

QUALITY CONTROLLED HOT DIP GALVANIZING
AND
PHOSPHATE ETCHING

by
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A THESIS

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ABSTRACT OF THESIS
ON
QUALITY CONTROLLED HOT DIP GALVANIZING
AND
PHOSPHATE ETCHING

This thesis covers the results of research in determining the value of accurate controls in the hot dip galvanizing of ferrous products.

Specifically it deals with equipment design, cleaning procedure, rinsing, flux coating, controlled galvanizing, phosphate treatment and economy.

It compares the results of tests on normal and forced alloy growth coatings, of uniform and uneven coatings, of ductile and brittle coatings, of plain and phosphate treated coatings and of coatings over different composition steels.

It covers the value of the accurate control of all phases of the process in the reduction of dross formation and rejects in the interest of economy.

It indicates the proper hanging and handling of work to insure quality galvanizing and minimum labor requirements.

It shows a method of determining proportionate dross formation from the work and the galvanizing kettle and correct production for minimizing the amount of dross formed per ton of material processed.

It covers salt spray and humidity tests on quality controlled coatings clearly showing the value of phosphate treatment.

A reference table of comparative characteristics of all types of zinc application is included to properly classify hot dip galvanizing as a protective coating.

F O R E W O R D

After many years of interest and research in the protection of steel by hot dip galvanizing with investigations of galvanizing plants in the United States and England, the technical staff of the Detroit Steel Products Company designed, constructed and put into operation a fully controlled and mechanized hot dip galvanizing plant for the protective treatment of steel window frames.

This is the first plant so designed in this country and has afforded a large field for research work in quality control.

The very fact that hot dip galvanizing in its crudest form provides considerable protective value, has clouded the necessity for controls to obtain uniformity and economy.

As the name implies, galvanizing (hot dip galvanizing) is the electro-chemical formation of a zinc-iron alloy crystalline coating on base metal formed during submersion of this metal in molten zinc, coated with free zinc as the work is withdrawn.

The name galvanizing comes from experiments recorded in 1786 by Luigi Galvani, Italian Physiologist, covering his work in showing the difference of electrical potential in dissimilar metals.

Zinc is higher in the electromotive scale than iron and protects the iron from corrosion by becoming the anode of an electrical couple when in the presence of an electrolyte. The iron will not corrode when coupled with zinc so that small voids in a zinc protection do not destroy its protective value as is true with many other metal coatings.

K. S. FRAZIER

Chief Research Engineer

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QUALITY CONTROLLED HOT DIP GALVANIZING
AND
PHOSPHATE ETCHING

Weight and Composition of Coating

It is generally recognized by authorities that the life of a zinc coating over steel under given atmospheric conditions is directly proportional to the thickness of this coat.

Exceptions to this rule of thumb have, however, considerable bearing on coating life and it is these exceptions which we wish to consider in this thesis.

In the handling of these items it will be shown that rigid controls in the Hot Dip Galvanizing process are not merely good house-keeping practices but are profitable to both the galvanizer and the customer of galvanized work.

Hot Dip Galvanizing is well into its second century of use and its proven value of protection over steel is established. It is generally conceded, however, that since reasonable cleaning of the base metal and the dipping of this metal into molten zinc will generally produce a good protective coating, close controls of the process have been very slow in finding their way into industry.

In the modified hot dip process generally known as Galvannealing, advances in control have been much more rapid. Galvannealing, generally associated with sheets and strip where forming is required after zinc coating, has forced the hand of industry in developing controls of coating thickness, zinc iron alloy growth and annealing. The limits of coating thickness in this process divorce it from immediate consideration where maximum weight "quality coating" is desirable

for long life protection particularly where adverse atmospheric conditions exist.

Since the zinc-iron alloy growth of hot dip galvanizing forms while the base metal temperature comes up to the temperature of the zinc bath it follows that heavy materials such as structural steel will accept normally a heavier coating than light weight sections such as used in steel windows. Although the findings shown here will apply in many instances to the heavier material all tests were made with the lighter sections and were pointed directly to that field.

In order to clarify this point a simple test was made. Coupons of 16 gauge (approximately $1/16$ "), $1/8$ " and $3/16$ " in thickness were prepared. After thorough cleaning they were placed on the same rack and lowered into molten zinc at 850° F. for a period of one minute. These coupons were then stripped in accordance with American Society of Testing Materials (A.S.T.M.) Procedure A-90 to determine the weight of accepted coating.

Three separate tests, each containing three coupons, were run of each weight of plate. The three tests showed the following closely parallel averaged results: the 16 gauge coupons picked up 2.85 ounces of zinc per square foot of plate or 1.42 ounces of zinc per square foot of surface; the $1/8$ " coupons picked up 3.28 ounces of zinc per square foot of plate or 1.64 ounces of zinc per square foot of surface, a gain of .22 ounces of zinc per square foot of surface; the $3/16$ " coupons picked up slightly more coating than the $1/8$ " coupons.

Subsequent tests indicated that this growth of zinc-iron alloy

was peculiar to thin sheets and that beyond 3/16" thickness this change in alloy growth was not material.

It is common practice in industry to record the weight of zinc coatings in relation to weight of black steel being galvanized. This must not be confused with the above findings.

A 16 gauge steel sheet will have approximately 100% more surface per pound of black steel than a 1/8" sheet while the zinc coating per square foot of surface will only be approximately 13% less. From this we find that the weight of zinc coating accepted on 16 gauge steel will be approximately 75% more per pound of steel than on a 1/8" steel sheet.

Carrying this trend of thought into the field of light irregular sections a testing program was set up using 18 samples each of four different sections of different weights or a total of 72 test samples.

Units of this group were galvanized at three different temperatures of molten zinc, namely 840° F., 850° F., and 860° F. and with different periods of submersion approximately 1 minute, 1 1/2 minutes, 2 minutes and 2 1/2 minutes. All accepted coatings were photomicrographed and stripped to determine weight of coating.

Several things were apparent from the microphotographs.

1. Within this range of temperatures and submersion time, the coatings were well proportioned between zinc-iron alloy growth and free zinc and were relatively uniform.

2. Excessive tramp particles of alloy did not show in the free zinc layer excepting where a rough steel surface caused palisading of the crystalline zinc-iron alloy growth.

3. The increase in alloy growth was consistent at a decrease-

ing rate with increase in time of submersion in the molten zinc.

4. The heavier sections produced a greater growth of zinc-iron alloy with the same time of submersion in molten zinc.

5. The variation in temperature between 840° F. and 860° F. had very little influence on the weight of accepted coating.

The weight of coating as determined by stripping, substantiated points 3, 4 and 5 and added credence to earlier tests.

Fig. 1 shows graphically the results of these tests. The curves in this graph were constructed using the average results of all test pieces involved and are accurate only for the conditions of this test or for comparative results between different weights of bars in the light classification.

From tests conducted by Heinze Bablik¹ and from our own observations we find that the free zinc layer accepted by the work as it is withdrawn from the molten zinc is relatively uniform under given conditions regardless of the time of submersion. We can therefore cut this free from our chart leaving just the alloy growth as indicated in the graph.

Having established the general characteristic of zinc-iron alloy growth on light sections it appeared advisable to establish this growth for longer periods of submersion in molten zinc duplicating all tests in order to eliminate recognizable errors.

1 - A lecturer at the Technical University of Vienna and manager of a large galvanizing factory.

