

INTERNATIONAL CONFERENCE  
ON  
HOT DIP GALVANIZING  
HELD AT  
COPENHAGEN 17-21 JULY 1950

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AN ACCOUNT OF THE PROCEEDINGS  
AT THE CONFERENCE WITH REVISED TEXTS  
OF THE PAPERS PRESENTED AND  
OF THE DISCUSSIONS ON THEM

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HOT DIP GALVANIZERS ASSOCIATION  
AN AFFILIATED MEMBER OF THE  
ZINC DEVELOPMENT ASSOCIATION  
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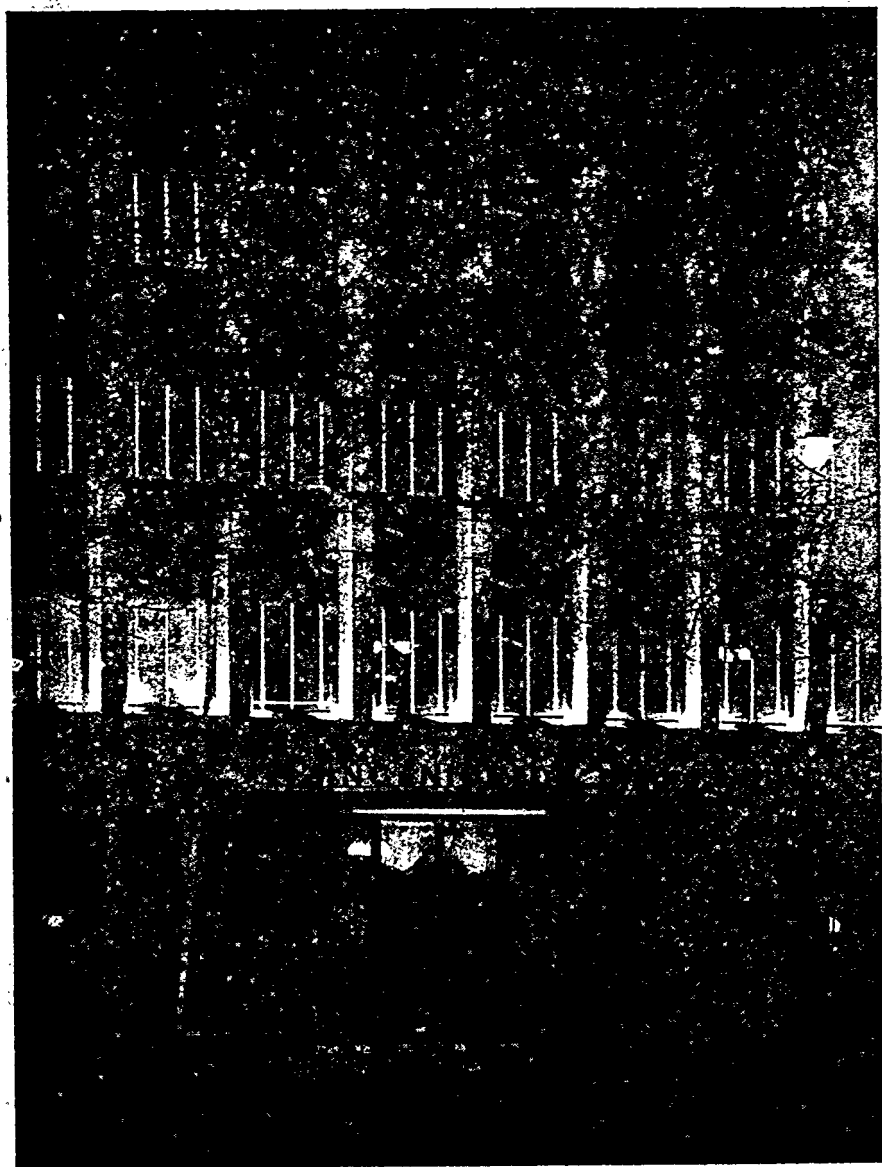
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Ingeniør Hus, Copenhagen

## PREFACE

*The first International Conference on Hot Dip Galvanizing was held under the auspices of the Hot Dip Galvanizers Association during July 1950, when more than 80 galvanizing experts from many parts of Europe met in Copenhagen to discuss the hot dip galvanizing process and the properties and uses of galvanized coatings.*

