 1½" studs with an asbestos gasket. The top of the drum was also equipped with an asbestos gasket, and the cover was held in place with two large iron bars passing through two inverted U's at each end, and wedged there with two large set screws near the end of each bar. (Picture and sketch attached).

PROCEDURE

We loaded the container with a charge of 35# of Blue-Powder to 700# of cleats. Loaded it into the drum with chainfalls, and brought it up to a temperature of 350°. This required about 3½ hours. The metal being so thin compared to the usual charge of bolts, nuts and etc., we thought it better to start with a lower than normal temperature, and held it at this temperature for three hours. After cooling and examining the results, we were very much disappointed, as there was very little evidence of any coating. We then tried the same thing at 380° at four hours duration with little better results, and then at 410° with four hours duration, with only slightly better results.

It was evident that some other factor was producing this lack of results. We noticed evidence of the cleats nesting, and we decided that perhaps we had too much metal and powder in the container which prevented the cleats
CURVE OBTAINED AT - A. R. JOHNSON

ELECTRICALLY HEATED SHEARAGING DRUM

TEMPERATURE VS. POWER CURVE
from tumbling freely. We therefore reduced our charge to 500# of cleats with 25# of Blue-Powder. The net result was anything but gratifying; the coating was not improved and the cleats had evidently tumbled too freely and a certain percentage of them were bent and twisted to such an extent as to be worthless. Our difficulty no doubt was due to the fact that the roofing cleat had several times the surface area per unit of weight as compared to the usual articles which were being sherardized; and therefore, needed a much larger quantity of the zinc dust to give proper contact. This we had failed to take into consideration when we made up our first few charges.

We then decided we were off on the wrong track, so we determined to increase the amount of Blue-Powder. We made up a charge of 700# of cleats and doubled the charge of Blue-Powder to 70# instead of 35#. There was an immediate improvement in the coating and our next charge was 700# of cleats and 125# of Blue-Powder. This gave us more than a sufficient coating, in fact it was so heavy as to show signs of chipping or peeling. It micrometered over .005 inches in thickness.

We then decided to reduce the time. We cut this to three hours instead of four and had fairly satisfactory results, but the coating was still a trifle heavy. It micrometered over .004 inches in thickness. We then cut the time to two and one half hours, maintaining our temperature to 410, which gave us a coating of from .003" to .004" in thickness, and afterwards on test by the salt spray method, we decided was the proper amount for our requirements.
Curve obtained by: A.R. Johnson
Electricaly heated shellardizing drum
Rate of deposit & temperature
Our next trouble was in the variation of the zinc content of the Blue-Powder. Also the gradual increase in the percentage of ZnO above the 10% limit, and in the increase in the iron content and other impurities.

It was customary to add a quantity of fresh Blue-Powder to the old to make up each new charge to maintain the proper balance of the ZnO, Metallic zinc and etc. But, due to the variation in zinc content of the Blue-Powder itself we decided to experiment with the zinc powder put out by the Grasselli Chemical Company.

This powder had the following chemical analysis:

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si O2</td>
<td>.01%</td>
</tr>
<tr>
<td>Sn &amp; Cu.</td>
<td>.05%</td>
</tr>
<tr>
<td>Pb.</td>
<td>.39%</td>
</tr>
<tr>
<td>Fe.</td>
<td>.56%</td>
</tr>
<tr>
<td>Zn O</td>
<td>5.84%</td>
</tr>
<tr>
<td>Metallic Zinc</td>
<td>93.18%</td>
</tr>
</tbody>
</table>

Giving a total zinc content of 98.82%.

We knew it was necessary to have a ZnO content of from 8% to 10%. (Recommended by G.E. Bulletin & Flanders Metallurgy of Zinc.). We found it advisable to run the new zinc powder for two or three heats with just scrap iron to bring it to the proper ZnO content. After a number of trials we found that by the addition of 10% of our charge in the new zinc Powder we were able to maintain our powder at a very satisfactory standard.
We found we obtained the best results in keeping our zinc powder to the following percentages:

- Zn: between 85-90%
- ZnO: 3-10%
- Pb: 1-1.5% (Not over 1.25 for good results)
- Fe: 1-2%

Other impurities between 0.5-1%

Lead must be kept down to a minimum or a lumpy coating will result. Any appreciable increase in the ZnO content above the allowable 10% resulted in the coating becoming fuller as the ZnO content increased. The higher the Zn content in the powder, the lower the temperature and the shorter the duration of the heating period.