QUALITY RANGE

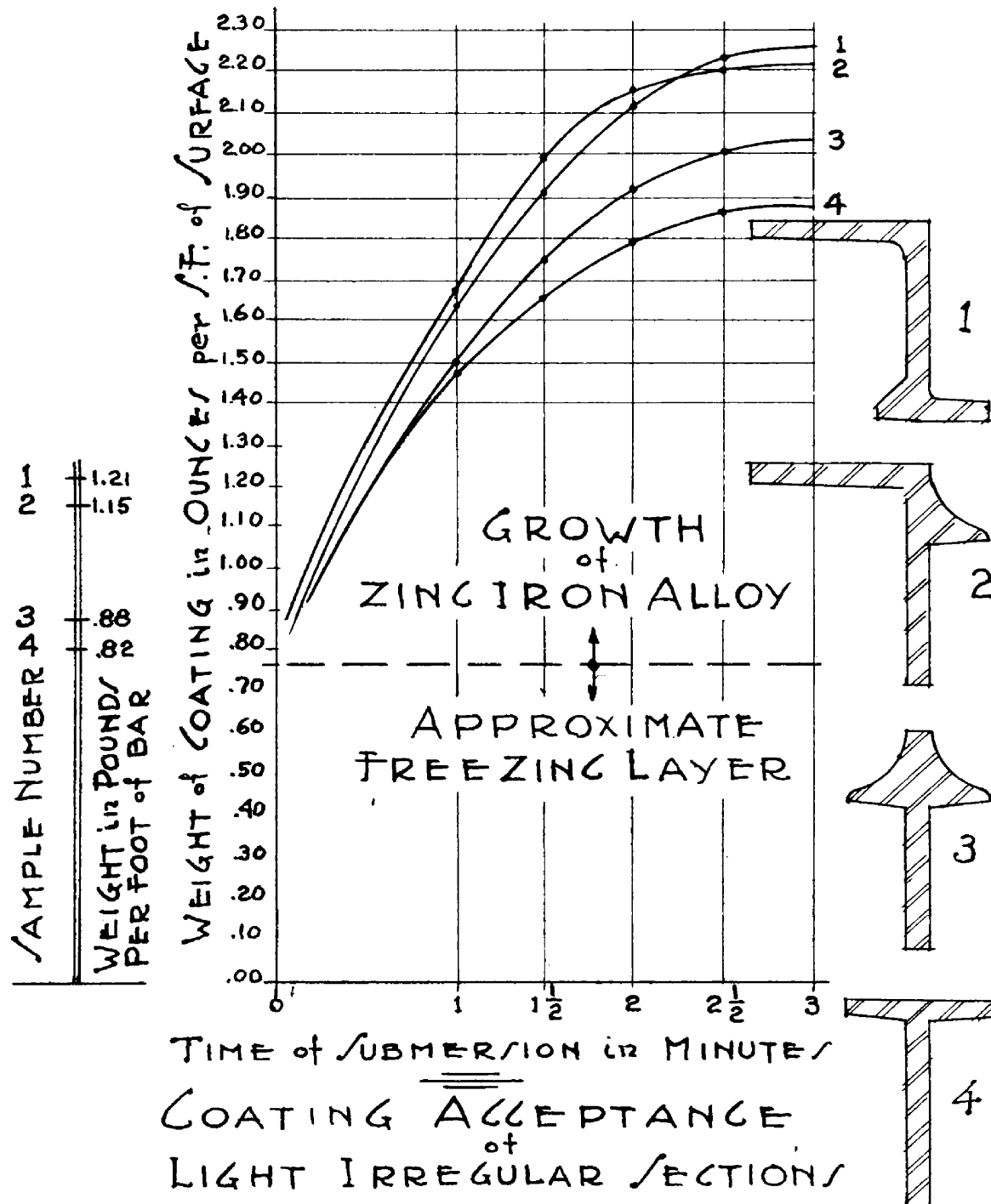


Fig. 1

K.F.

1/8" by 1" hot rolled low carbon bars were used in this test. All bars were hung on the hooks of a single rack, thoroughly degreased, pickled, rinsed, coated with a zinc ammonium chloride ($\text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl}$) and lowered into molten zinc at 850° F. At regular time intervals 2 bars were removed from the zinc and air cooled. The time intervals were 10, 10, 10, 10, 10, 10, 20, 20, 20, 60, 60, 60, 60, 60, 60 and 60 seconds so that the final bars were removed after 10 minutes of submersion.

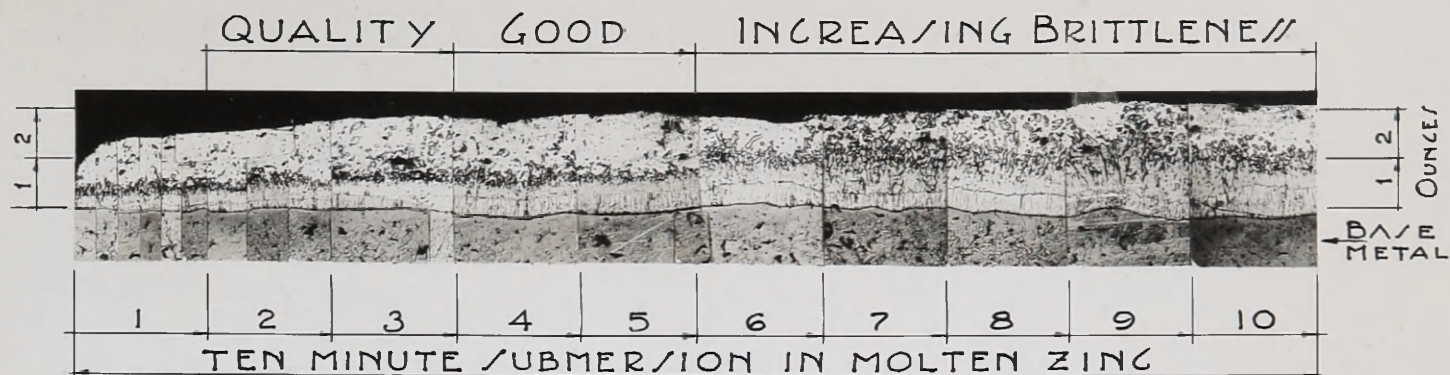
Sections taken at the center of each of these bars were photomicrographed and adjacent sections were stripped to determine weight of coating.

In Fig. 2 we have shown a composite picture of this growth having carefully selected the width of microsections used to represent time in the zinc bath. It develops a picture story of the zinc-iron alloy growth in ten minutes of submersion. Since a galvanized surface is not entirely uniform and since each microsection at 125X covers only a fraction of an inch, any individual section may not be truly representative of the total coating but are averaged out in a picture of this type.

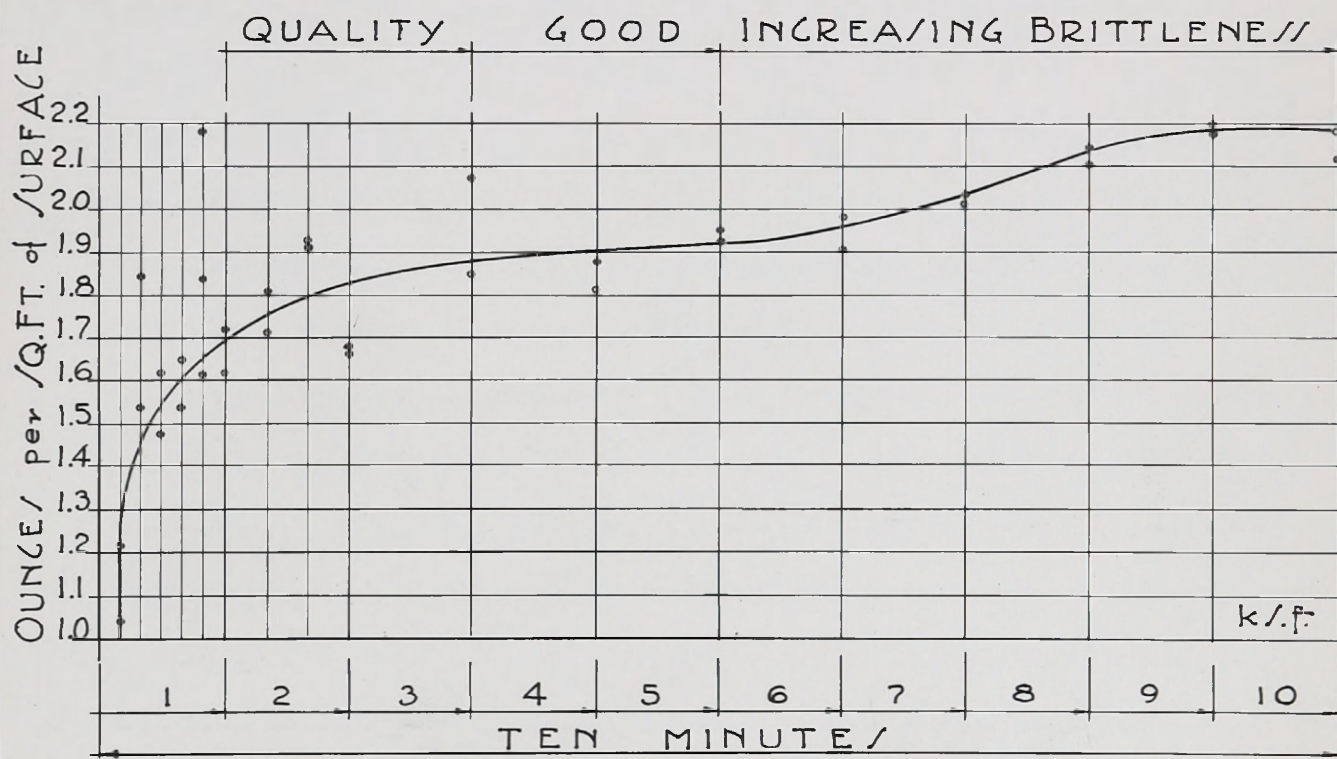
Independent of this composite picture a graphic representation at the same scale as the picture was developed from the weights of coatings obtained by stripping the samples.

It will be noted that the results indicated by these two independent methods of portrayal parallel very closely.

From this information we find a very rapid zinc-iron alloy growth during the first minute of submersion.



A COMPOSITE PICTURE SHOWING ALLOY GROWTH
THROUGH TEN MINUTE CYCLE
125 X



ZINC GROWTH and ACCEPTANCE by WEIGHT
DETERMINED by STRIPPING

QUALITY HOT DIP GALVANIZING CHART
LIGHT SECTION

Fig. 2

This is very important since a few seconds either way shows up appreciably in the weight of accepted coating and coating weight would therefore be hard to control in this area.

This vertical columnar-crystalline growth which is brittle in nature slows down rapidly after a minute of submersion to almost no growth at about three minutes probably due to the increasing resistance of free zinc and base metal to contact each other and alloy.

According to Daesen² this alloy growth starts as $\text{Fe}_3\text{Zn}_{10}$ in cubic crystals of a very thin layer and graduates through FeZn_7 to FeZn_{13} in the columnar form.

At three minutes of submersion time the normal alloy growth is apparently complete, uniform and leaves a base for uniform reception of the free zinc.

For the next two minutes of submersion, from 3 minutes to 5 minutes, the alloy growth is barely apparent, the quality of the coating remains good.

Photomicrographs do not indicate excessive tramp particles of zinc-iron alloy but through this retarded alloy growth zone there is unquestionably some breaking away of the uneven ends of columnar crystalline growth. These broken crystals of alloy being heavier than zinc settle to the bottom of the zinc bath to form dross, picking up zinc in their descent and showing about 97% zinc to 3% iron in the dross form.

This factor is recognized in the old axiom, "Dross begets dross."