*The Hot Dip Galvanizers Association was founded early in 1949 by a group of U.K. general galvanizers as a non-trading organization affiliated to the Zinc Development Association, the well-known technical information bureau on all the uses of zinc. Membership grew rapidly, and at the time of the Conference comprised some 90 firms in the U.K. The new Association had the twin aims of increasing the use of hot dip galvanized coatings by the spread of information about their properties and uses, and of improving technical efficiency and working conditions throughout the industry, including work on reducing galvanizing costs. It was clear that the free exchange of technical information for the common good would be the best method of achieving these aims; and this has been the basic policy of the Association and its Members. Much work has already been done in this spirit, notably by technical surveys of the industry and the issue of technical publications. The principal object of the Association may perhaps be summed up as that of making its Members the best informed in the world. Its Council believes that this can only be done by creating a pool of knowledge to which all Members have already generously contributed.*

*Great interest in the work of the Hot Dip Galvanizers Association was shown by many friends of the Zinc Development Association in various parts of Europe and in the U.S., and it was the widespread desire to share in it by the exchange of information on galvanizing techniques which led the Hot Dip Galvanizers Association to call the Conference.*

*The organization of the Conference and all the arrangements connected with it were carried out by the Zinc Development Association which sent three representatives. The following two*

## PREFACE

*pages contain a full list of those who were present; and this list would have been considerably longer if travel difficulties or urgent affairs had not prevented the attendance of several people at the last moment.*

*Copenhagen was chosen for the meeting, not only as a convenient centre well provided with hotel accommodation, but because it was a city where the Zinc Development Association already had many friends among the Danish galvanizers. Special thanks are due to their hospitality and kindness in opening their works to the Conference members, as well as to the Institution of Danish Civil Engineers for putting its modern headquarters at the disposal of the Conference.*

*The Technical Sessions were held on four successive mornings in the beautifully appointed conference room of the Engineers House. Authors were given ten minutes in which to introduce themselves to the meeting and to review the main points in their papers likely to lead to discussion. One of the most noteworthy features of the Conference was the full attendance at all the Technical Sessions, and the liveliness and pertinence of the discussions. The success of the Conference is not, however, to be attributed solely to the quality of the papers or the discussions, although these have clearly contributed much to the store of information available to practical galvanizers and those working on related problems. A powerful factor was the meeting together of international experts in a friendly atmosphere which was of the greatest advantage not only to the Association but to all those who came to Copenhagen.*

*For the reader's convenience, and to make this Report a reference book of some permanent value, the account of the proceedings has been rearranged to fall into six chapters, each of which is divided into sections. The Contents pages show the general grouping of the subject matter, details of which are given in the Index. A few minor alterations have been made in the text of the papers, while that of the discussions has been carefully checked by the speakers themselves. Some contributions since made in writing have also been included, and where work already published was mentioned, the full reference has been added to the text.*

## List of those present

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\* Member of the Council of the Hot Dip Galvanizers Association

# INTERNATIONAL CONFERENCE ON HOT DIP GALVANIZING

## Chapter I

### FUNDAMENTAL ASPECTS OF HOT DIP GALVANIZING

Many remarkable improvements in the century-old galvanizing process have been introduced during the last ten years or so as a result of the fundamental research which has led to a fuller understanding of the process. It seemed therefore fitting that the first Technical Session should be devoted to consideration of the two research papers presented. Mr. F. C. Braby, Chairman of the Hot Dip Galvanizers Association, took the chair during the discussions which were mainly concerned with the effect of aluminium and other alloying elements in the molten zinc on the quality of the coating. Steel compositions were also considered in relation to the coating and to pot life.

#### Author's Introduction

MR. D. N. FAGG, of the British Non-Ferrous Metals Research Association, introduced the paper 'Twenty Years of Research for the Galvanizing Industry' by describing the close relationships which his Association had maintained with the galvanizing industry for the last 20 years, during which it had been continuously engaged in fundamental work on the mechanism of the reactions occurring in the galvanizing process. He thought that this work had made a substantial contribution towards the elucidation of galvanizing problems, and had established the relationships between many of the variables involved in galvanizing. From this fundamental background it had been possible to make recommendations which had led to substantial improvements in galvanizing practice.

Turning to the work described in the paper, he underlined some of the more important practical points which emerged from it. It was evident, he said, that the temperature of galvanizing was the most important single factor in determining pot life under the conditions usually met with in practice. Every effort should be made to ensure that at no place in the pot did the temperature exceed 480°C.