We had the powder analyzed once a week to check the contents. And we eliminated the iron to a great extent by passing the powder through a magnetic separator once every two weeks, and then ran it through a 60:1 riddle to prevent any tendency to become lumpy.

After establishing this uniform base for our powder we tried to obtain the most economical combination of temperature and duration of the heating period, and exact amount of the charge. We finally, after a number of variations, adopted the following combination:

- 1000# Cleats
- 155# Zinc Powder with a 10% of new powder to prevent it becoming impoverished.

A duration of two hours at a temperature of 410° C. Power shifted from High Load to Low Load at 400° as temperature
would continue to rise until it reached $410^\circ$ C before leveling off.

The increase of the amount of powder in the charge, beyond the amount necessary to give the desired coating is only a waste of zinc dust.

A sufficient time must be given to allow the container and its contents to cool to about $100^\circ$ C. If the container is opened before sufficient cooling has taken place the Sherardized metal, instead of being a bright grey or silver color, will have a decided bluish color. And, while this will in no way affect its rust resisting properties, it most certainly will be very detrimental to its appearance and no doubt cause it to be rejected when the Sherardizing is done for any other than your own concern.

In order to prevent the loss of time necessitated by the length of time required to cool the container before opening, we had a number of these containers built, so that we always had one or two containers loaded and ready for the drum as soon as the previous one had been removed. In this way we were able, due to the heat retained in the drum, to bring the temperature of the container up to the required $410^\circ$ C. in 1 1/2 hours instead of 3 1/2 hours, and to maintain it at this temperature for two hours and replace it with a new container in 1/8 hour or less, giving us a complete cycle of operation in four hours. And, by running continuously we could run 6 heats in 24 hours, and cut our electric current cost about in half.
Comparative Temperature & Power Curves
of Electrically Heated Sherardizing Drum
24"x24"x40"

Starting with Cold Drum       Starting with Hot Drum

Curves obtained by MP Brazill Jr

Temperature Curve
Power Curve

105 K.W.H.
205 K.W.H.

Hours Run
Attached you will find power curves for the 50 K.W. drum which we used in this work, showing the K.W. input when it was necessary to heat on high power for 3 1/2 hours, when the drum was cold, to bring it to the necessary temperature and then 2 hours on low power to maintain this temperature, as compared to heating it in 1 1/2 hours with a hot drum.

<table>
<thead>
<tr>
<th>Time</th>
<th>Power</th>
<th>K.W.H.</th>
</tr>
</thead>
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<tr>
<td>3 1/2 hours</td>
<td>50 K.W</td>
<td>175 K.W.H.</td>
</tr>
<tr>
<td>2 hours</td>
<td>15 K.W</td>
<td>30 K.W.</td>
</tr>
<tr>
<td>1 1/2 hours</td>
<td>50 K.W</td>
<td>75 K.W.</td>
</tr>
<tr>
<td>2 hours</td>
<td>15 K.S.</td>
<td>30 K.W.</td>
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Our costs on the basis we at first ran our heats, on the proportions of zinc to cleats, and the time and temperature at which we obtained our first satisfactory coating, were about $.07 per pound of finished cleats. At this rate it was not much of a saving over making the cleats from galvanized sheets. However, after we established our final charge, temperature, and duration, along with our saving of electric energy, overhead and etc. on the 6 cycles per day, we had the satisfaction of seeing our costs drop to .0357 per lb, which was a material saving over galvanized sheets.

I understand today that the General Electric Company are recommending a charge of Graselli Zinc Powder very similar in proportion to that we used on light gauge stampings, for the regular charge in Sherardizing nuts, bolts,
screws and small castings which is a considerable increase over the accepted standard charge used in 1920 and 1921.

Practically all Sherardizing today is done in containers that can be removed from the drum or oven, in order to save the time lost by cooling, and to retain the heat in the drum or oven for the next charge, thereby saving the cost of heating from room temperatures to operating temperatures.

ADVANTAGES OF SHERARDIZING OVER GALVANIZING

Dr. Hinchey, of the Faraday Society, has determined that 1/2 ounce of Sherardizing coating per square foot is equal in protection to the underlying metal to 1 1/2 ounces of hot galvanized coating.