2 - Consulting Metallurgical Engineer

From this coverage it can readily be seen that any reduction in submersion between 3 minutes and 5 minutes will not materially reduce the weight and quality of coating but will reduce the dross formation and will improve the economy of operation.

Increasing the submersion time beyond five minutes shows a rapidly accelerating new zinc-iron alloy growth which tapers off again at around nine minutes to practically no increase. In this range of submersion photomicrographs show a decided increase of tramp particles of alloy in both quantity and size in the free zinc layer which remain in the coating only by virtue of having been trapped by the free zinc. These particles are much larger than found with the shorter submersions. The indication is that much more dross is formed in the zinc bath in this extended submersion period.

To establish this criteria, bars of each submersion period were bent 180° over a soft mandrel. It was found that the radius of the bend increased in approximate direct proportion to the thickness of the alloy growth.

Examining these coatings after bending it was found that up to five minutes of submersion time a coating was produced that remained smooth and showed no checking with the bending. With submersion times of six minutes through ten minutes the coating showed increased wrinkling and checking in the bending. At ten minute submersion, this fracturing of the coating was quite severe.

To reveal the extreme, test bars were submerged in molten zinc at 850° F. for fifteen minutes. When these bars were bent over the soft mandrel, the coating flaked off in large areas showing

extreme brittleness and poor adhesion.

Using this extreme comparison again, two 3/4" x 3/16" steel bars were selected; one of these was submerged in molten zinc at 850° F. for 45 seconds and one for 15 minutes. The coatings were photomicrographed, Fig. 3, and stripped to determine weight of coating.

From a study of the microsections at 250 magnifications, it was found that for sample one, the alloy growth is the initial normal alloy growth found in good galvanizing. The tramp particles of alloy are small and not well defined. In bending this sample showed excellent adhesion of the coat with no checking.

For sample two, the initial normal alloy growth is well defined at about the same level as for sample one. There is then a forced alloy growth which becomes very ragged with large well defined tramp particles at and above its surface. These tramp particles show a considerable breaking away from the base alloy growth and much of this has freed itself into the bath to form dross. The increased surface zinc applies because of the roughness of the alloy growth. In bending, large areas of this surface flaked off partly due to its extreme thickness and partly due to increased brittleness from the proportion of alloy to free zinc.

Comparison Chart

	Submersion Time	Weight Coating Per Sq. Ft.	T h i c k n e s s		
			Coating Ave.	% Alloy	% Free Zinc
Sample #1	45 Sec.	1.7 Oz.	.0027 in.	54	46
Sample #2	15 Min.	4.0 Oz.	.0070 in.	71	29

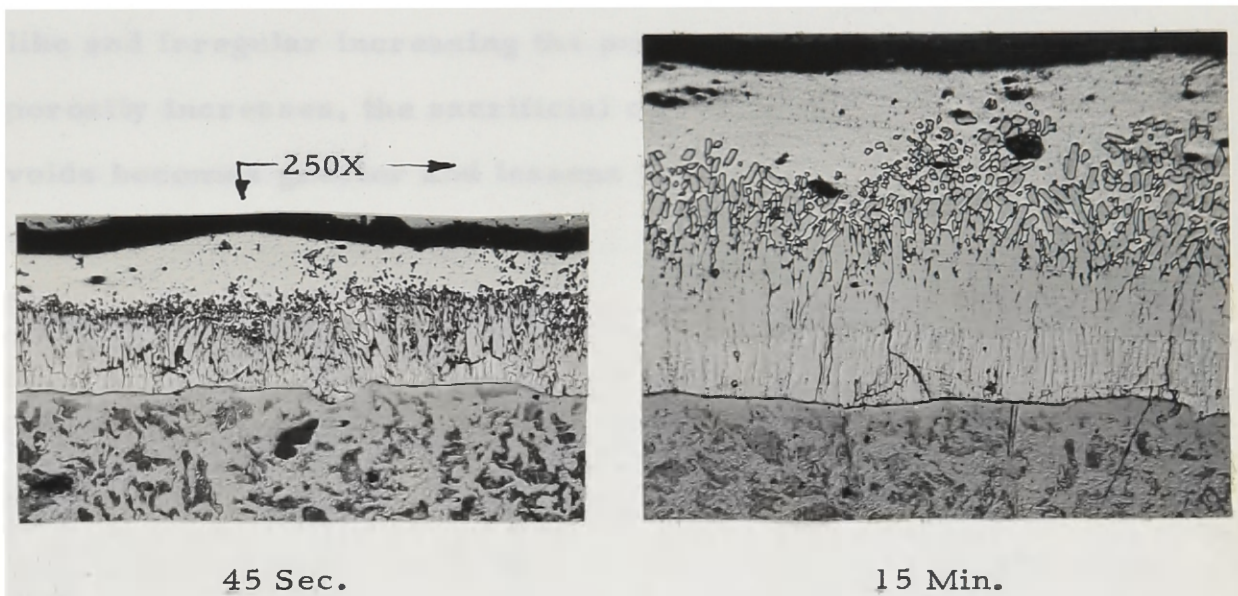
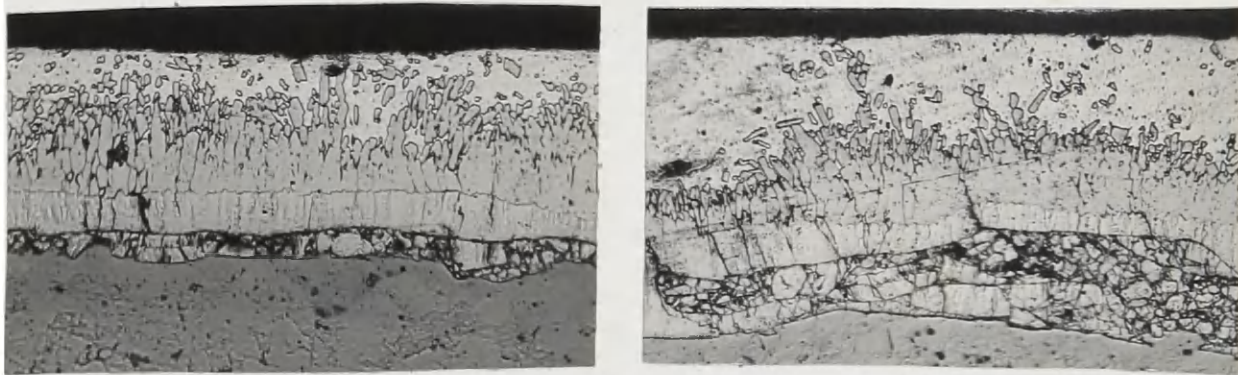


Fig. 3



Breaking away of base layer on long submersion

Fig. 3a

It is recognized that the very nature of applying zinc by the hot-dip method due to the alloying action of zinc and iron produces a denser coating than in any other form of zinc application.

This density is an added protection against corrosion and gives greater life since it slows down the sacrificial requirement of the zinc to protect the iron.

As the alloy growth is allowed to continue after its normal original growth the compact vertical crystals become more tree-like and irregular increasing the porosity of the coat. As this porosity increases, the sacrificial corrosion of the zinc to fill the voids becomes greater and lessens the effective advantage of this thicker coat.

Flexibility of Coating

Authorities indicate that for the usual galvanizing method it is mainly the thickness of the alloy layer which governs the flexibility of the coating.

We have found some indication, however, of the breaking up of the adherent alloy layer on 1/8" x 1" open hearth steel strips after submersion for 10 minutes in molten zinc at 850° F., air cooled.

This condition as shown in microsection, Fig. 3a, reduces the adherent quality of the coating and makes it more subject to flaking away to base metal under stress.

Although this condition is usually found from rapid cooling, this was not the case in these tests and the proportion of surface thus affected was comparatively small.

We must assume from subsequent tests that the condition as shown would be increased by either longer submersion or faster cooling.

In justice to the above statement a ten minute submersion with these light sections gives a relatively heavy alloy growth, the point being that the heavy alloy which decreases flexibility may be further handicapped by the breaking down of the adhesive layer.

DROSS

It is recognized in the industry that one of the major economies in hot dip galvanizing is obtained by reduction in dross formation.

It is paradoxical that the controls required in timing, temperature and cleanliness of work to control dross formation automatically improve the uniformity and quality of the galvanized work produced.

Or in reverse - controls required to produce a more uniform product of better quality tend to reduce the amount of dross formation.

The size, shape, method of heating of the kettle, type of production and installation details all affect the characteristics or personality of any selected galvanizing kettle.

In discussing this subject therefore any installation must be considered on its individual merits and any data acquired will only apply directly to the unit from which it was secured.

This data may be used in format and to some extent comparatively for use with other installations.

Accepting the data from a regular production schedule for a period of one year we find that by rearrangement we can graph a straight line of increasing production. A graph of dross formation is then superimposed on the same chart.

Both of these lines are extended by extrapolation to zero production.

At this point we find a dross production of 5500 pounds per month which represents the dissolution of iron from the sides of the kettle into molten zinc at 850° F.

Fig. 4 is taken from a chart prepared by E. Diegel of Julius Pintsch Corp.¹ This chart indicates the comparative solubility of iron in molten zinc at different temperatures within the range of 850° and 1000° F. for a particular steel. This curve will remain constant for the lower temperature with various steels but will vary considerably with the higher temperatures.