The paper also emphasized the importance of removing adhering iron salts from the surface of the work before immersion in the galvanizing bath, since for each part of iron carried into the bath in this way, approximately 25 parts of zinc were ultimately removed in the form of dross. The danger of iron salts being carried over from the pickling tanks was, he thought, fairly widely appreciated nowadays but there was not the same awareness that the drying operation which followed prefluxing could also be a serious source of iron salts if the drying temperature were not carefully controlled. Obviously there was little point in washing the work after pickling if large quantities of iron salts were produced by reaction between the flux and the steel during the drying of the flux coating.

In practice therefore the maximum drying temperature was determined not so much by the quality of the galvanized coating — since good coatings could

be produced even after drying at relatively high temperatures — but by the amount of iron salts produced. The temperature above which iron-salt formation became excessive, which was about 150°C. for a zinc ammonium chloride preflux, should therefore be regarded as the maximum permissible drying temperature.

## TWENTY YEARS OF RESEARCH FOR THE GALVANIZING INDUSTRY

by W. L. HALL,\* B.Sc., A.R.S.M., A.R.I.C., and D. N. FAGG,\* B.Met., A.I.M.

### Introduction

Twenty years ago, at the suggestion of a few British galvanizers, research on problems of the production and use of galvanized coatings was started by the British Non-Ferrous Metals Research Association. In the intervening years, much useful work has been completed and an increasing number of British galvanizers have joined the Research Association to support its efforts to increase our knowledge of galvanizing and galvanized coatings until, at the present time, among the 500 members there are some 65 firms directly interested in the production of galvanized coatings. It is these firms who have borne the main cost of the research aided by supplementary grants from the British Government.

Mr. F. C. Braby, the Chairman of the Hot Dip Galvanizers Association, was the chairman of the Association's first advisory committee for work on galvanizing and has maintained an active interest in all the efforts of the Association to improve our knowledge of the galvanizing process. The work reviewed in this paper owes much to Mr. Braby's interest and encouragement.

The research results of the B.N.F.M.R.A. are in the first place communicated to members in the form of confidential research reports but, after an appropriate period of confidential release, the results are subsequently published in the scientific and technical journals. In what follows, the main published results of the Association's work on the galvanizing process and on the resistance to corrosion of galvanized coatings are briefly summarized. It will be apparent that many of the changes in galvanizing practice which have taken place in the last ten or fifteen years are the direct outcome of the pioneer research carried out by the B.N.F.M.R.A.

An Appendix to the paper lists the references to published papers which should be consulted if more detailed information regarding the research work is desired.

Growing competition from new coating processes coupled with high running costs compared with pre-war conditions have compelled many galvanizers to seek ways of bringing the process under closer control, not only to reduce zinc losses, which frequently exceed 40 and 50 per cent of the total zinc consumption, but also to produce galvanized coatings with a combination of properties best suited to any particular service condition.

For example, according to the nature of the work, preference may be given to a coating having maximum corrosion resistance, or flexibility, or a bright surface appearance with perhaps a pronounced spangle.

The coating characteristics are decided by the galvanizing technique and the composition of the materials used, and a great deal of the work described in the published literature has been devoted to establishing the exact relation

\* British Non-Ferrous Metals Research Association.



between the many variables involved. The conclusions drawn from much of this work, however, particularly on the effect of compositional variations, are contradictory; failure to take all the existing variables into consideration is no doubt responsible for many of the apparent anomalies.

The need was apparent therefore for an investigation of a fundamental nature to establish the exact effect of the variables, both individually and collectively, and it was with this broad objective that the work described below was undertaken by the B.N.F.M.R.A.

## 1. Reaction between the Zinc and Steel

### The Effect of Temperature (1)

Specimens of mild steel sheet were stripped after galvanizing at various temperatures and the loss in weight determined.

The rate of loss in weight decreased progressively with the time provided that the temperature was below 480°C., the weight removed being roughly proportional to the square root of the time of immersion. Further increments in temperature brought about a marked change in the relationship, the rate of loss at 500°C. being substantially constant, so that the weight of steel dissolved was directly proportional to the time of immersion. The results are shown graphically in Fig. 1.