Another advantage that is of particular importance to our particular product is that paint or enamel will not adhere to either the hot or electro-galvanizing with any degree of permanence. Due to the rough exterior of Sherardized surfaces, paint and enamel adhere firmly to it, which you can readily see is of great importance to a roofing cleat.

Dr. Richard Moldenke in his book, "The Production of Malleable Castings", shows us another decided advantage of Sherardizing over Galvanizing. In hot Galvanizing the casting is plunged into the molten zinc, the temperature varies from 900° to 1000° F. The casting is left in the bath until its temperature reaches the same temperature as
that of the bath, so that the coating will be smooth, then removed and generally plunged into cold water. The result is a hard or crystalized casting, in which the temper carbon has gone back. This reduces the strength of the casting. The amount of zinc which the casting has taken on cannot be regulated and in most cases there is an excess and therefore a consequent loss.

In Sherardizing these disadvantages are eliminated. As zinc dust has a low factor of heat conductivity, it is impossible to subject the casting to sudden changes of temperature. This avoids crystallization and cracking of castings. Hot galvanizing as a rule reduces the strength of the casting, while Sherardizing has, in some cases, slightly increased the strength as compared to plain castings.

Some authorities claim a saving of from 25% to 40% for Sherardizing over Galvanizing for castings. They distribute it through six different items.

1st. Less fuel per pound of coating.
2nd. Less labor required for equal tonnage.
3rd. Less zinc required for equal protection.
4th. Loss of material practically nothing.
5th. Maintenance of plant much lower.
6th. No loss from crystallization or cracking.
SUMMARY OF OUR FINDINGS

The following facts have been demonstrated by various Metallurgists and authorities on Sherardizing, and we have checked their results in the most part part with the exception of the 3rd and 4th paragraph, which is a little deeper than we went into the problem.

1. If the metallic zinc content in the dust is kept constant we will get on the same class of material equal weight or thickness of coating under the same temperature and time treatment.

2. Zinc does not begin to deposit until the material has reached the temperature at which sublimation takes place, and also the magnetic oxide of iron appears.

3. That iron which oxidizes with difficulty Sherardizes with difficulty.

4. (Paper by Thomas Liggett, Jr. in American Foundrymen).

The coating is a true zinc iron alloy. The magnetic oxide of iron which forms on the material is reduced to metallic iron by contact with the zinc, which alloys with the excess zinc and exactly replaces the film of magnetic oxide that was first formed.
In conclusion I will say that I believe Sherardizing will gradually replace hot galvanized on a great many of the smaller metal articles needing a protection coating. Of course for large bulky castings, etc., the cost of building Sherardizing equipment to handle it would be out of proportion to the economic results, and in this field galvanized will hold its predominance.

Due to the fact that sublimation takes place at a lower temperature under a vacuum it is very possible that some work may be done under this condition, and I understand some patents covering this phase of Sherardizing have been applied for.

But, unless the cost of electric current reverses its trend toward lower prices, I can see no economic advantage in applying the zinc coat under this condition.
NOTE: In the attached graphs you will see a variation between the curve obtained by A. R. Johnson and W. R. Woolrich and the one we obtained, in that they only reached a temperature of 375° in 3 1/2 hours heating using 52 1/2 K.W. per hour, while we reached 410° with only 50 K.W.H.

This is due to the fact that their equipment was designed and built previous to 1916. Due to improvement in the heating units and insulation of the drum, those built after the war were more efficient.

The cooling curve they obtained was made with the charge remaining in the drum and allowed to cool. In a separate container, such as we used, the charge cools much more quickly, as there is no insulation around it to retain the heat.

We determined whether a container was sufficiently cooled to open by laying our hand on it and if we could hold it there for 1/2 minute without any real discomfort, we considered it cool enough.
NOTE: This picture shows a battery of Sherardizing drums in operation at the General Electric Company plant at Schenectady, New York.

They are identical with the one we used in our work except they were operated without using containers.

The one at the extreme left shows a drum ready to be loaded. The top and bars for holding it, placed on the floor to the right of the drum.

The second drum has been opened and the finished product is being unloaded.

The drum at the extreme right is in operation.