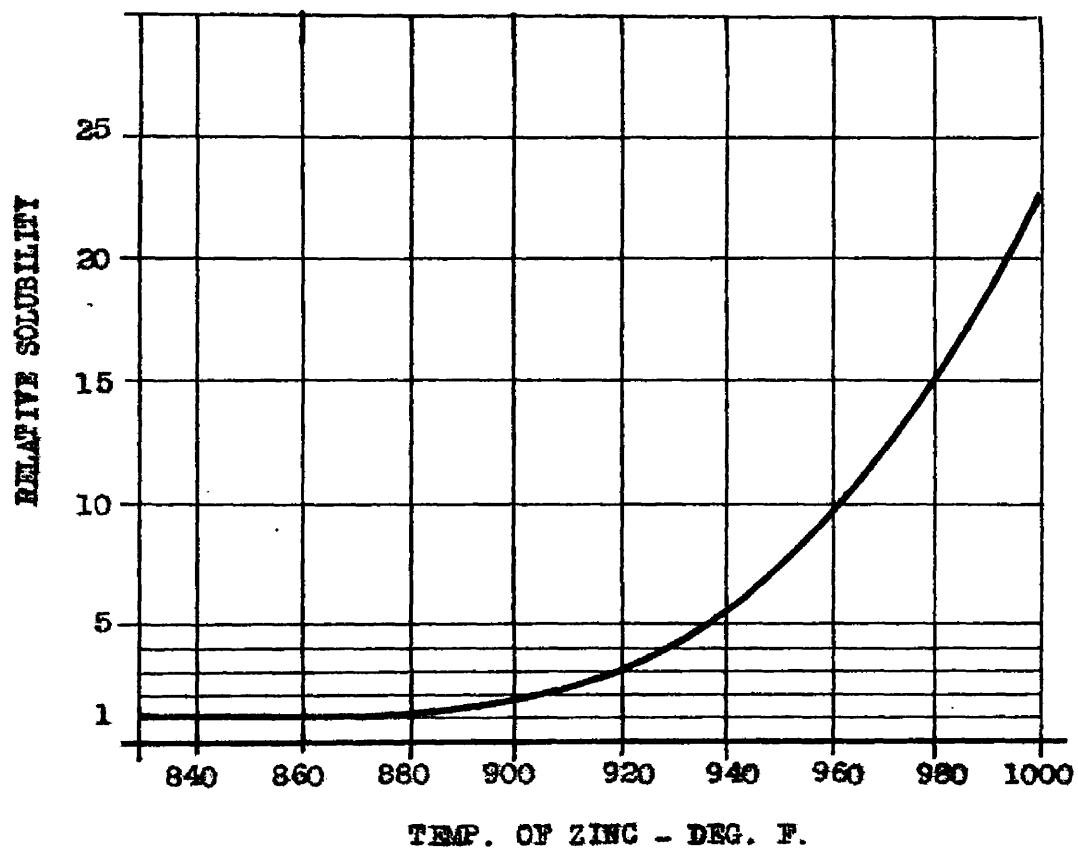
With the introduction of production into the kettle, two other major sources of dross are found. First the dross formed from the work itself which is generally in proportion to the work put through. Secondly, the additional dross formed from the sides of the kettle due to the increased heat input through the sides of the kettle to replace the heat absorbed by the work, the radiated heat from the top of the bath and the washing action of the molten zinc on the sides of the kettle during production.

Considering this second source from the kettle and referring to chart Fig. 4 it can be readily seen that the dross formation will increase by a rapidly accelerating curve with increased heat transmission through the sides of the kettle due to increased production of work. This curve with excessive production will rise so rapidly that it becomes incompatible with good economics through dross formation, handling and kettle life.

We have found that if the molten zinc is held at 850° F. by electrical control of the heating units a thermocouple placed close to the outer wall of the kettle will register 860° F. with no production. As production is increased this temperature will rise to about 1100° F. Since the production galvanizing is a periodic procedure

1 - Published in Zeitschrift Des Vereines Deutscher Ingenieure
May 1, 1915.

SOLUBILITY OF IRON IN ZINC



This curve will vary in the higher temperatures with steels of different analysis.

Fig. #4

this increase is fluctuating in nature and the average with definite production can only be estimated. This, however, gives us a reasonably close picture.

Since with no production the temperature of the air at the outside of the kettle is 860° F. and of the molten zinc is 850° F., the temperature of the inside of the kettle will average only a few degrees above the zinc temperature, say 852° F. At this temperature the additional alloying action of the steel kettle over normal standing corrosion can be considered negligible.

From this point we establish an area of increasing solubility of iron and zinc with increasing kettle wall temperature due to increasing production in keeping with the solubility curve in Fig. 4.

Subtracting area of dross for standing kettle and area of dross from kettle due to production from total dross formation, we have the area of dross from the production itself as shown in Fig. 5.

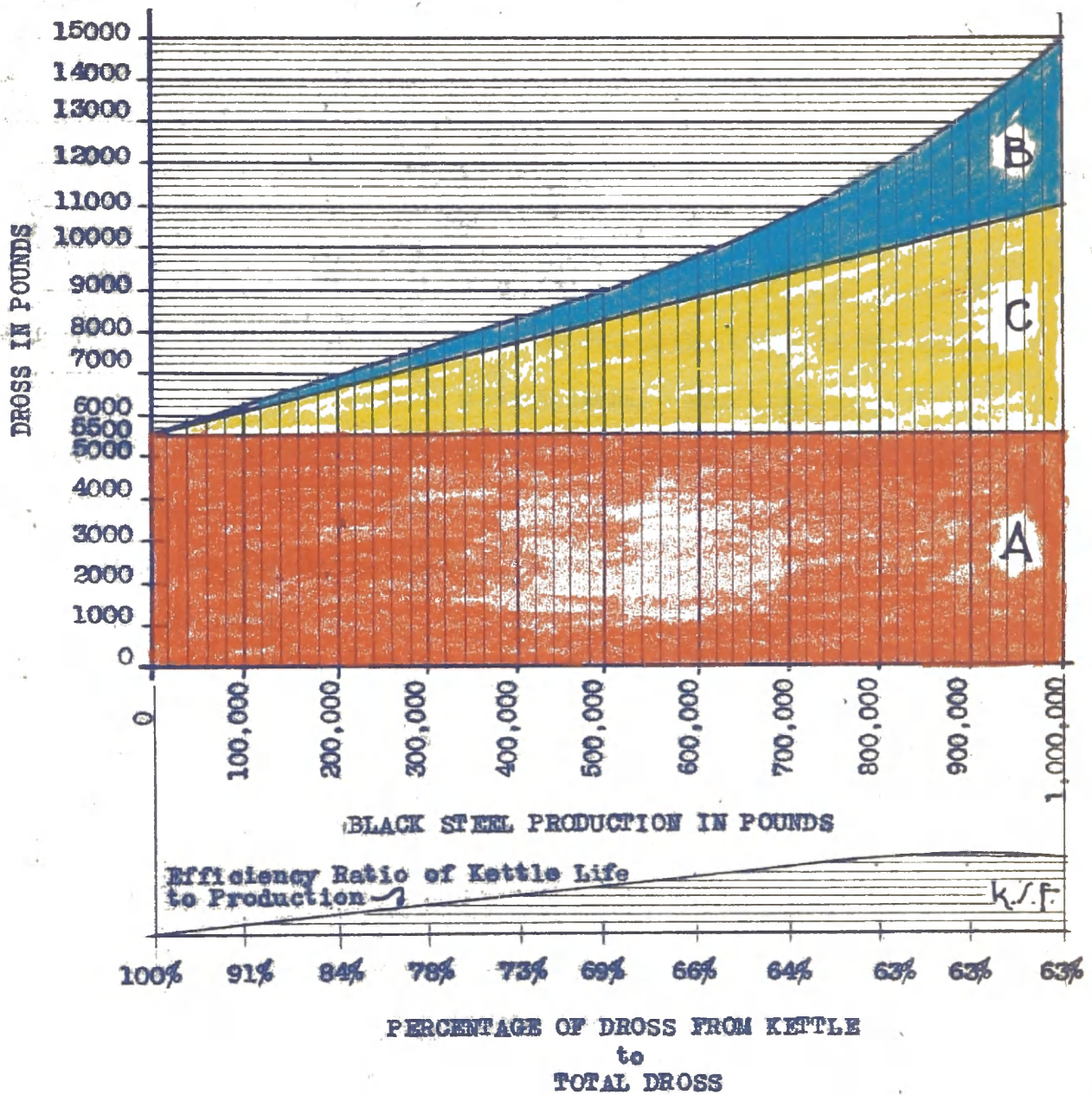
These areas of dross shown as A - for normal dross from the kettle, B - dross from the kettle due to production, and C - dross from production are subject to individual and combined consideration.

The area A must be considered mostly in the original design of equipment and when once established, dross from this source will be reasonably uniform throughout the life of the setting.

Mr. W. H. Spowers, Jr.,¹ has done considerable work in this field and finds that a ceramic non-alloying surface on the inside of the kettle eliminates dross from this area and in reducing contamination of the bath improves the quality of the work.

1 - President, Spowers Research Laboratories, New York.

DROSS BASED ON MONTH'S PRODUCTION



- A- [Orange Box] - NORMAL DROSS FROM KETTLE
- C- [Yellow Box] - DROSS FROM PRODUCTION
- B- [Blue Box] - DROSS FROM KETTLE DUE TO PROD.