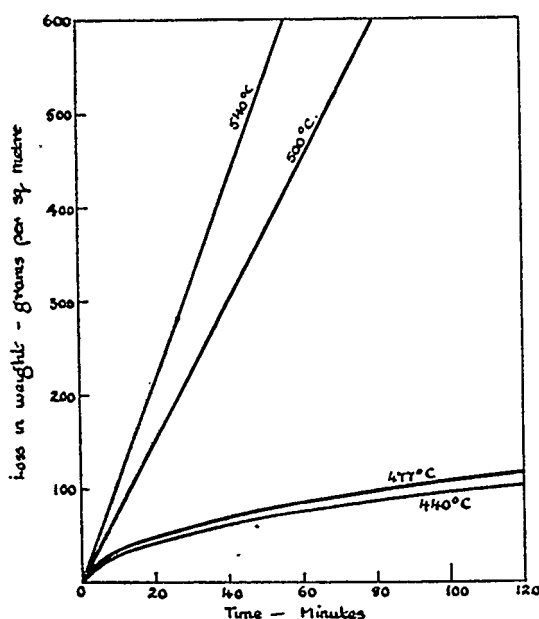


FIG. 1. Rate of attack of mild steel by molten zinc at different temperatures

It is interesting to observe what these results mean in terms of kettle wastage. At 500°C. the steel would be dissolved to a depth of  $\frac{1}{10}$  in. in two days, whereas at 477°C. the same amount of attack would necessitate seven years use. With such a drastic change in behaviour in a temperature range of about 20°C., the wide differences in pot life obtained in practice are scarcely surprising. To avoid premature pot failure, therefore, 480°C. may

be regarded as the maximum permissible temperature both locally and in the bath as a whole. Electrical heating or indirect heating by the products of solid or gaseous fuel combustion are preferable in this respect to direct coke-firing where hot spots are difficult to avoid.

As might be expected, the change in rate of attack is reflected in the microstructure of the coatings; the alloy layer has a uniform adherent structure when formed at temperatures below 480°C. but tends to break up into discontinuous non-adherent fragments when the temperature exceeds 500°C. The rate of attack on the steel in the first case is controlled by the speed at which the reacting ions diffuse across the alloy barrier, whereas in the second case, the zinc has free access to the basis steel and the reaction can proceed uninhibited. Between 480° and 500°C., the alloy layers are probably in a transition stage, and the rate of attack is observed to be greater than would be expected if the alloy layers were continuous.

### The Effect of Immersion Time and Rate of Withdrawal (2)

The total thickness of a coating and the amount of alloy layer present may be varied by adjusting the galvanizing conditions such as the temperature of the bath, the time of immersion and the rate of withdrawal.

The relationship between these factors was studied for three different temperatures, 435°, 455° and 475°C., with dipping times ranging from 0.5 to 10 minutes, and rates of withdrawal from 2.5 to 50 ft./min. The galvanizing bath was charged with high grade zinc to which approximately 1 per cent lead was added to simulate commercial practice. Variations in the weight of coating at temperatures of 435° and 475°C are shown graphically in Fig. 2. The curves for 455°C. were intermediate. The specimens were 24 S.W.G. steel sheet.

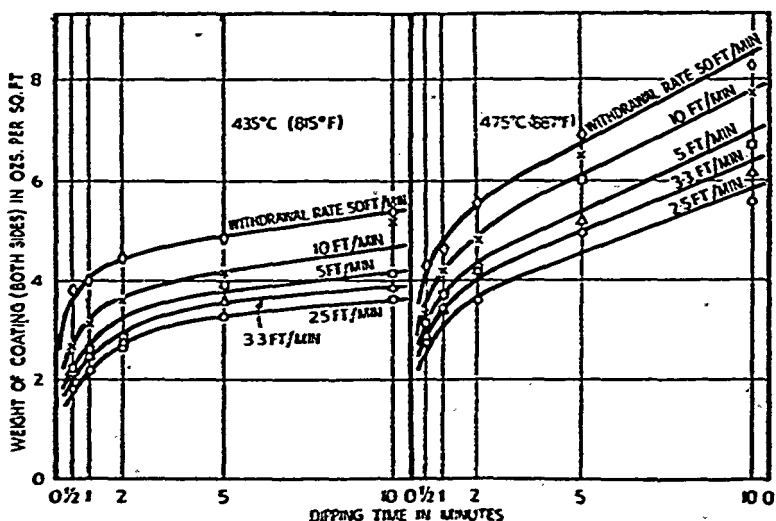


FIG. 2. Effect of galvanizing conditions on weight of coating

The thickest coating of 8.2 oz./sq. ft. (total of both sides of the sheet) was obtained at 475°C. with a dipping time of 10 minutes, and a withdrawal speed of 50 ft./min.; the thinnest coating was 1.8 oz./sq. ft., after dipping for  $\frac{1}{2}$  minute at 435°C. and withdrawing at 2.5 ft./min.

It will be seen that increasing the bath temperature, the rate of withdrawal and the dipping time all tend to produce heavier coatings. Within the range of immersion times normally used in practice, there is considerable scope for varying the coating thickness by adjusting the other two conditions.

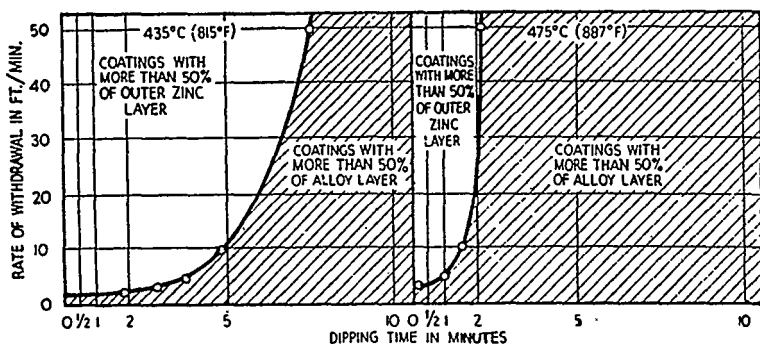


FIG. 3. Effect of galvanizing conditions on thickness of outer zinc layer and alloy layer

A micrographic determination of the amount of alloy layer present in the coatings indicated that increasing the galvanizing temperature makes it increasingly difficult to produce coatings containing less than 50 per cent alloy layer. This point is illustrated in Fig. 3 which shows that at 475°C. this condition cannot be met if the dipping time exceeds 2 minutes. On the other hand much greater latitude is gained by reducing the temperature to 435°C., the effect of long immersion times being more readily counteracted by increasing the rate of withdrawal.

Another important result found in this examination is that the thickness of the outer layer of a galvanized coating is, for a bath of given composition, almost entirely a function of the rate of withdrawal, the effect of dipping time and temperature being relatively slight.

### The Effect of Additions to the Galvanizing Bath (2)

Certain elements dissolved in the galvanizing bath exert a considerable influence on the characteristics of the coating.

Clearly no effective control of the galvanizing process is possible without knowing the exact effect of these elements, whether they are present as deliberate additions to the zinc or merely as incidental constituents of impure metal.

The effect of additions of aluminium, tin, antimony and cadmium, both singly and in combination with one another, have been studied. Throughout this work the galvanizing temperature was 460°C. and the dipping times were varied between  $\frac{1}{2}$  and 10 minutes.

**Aluminium.** The effect of aluminium on the properties of the coating and the attack on the basis steel was examined for additions of from 0.02 per cent to 2.5 per cent.

Attack on the steel, as indicated by the loss in weight of mild steel sheet specimens, decreased progressively with increasing aluminium contents for

# FUNDAMENTAL ASPECTS OF HOT DIP GALVANIZING

short time immersion up to about 2 minutes. Longer dipping time caused a marked increase in the rate of dissolution as is evident from the curves shown in Fig. 4.

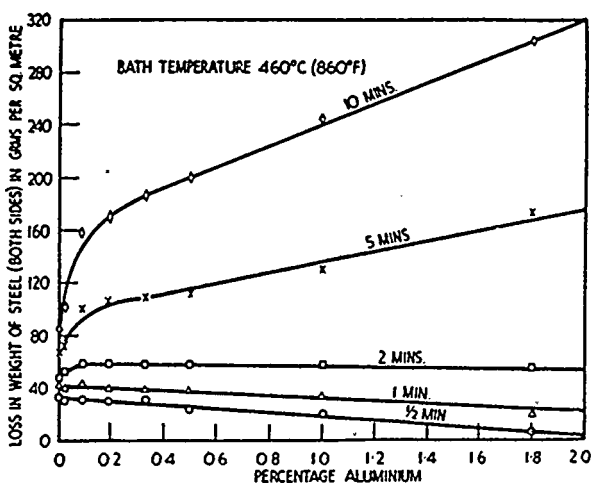


FIG. 4. Effect of aluminium on the attack on the steel base

Although these results suggest that aluminium is detrimental to the life of galvanizing pots, it should be remembered that the range of aluminium contents investigated in this work far exceeds that normally encountered in practice. Hence, any shortening of pot life from this cause is likely to be very slight.