Fig. 5

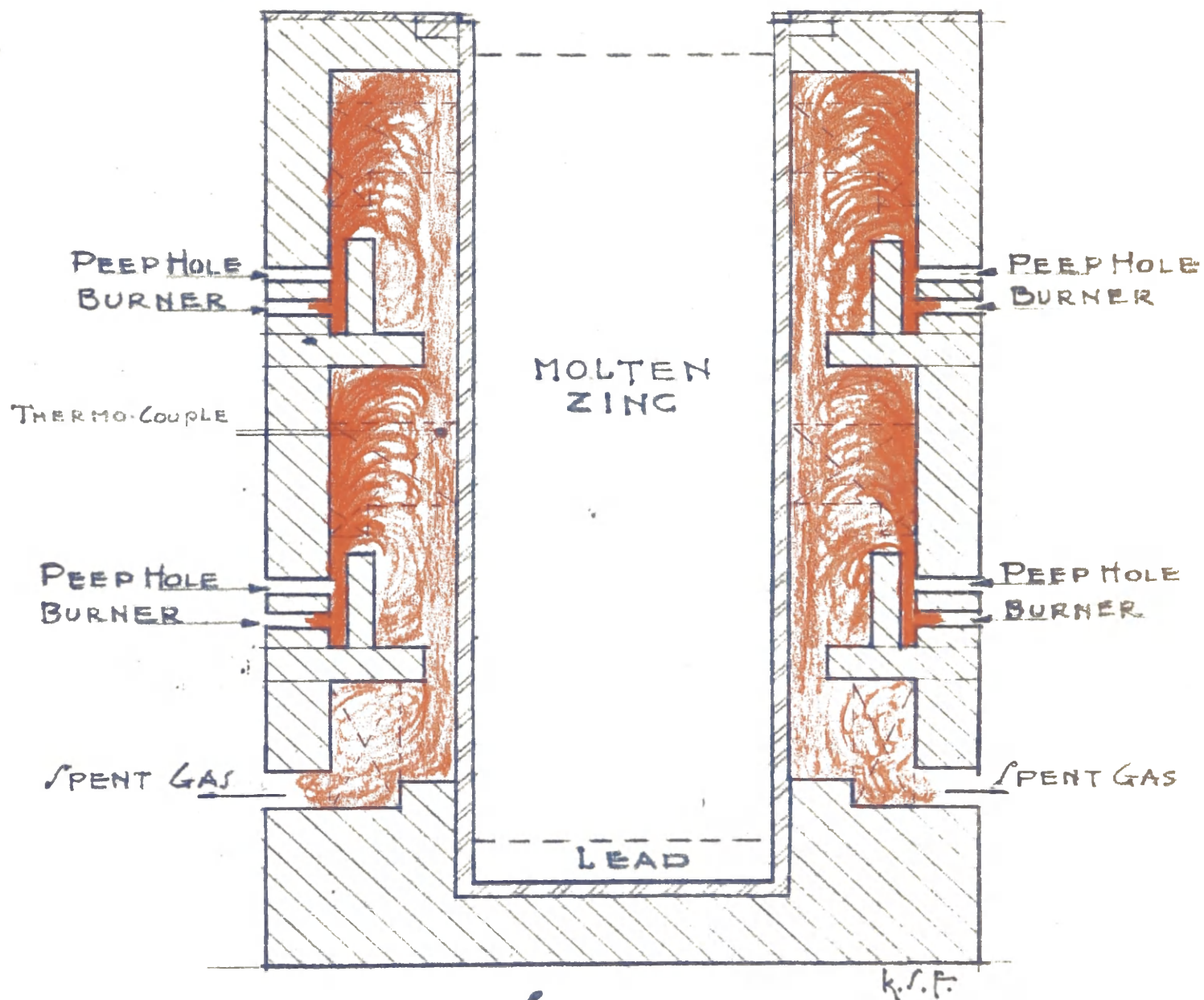
Certain difficulties in the application and maintenance of this ceramic lining have held it from universal acceptance in the industry but from the immediate standpoint of theory and possible future use it would seem to be a contribution of major importance.

Uniform heating of the heat transmission area of the kettle, see Fig. 6, minimum exposed surface radiation area of molten zinc and proper steel in the kettle itself all contribute to low dross formation.

The area B is affected by the same consideration plus several more. The keeping of the work away from the sides of the kettle to minimize wash is mostly a design item. The control of production to remain below critical heat-replenishment to the bath and the holding of the work above the settled dross area all keep the zinc bath cleaner, tend to reduce dross formation, and allow for better quality work.

The area C of dross formation from the work depends on the preparation or cleanliness of the work, the speed of submersion and withdrawal, the length of time of submersion, and the cleanliness of the bath from suspended dross.

It is noted that the inside surface of the kettle is consistently hotter and therefore more soluble in zinc than the surface of the work being galvanized. This is not a desirable situation from the standpoint of dross formation, but would be much worse if it were not reduced by the following alloying action. An alloy crust forms on the inside surface of the kettle which if not washed or scraped away deters the alloying action, whereas work being galvanized continually presents a clean surface to the molten zinc for alloying,



SECTION
HOT DIP GALVANIZING KETTLE
Fig 6

most of which becomes a permanent part of the finished coating.

It is readily seen from the foregoing discussion that automatic controls of time and temperature, scheduled controls of production and bath analyzation all contribute to both the economy and quality of production.

The Kettle

Because of the comparatively heavy cost of replacing a burned out or dissipated kettle, kettle life has always been a subject for a great deal of study.

The composition of metal used, method of welding, annealing, construction of the setting and uniformity of heating are all design problems that should be given much thought.

Production schedules and methods, however, bear greatly on kettle life.

From Fig. 5 we find that with no production approximately 100% of dross formed comes from the inside surface of the kettle and with uniform heating the practical life of an idle kettle at maintained temperature of molten zinc could be calculated with considerable accuracy.

As production is increased the total dross increases, both from production and from the kettle, reducing the life of the kettle. The percentage of dross from the kettle to total dross reduces in this setting to only 63% with full production. This actually shortens the kettle life but increases the life in terms of tons of production.

At a certain point in the increase of production the transmission of heat through the kettle wall increases the solubility of this steel in zinc to a point where the increase in dross formation from the

kettle in percentage to total dross rises sharply, reducing again the kettle life in terms of production tonnage. This condition is known in the industry as "beating the pot."

We find then that either a low production or a high production in terms of the setting characteristics is not economical, and particularly in the high area tends to keep dross particles in suspension thus reducing the quality of the produced coating.

With careful analysis of any galvanizing setting and production requirements, and barring accidents, the kettle life can be closely anticipated.

EFFECT OF CHEMICAL TREATMENT ON CORROSION RESISTANCE OF GALVANIZED SURFACES

Phosphate Etch After Galvanizing

It is recognized from the results of many tests that the initial corrosion of a new zinc surface in moist atmosphere is comparatively rapid. However this initial corrosion or oxidation forms a surface that materially slows down the corrosion process.

Certain atmospheres have been found in England that do not allow this oxidized surface to form, in which case the dissipation of the entire zinc protection continues at a comparatively rapid rate.

It may be assumed that if the initial corrosion could be retarded effectively, considerable protection could be saved and the effective life of the coating lengthened.

Many organizations have worked to this end and their findings have been reviewed.

Even in the field of phosphate etching there are many variables to be considered in the exact formulation, pretreatment temperature requirements, submersion time, resultant appearance and end use of the product thus treated.

We will confine our findings to one set of conditions which are comparative and indicative of the value of this process.

For the purpose of our examinations, bars 1" x 1/8" x 16" were used. All bars were hot dip galvanized at 850° F. at the same submersion time.

Half of these bars were then dipped in a phosphate bath @ 170° for three minutes.

One-half of the galvanized bars and one-half of the galvanized,

phosphated bars were placed in a salt spray chamber in a 20% salt spray at 100° F. The remainder of the bars were placed in a humidity chamber at 100% humidity at 100° F.

At the end of each twenty-four hour period one bar each of galvanized, and galvanized phosphate-treated was drawn from each chamber.

Visual inspection of these bars was recorded and stripping showed the remaining weight of coating which was also recorded.

The results from this testing were definite and showed our earlier premise to be correct. See Fig. 7.

1. The slight phosphate etching and application of phosphate salts did not perceptibly reduce the original weight of coating.

2. The initial corrosion of the zinc coating of the galvanized bars was comparatively rapid.

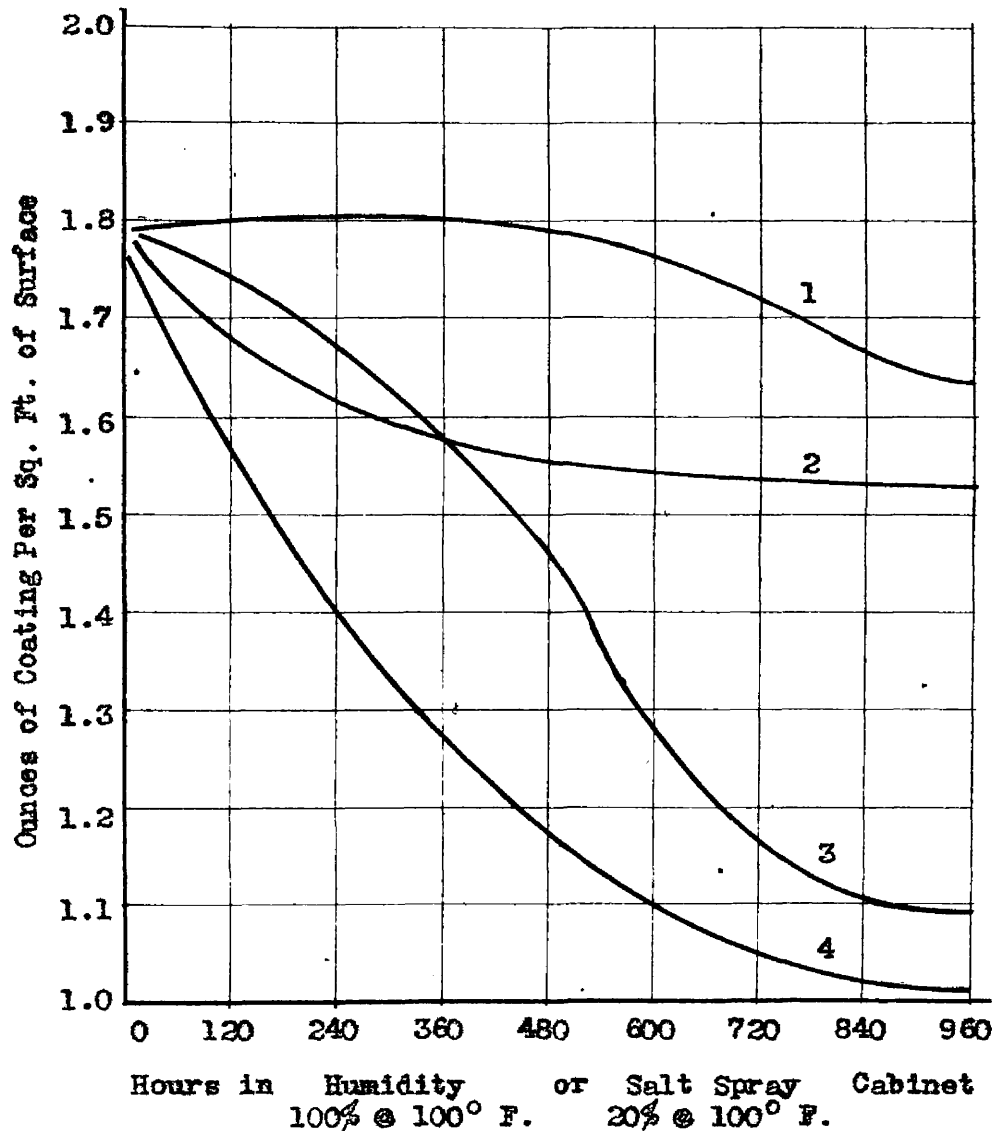
3. The initial corrosion of the surface on galvanized, phosphate-treated bars was retarded beyond the normal corrosion after oxide protection formation.

4. The normal corrosion rate after some three hundred hours in both chambers became uniform and parallel for both coatings.

5. In retarding the initial corrosion of zinc a protective thickness of coating approaching a recognized commercial electro-galvanized coating had been saved, comparably extending the anticipated life of the protection.

These tests were conducted in the laboratory test chambers and under the supervision of qualified technicians of a recognized

**COMPARATIVE CORROSION RATE OF PROTECTIVE COATINGS
UNDER ACCELERATED TESTING.**



HUMIDITY TEST

- 1 - Hot Dip Galvanized and Phosphate Treated
- 2 - Hot Dip Galvanized Only

SALT SPRAY TEST

- 3 - Hot Dip Galvanized and Phosphate Treated
- 4 - Hot Dip Galvanized Only

Fig. 7

surface protection organization¹ and checked in the laboratory of a galvanizer².

In addition to the corrosion retarding effect, properly compounded solution and temperature and time controlled phosphate treatment reduces the spangle or flowers of zinc to a uniform grey surface. It also provides an adhesive base for decorative paint and for glazing compounds which will not adhere to a new untreated zinc surface.

Subsequent tests of complete steel window units control galvanized and phosphate-treated have shown that in a 20% salt spray at 100° F. normal zinc oxidation or white rust is apparent up to about 200 hours representing the free zinc surface.

From 200 hours to approximately 800 hours through the zinc iron alloy growth discoloration becomes more apparent.

At approximately 800 hours red rust appears showing a complete but spotty breakdown of the coating to base metal.

Up to 1100 hours there is still sufficient zinc on the surface to stop any pit rusting through its characteristic sacrificial action.

Fig. 8 is a microsection of galvanizing modified to show the reducing action of salt spray indicating the long life of the treated zinc protection.

1 - Parker Rust Proof Company

2 - Detroit Steel Products Company

MATERIALS AND METHODS

Base Materials

In order to protect the many economic and quality advantages in controlled hot dip galvanizing, it becomes imperative that all phases of base materials and processes used in the preparation of this material for galvanizing be thoroughly investigated.

It is generally recognized that low-carbon open-hearth steels are most suitable for hot dip galvanizing. For control of uniformity in the acceptance of this coating even low-carbon steels vary to a considerable degree. Some of these variations show embrittlement of the base metal in the process while others produce a long rapid growth of noninter-adherent columnar zinc-iron alloy crystals with excessive porosity, which due to the iron content darken rapidly at the surface.

From research by many individuals in this field it can be logically assumed that the excessive nascent hydrogen intake of certain steels during the sulphuric-acid pickling is partly responsible for these conditions. The constant release of hydrogen from the steel through the forming zinc-iron alloy growth during submersion in molten zinc partly relieves embrittlement of base metal but creates unorthodox zinc-iron alloy growth.

Sample bars were selected for analysis as follows:

PROGRESSIVE CORROSIVE DISSIPATION OF
PHOSPHATE TREATED ZINC COATING
IN SALT SPRAY

Reconstructed from Test Data

(See Fig. 7)

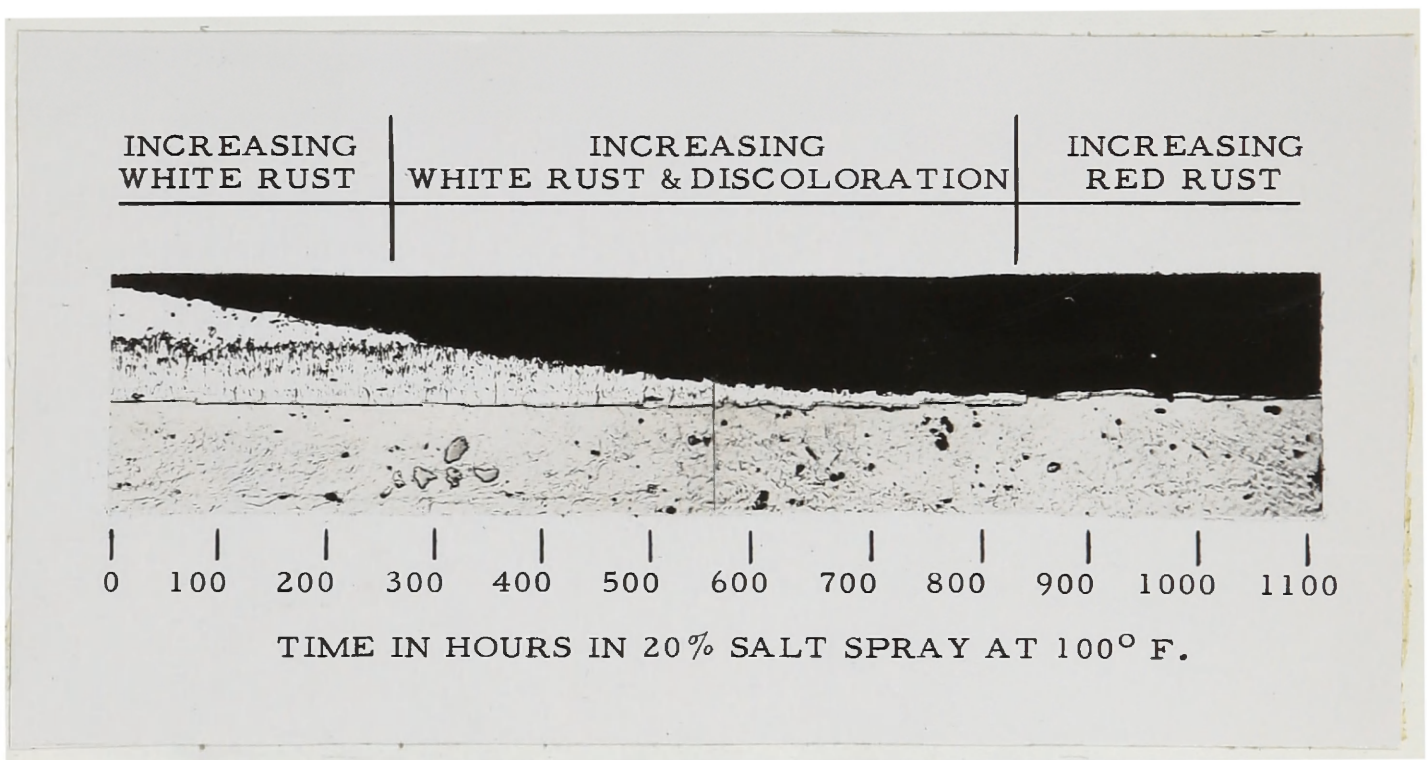


Fig. 8

1. Bars of good ductility and uniformly ductile coating.
2. Bars showing rapidly darkening surface.
3. Bars showing embrittlement.

The steel of these bars was analyzed and microsections photographed. Fig. 9.

In general the bars producing the best galvanizing without becoming brittle and showing a uniform surface of nearly pure zinc were of open hearth of .05 to .13 carbon, .040 phosphorus or less and silicon of .02 or less. Bessemer steel showing higher phosphorus to .09 showed considerable brittleness after galvanizing, resulting in broken bars under normal stress.

Bars with high silicon content to .09 showed strong attack by the zinc and an abnormal zinc-iron alloy growth with practically no free zinc acceptance on the surface. Due to the iron in the surface zinc and extreme porosity, this coating darkened rapidly with oxidation.

This itemizes only a few of the major requirements in steel for quality galvanizing but definitely indicates the need for continuous and careful analysis and testing in the selection of base metal.