The relationship between the aluminium content and the thickness of both coating and alloy layer is shown in Figs. 5 and 6.

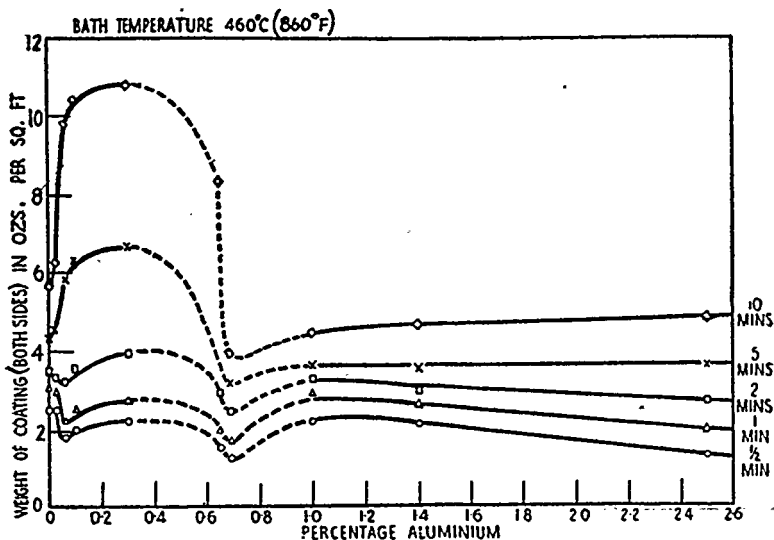


FIG. 5. Effect of aluminium on weight of coating

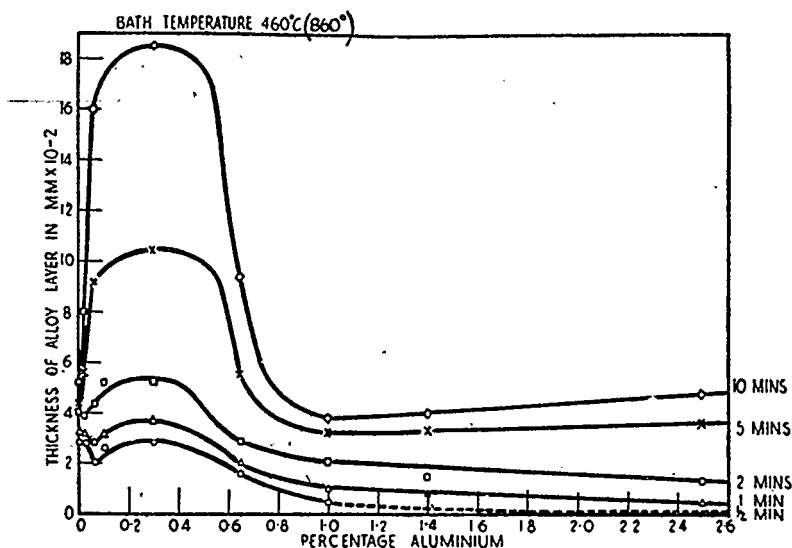


FIG. 6. Effect of aluminium on thickness of alloy layer

Aluminium additions up to 0.06 per cent produced a progressive reduction in coating thickness for short time immersion up to 2 minutes. Prolonging the time beyond 2 minutes, however, increased the thickness owing to the greater rate of attack on the steel referred to previously. The marked effect of larger aluminium additions between approximately 0.05 and 0.8 per cent even for comparatively short dipping times, is evident from the graphs.

The steep negative gradient of the curves at approximately 0.6 per cent aluminium marks a radical change in the structure of the alloy layer. The absence of a corresponding reduction in the rate of dissolution of the steel at this point suggests that the iron/zinc compounds continue to be produced but in a form which is readily detached from the surface of the work. Micrographic examination of the coatings supported this theory.

The minimum thickness of alloy layer was obtained with 1 per cent aluminium, the coating consisting of a thin compact layer of zinc with an almost imperceptible layer of alloy adjacent to the steel.

The aluminium concentrations required to produce the changes in coating structure described above may be modified by the presence of other elements in the galvanizing bath. The apparent discrepancies between this work and that carried out on the effect of aluminium additions by the British Iron and Steel Research Association and by other workers are probably explicable on this basis. Further experimental work is in progress to examine this point.