Fabrication

Many factors should be considered in the fabrication of materials for hot dip galvanizing.

Cold upsetting or sharp bending tends to create internal stresses that brittelize in the galvanizing process.

Annealing of this work after forming or hot bending and hot pressure upsetting eliminates these internal stresses and minimizes rejects.

Arc welding with coated rods leaves a flux residue surface difficult to clean and one that will not be adherent to zinc if not cleaned. Wire brushing after welding improves this condition. Light coated or bare wire in welding leaves a surface that zinc will adhere to.

Pressure butt welding of oily bars burns the oil from the weld but impregnates it into the steel close to the weld.

Extensive experimenting shows that most caustic cleaning operations will not completely remove this impregnated oil and bare spots will occur in the galvanizing.

Cleaning with a suitable vapor degreaser such as trichlorethylene removes this impregnated oil effectively.

If thorough degreasing of all bars is done before welding this impregnation will not occur and the lesser cleaning mediums are sufficient.

Applied materials covering surfaces before galvanizing must be closely attached and tight fitting to prevent the holding of pickling acids and moisture. With this condition the zinc in galvanizing will completely seal the edges of the joined pieces and the closeness of the attaching will tend to eliminate warpage.

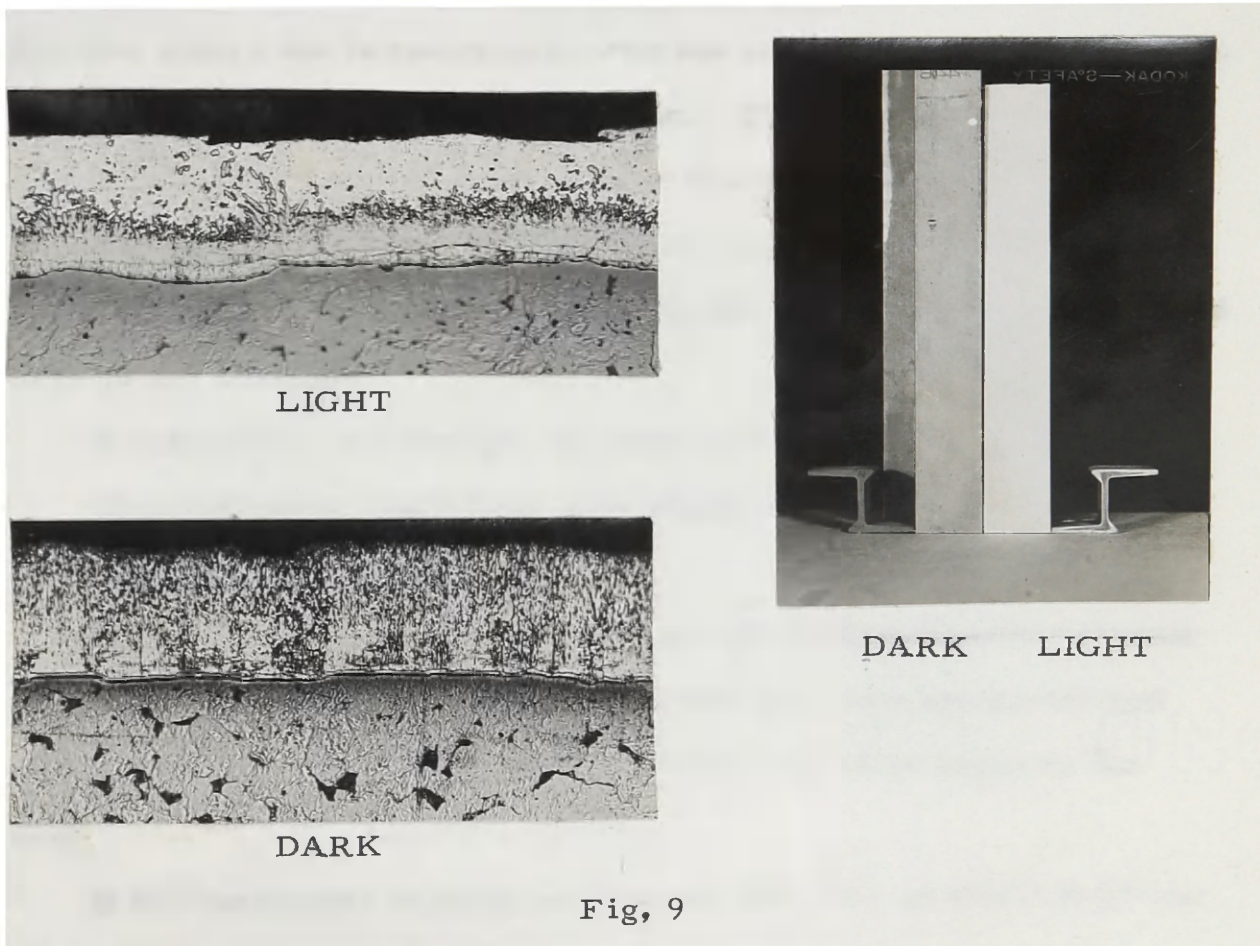
Hanging of the Work

It is quite obvious that hanging devices and the manner of the hanging of work to be hot dip galvanized is important.

The degree of this importance is borne out in repeated testing and defines itself in the results.

**STEEL CHARACTERISTIC AND APPEARANCE
AFTER HOT DIP GALVANIZING AND PHOSPHATE ETCHING**

Coating Base Metal	1 Light Ductile	2 Dark Ductile	3 Light Brittle	Desirable
Carbon	.07	.08	.04	0.05 - 0.13
Manganese	.38	.38	.33	
Phosphorus	.010	.010	.065	0.04 Max.
Sulphur	.040	.031	.041	0.02 Max.
Silicon	.02	.09	.01	
Chromium	.02	.02	None	
Copper	.11	.12		
Nickel	None	None	None	
Molybdenum	None	None	None	



In all of the cleaning baths proper drainage of the work tends to minimize the contamination caused by the liquid from one bath passing into the next.

This both aids in the economy and in the effectiveness of the process.

This correct drainage becomes imperative in the molten zinc bath since uniform protection depends on proper zinc flow as the work is withdrawn from the bath.

Many experiments indicate that in an open framework, no individual bar should have a slope of less than 30° to the horizontal for proper flow.

When work is ~~thus~~ hung and slowly and evenly withdrawn from the zinc, the flow of zinc takes place uniformly at the surface of the zinc where the temperature remains uniform and at about 60° F. above the melting temperature of zinc. The surface becomes stable from air cooling closely above this line.

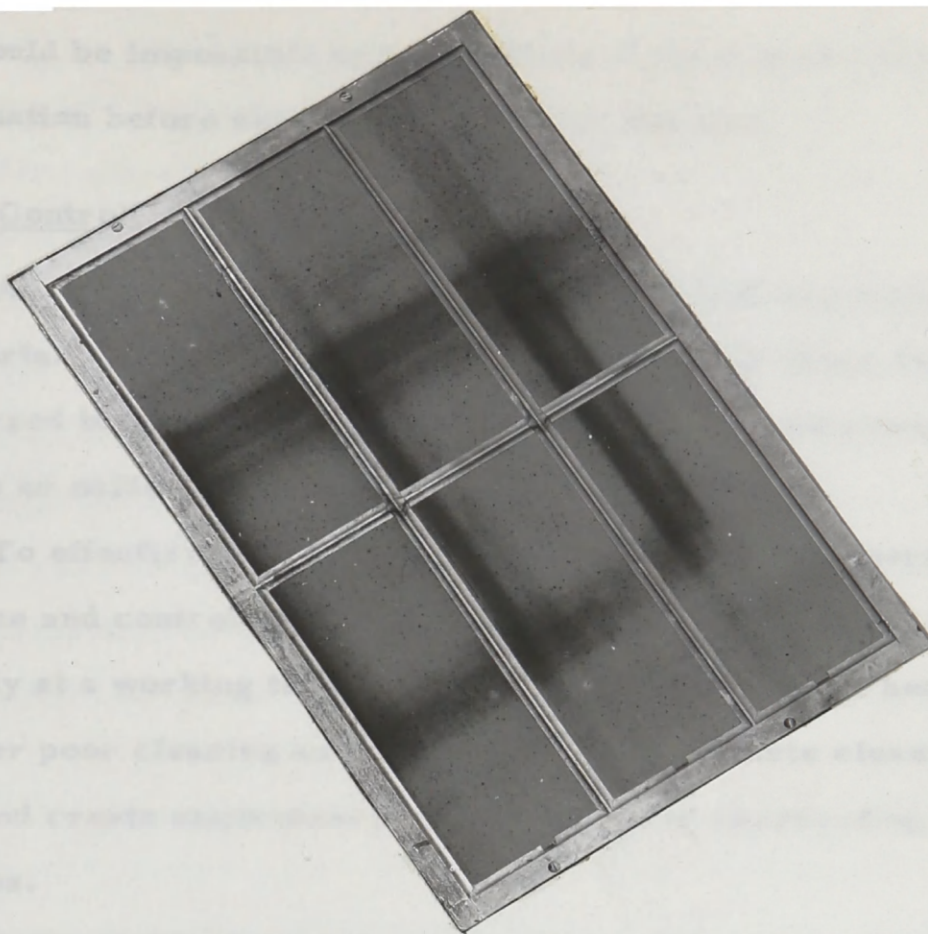
If the work is withdrawn quickly, it carries excess zinc well above the bath allowing chilling during the flow and causing runs and sags in the coating.

If withdrawn erratically, lap lines and ridges will be apparent.

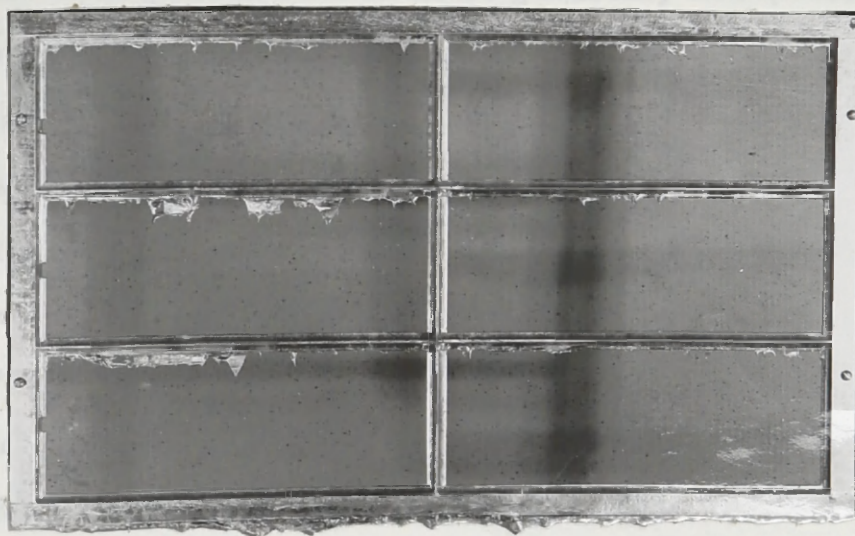
This indicates clearly the advantages of controlled mechanization.

Fig. 10 illustrates the extreme comparison of results between the hanging of a frame so that part of the bars are horizontal and with frames that are hung so that all bars are at an angle to the bath.

If the horizontal hanging were to be done in a production group,



PROPER HANGING



IMPROPER HANGING

Fig. 10

it would be impossible to fettle off all of the drip or stalactite formation before setting or freezing of the zinc.

The Controlled Process

As indicated before, the proper cleaning of materials is as important as any other phase of the work. The vapor degreasing referred to removes all oil and grease but does not remove dirt, scale or oxides.

To effectively and consistently do this work, temperature source and controls must be sufficient to keep the vapor in plentiful supply at a working temperature of 190°. Inadequate heat will render poor cleaning and excessive heat will waste cleaning materials and create unnecessary contamination of surrounding atmospheres.

In the pickling process for removing scale rust and oxides many acids and combinations of acids are used. For economy and close control sulphuric acid is most generally accepted.

With production work of a consistent nature, controls of temperature and time should be used for uniform work. Since this bath deteriorates by loss of acid concentration and pick up of iron, uniformity of pickling can only be obtained by scheduled analysis of the liquid with proper correction.

Increase of temperature of bath and/or increased concentration of acid, within limits, counters the retarding action of increased iron content.

For example, as the iron content increases with usage from 4% to 7%, the acid concentration may be increased from 8% to 10%. The temperature may be increased from 150° F. to 170° F. or time

of pickling may be increased. Beyond 7% iron content, it becomes economical to dump the bath and replenish it with fresh liquid. Shortly before dumping, acid percentage may be allowed to run down to say 4% for economy in neutralizing with lime.

Much above 150° F. the contamination of atmosphere from acid carried by released nascent hydrogen becomes a problem. Longer pickling time in a controlled system reduces the effectiveness of that system in production by idling other phases of the process.

It can be readily seen that close correlation of time, acid concentration, temperature, atmosphere contamination, balanced operation and operating costs are vital to both economy and quality.

Rinsing

As the work is removed from the pickle solution, acid and iron salts remain on the surface and must be thoroughly removed.

Hot water removes these more rapidly and thoroughly than cold and agitation assists materially. However, agitation holds this material in suspension and requires more water changes per hour.

At this point the base material is so thoroughly clean that short contact with the atmosphere will produce superficial red rust.

To alleviate this, one or two cold water rinses will reduce the material temperature retarding this tendency to rust at the same time insuring that all foreign materials are removed from the surface.

In order to protect this clean surface until it reaches the galvanizing kettle an immersion in a flux bath, usually zinc ammonium chloride, $\text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl}$, is provided for dry galvanizing or

in the case of wet galvanizing a flux foam blanket is built up directly on the molten zinc through which the work must pass.

In the dry process, the temperature of the flux bath and its concentration are relatively critical to quality galvanizing and here again rigid controls prove valuable.

Drying

Moisture carried from this bath into the zinc would cause steam spitting or explosions. A drying process before galvanizing is therefore required and it is found that fast moving air at about 150° F. does this effectively. Air below this temperature loses its economy and if above 180° F. tends to deteriorate the flux coating. Contamination of this air from fuel gases must be avoided.

When dry, the work will show a thin, shiny, brownish coat of flux protection which will oxidize or volatilize as it contacts the 850° F. molten zinc. We are then, in a controlled process, assured that work reaches the zinc clean and that good coverage and proper adhesion will be attained.

COMPARATIVE ZINC COATINGS

SHERARDIZING

In this process, the articles, after being thoroughly cleaned by pickling and sand blasting are placed in a metal drum together with zinc dust, heated to 500 to 600° F. and the drum rotated.

The resultant coating is about 90% zinc and 10% iron with a melting point of about 1260° F. and although it is highly resistant to corrosion develops a reddish or brownish color from the heavy iron content.

The system itself limits its use to hardware and other relatively small items.

The term electro-sherardizing merely relates to the method of heating the drum.

Coating weight is a function of time but becomes uneven in heavier coats.

ELECTROGALVANIZING

In this process the articles to be plated are usually placed in baskets and act as the cathode in the reaction. The anode used is metallic zinc. Both acid sulphate and cyanide baths are used and additional materials are added to obtain bright surfaces.

The high ductility of the pure zinc surface applied is its outstanding feature. For this reason it is successfully used in the coating of wire and is now being used in the plating of sheet steel. Coating weight is up to 0.2 oz. per square foot of surface beyond which the process is not economical and much thinner coatings are the usual practice.

ZINC SPRAYING

In this process zinc wire or powder is fed at a controlled rate into the flame of any oxy-gas or oxy-acetylene torch. The impingement of this atomized metal on a prepared surface produces a layer of flat interlocked particles which are mechanically bonded to the surface being coated.

The weight of coating is merely a function of the amount applied but is comparatively porous.

The coat because of this porosity makes an excellent paint base and is used effectively in repair surfacing of fixed items such as the inside surface of stationary tanks.

GALVANNEALING

A modified hot dip process where work is preheated by gas pickling or drawing through hot lead in lower portion of zinc bath and/or flame annealed and/or carried through furnaces up to 1200° so that total coating becomes zinc-iron alloy with excellent corrosion resistant properties.

Variations: Zenzimir Process, Sharon Process, etc.

HOT DIP

Wet Process

Cleaned material is immersed through a blanket of flux foam into molten zinc at temperature of approximately 850° F., allowed to come to the temperature of the bath and slowly withdrawn after flux blanket is skimmed back.

Dry Process

Cleaned material is dipped in liquid flux (Zn , $3\text{NH}_4\text{Cl}$), dried

and immersed in skimmed molten zinc bath at approximately 850° F., allowed to come to the temperature of the bath and slowly withdrawn.

Hot dip galvanizing produces a zinc-iron alloy coating with a corrosion-resisting vertical crystalline structure formed by an electro-chemical action during submersion. This alloy coating is covered with a ductile, smooth, flat crystalline nearly pure zinc coating as it is withdrawn from the zinc bath.

Surface crystal formation (spangle) can be amplified and brittlized for appearance with the use of small amounts of tin or antimony in the bath. On the other hand this formation can be enlarged, subdued in appearance and refined with the use of a small amount of aluminum in the bath.

COMPARISON CHART

Process	Usual Thickness Per Sq. Ft. of Surface	Coating	Comparative Corrosion Resistance Per Unit Thickness	Characteristics	Use
SHERARD-IZING	Varies with time to 2 oz., .0034"	10% Fe	Good	Turns brownish or dark	Small parts
ELECTRO-GALVANIZING	Varies with time to 0.2 oz., .0003"	Pure Zn	Fair	Ductile and even	Small parts wire, sheets
ZINC SPRAY-ING	Uneven to any weight	Pure Zn	Fair	Porous and uneven	Repair work and structures
GALV-ANNEAL-ING	to 0.375 oz. .0006"	ZnFe Alloy	Excellent	Ductile with oxidized finish	Sheets and strip
HOT DIP	to 2 oz. .0034"	1/3 to 1/2 ZnFe Alloy plus 2/3 to 1/2 Pure Zn	Good	Reasonable ductile and bright	All purpose for maximum protection

SUMMARY

To insure that any galvanizing system is both economical and capable of producing a uniform quality product many things must be considered.

1. All equipment must be studied and designed to facilitate the handling of the product or products to be galvanized.

2. Complete provision for the control of the movement of this material through the system is essential.

3. Ample provision for the complete cleaning of all base metal of all paint, grease, oil, rust, scale and dirt is of primary importance.

4. Adequate flux protection by predipping or flux blanket must be maintained.

5. Complete and automatic timing and temperature controls produce uniformity.

6. Provision for scheduled laboratory analysis and control of all chemical and elements used in the process is important.

7. Controlled analysis of base metal to be galvanized is valuable.

8. Considered and controlled fabrication of base metal insures against rejects.

9. Additives in coating performance, such as phosphating, are desirable on many products.

10. Good housekeeping and continuous research testing for improvement in the mechanical, chemical and electro-chemical processes will improve quality and result in improved economy.