In practice the difficulty of galvanizing by the normal techniques in baths of high aluminium content precludes the use of as much as 1 per cent. The upper limit is normally decided by one of two considerations. In the first place a mere trace of aluminium of the order of 0.005 per cent may be added to enhance the smoothness and lustre of the coating without significantly affecting its structure and other properties. On the other hand, further additions up to 0.05 per cent aluminium may be used to reduce the thickness of the coating and the alloy layer. These aluminium concentrations, however, can only be worked successfully with special techniques. Galvanizing by the

wet process (with a molten flux cover on the bath) is impracticable if the aluminium exceeds about 0.01 per cent, due to a reaction between the chloride flux and the aluminium present in the zinc which reduces the efficiency of the flux and also removes the aluminium from the bath as volatile aluminium chloride. The alternative is to galvanize by the dry process involving pre-fluxing in a flux wash. By exercising reasonable care, it is possible by these means to produce satisfactory coatings with up to about 0.05 per cent aluminium in the bath, but above this concentration the coatings tend to develop black uncoated spots.

*Tin.* Tin is frequently a constituent of the bath when coatings with a pronounced spangle are required.

Up to 3 per cent tin was found to have little effect on the weight of coating except for the longer immersion times. A marked reduction in the flexibility of the coating was observed which was attributed to the embrittlement of the zinc layer by the tin and a slight increase in the thickness of the alloy layer. It was concluded, however, that the effect was not significant if the effective dipping time was kept below 1 minute.

*Aluminium and Tin Together.* The likelihood of improving the appearance of galvanized coatings by simultaneous additions of tin and aluminium suggested that an investigation of their combined effect on the properties of the coating would be of interest.

It was found that tin tended to counteract the effects previously observed for aluminium alone; thus the reduction in weight of coating produced by 0.05 per cent aluminium after short immersion times was neutralized by the addition of 1 per cent tin, smaller additions having a proportionate effect.

However, the presence of tin had little effect on the detachment of the alloy layer in the critical region of approximately 0.6 per cent aluminium, or for that matter, on the rate of attack on the steel base.

In short, tin may usefully be added to baths containing up to approximately 0.1 per cent aluminium in order to reduce the danger of heavy rough coatings that would otherwise form after long immersion times and to improve the appearance of the work.

*Antimony.* Antimony additions up to 1 per cent had no appreciable effect on the thickness of coating or rate of attack on the steel, but caused a marked reduction in the flexibility of the coatings, particularly after long dipping times.

Spangling was very pronounced with more than 0.25 per cent antimony, but the coatings developed a yellow stain, due presumably to oxidation, when the antimony exceeded 0.05 per cent.

*Antimony with Aluminium and Tin.* Antimony, like tin, had a neutralizing effect on aluminium additions, 1 per cent antimony sufficing to counteract 0.05 per cent aluminium. The adverse effect of antimony on the flexibility of the coating persisted even in the presence of aluminium, although the yellow surface staining was eradicated. A combination of 0.01 per cent antimony and 0.03 per cent aluminium yielded coatings having bright, well-defined spangles, and these coatings were further improved by the addition of 1 per cent of tin. Further increments in the antimony and aluminium, however, had no significant effect on the appearance.

The addition of antimony to the zinc when other elements are absent is not recommended, therefore, because of the danger of stained coatings. A suitable combination of antimony, tin and aluminium, as mentioned above, would benefit the appearance, but would also necessitate short dipping times to obviate excessive embrittlement of the coating by the antimony.

**Cadmium.** The addition of cadmium up to about 1 per cent was virtually without effect on the weight of coating and rate of attack on the basis steel, but both were considerably increased by further additions, a maximum occurring in the range of 2.5-2.8 per cent cadmium see (Figs. 7 and 8). Longer dipping times served to accentuate this effect.

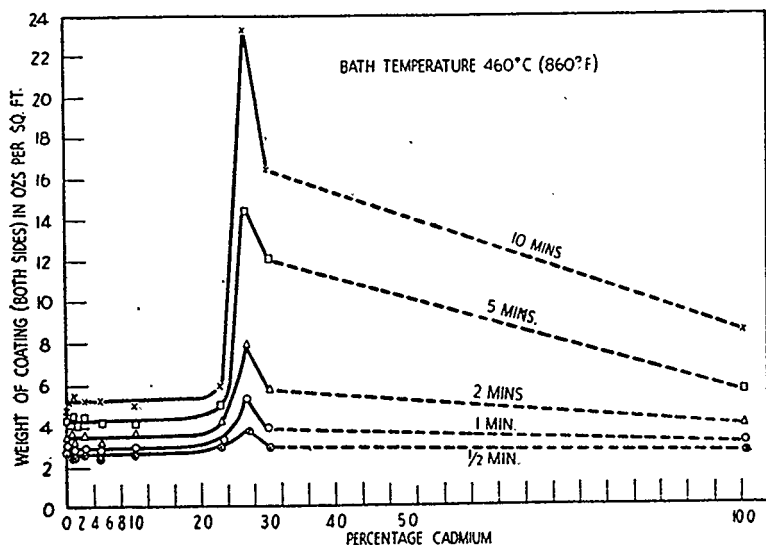


FIG. 7. Effect of cadmium on weight of coating

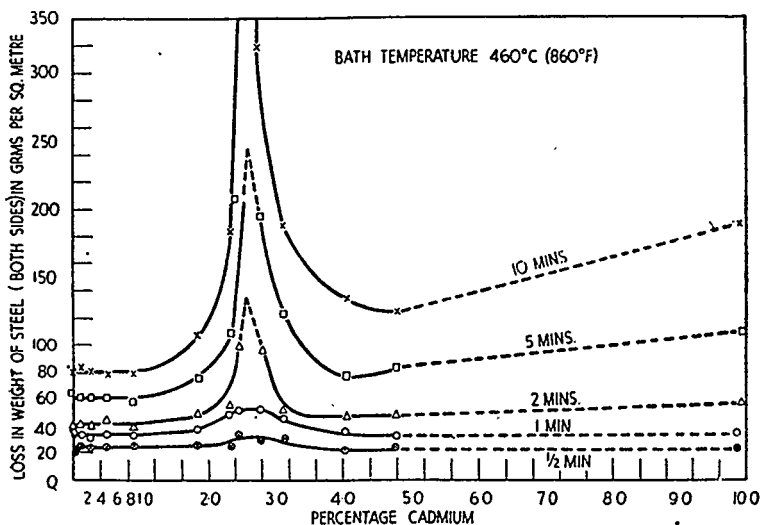


FIG. 8. Effect of cadmium on the attack on the steel base

Variations in the flexibility of the coatings followed the same trend as the attack on the steel; there was no effect for cadmium additions up to 1 per cent, but a reduction in the flexibility occurred in the range of 2.5-2.8 per cent due to the presence of increased alloy layer.

Spangling was evident in coatings produced in baths containing between 0.1 and 0.5 per cent cadmium, but with cadmium contents in the region of maximum attack the coatings became very dull and rough.

*Cadmium, with Aluminium, Antimony and Tin.* The influence of cadmium in the presence of aluminium was very similar to that already described for tin and antimony. 0.5 per cent cadmium appeared to neutralize the effect of 0.05 per cent aluminium, the two together producing smooth, very bright coatings with a sharp well-defined spangle. A further addition of 0.5 per cent tin caused no further improvement in the appearance of the coatings. There were indications that cadmium prevented the staining of coatings prepared in baths containing 0.25 per cent antimony.

### The Effect of the Basis Steel (2)

To complete the work on variations in the composition of the working materials, a brief study was made of the influence of various types of commercial iron and steel sheet on the weight of coating picked up and the rate of attack by the zinc. Five grades of cold rolled and close annealed sheet were investigated, having the analyses shown in Table I.

TABLE I

*Composition of Materials Used in Investigating the Effect of the Basis Metal*

Material	Carbon %	Silicon %	Sulphur %	Phos- phorus %	Manganese %	Copper %
Wrought iron	0.025	0.132	0.024	0.266	0.044	0.062
Ingot iron	0.030	trace	0.032	0.012	0.033	0.040
Rimmed basic open hearth steel	0.050	trace	0.034	0.008	0.297	0.154
Balanced basic open hearth steel	0.080	0.038	0.042	0.011	0.440	0.142
Copper-bearing balanced basic open hearth steel	0.090	0.038	0.037	0.012	0.033	0.372

Briefly, no significant differences were observed, in either the properties of the coatings or the rate of attack on the steel, which could not be explained by variations in the surface roughness of the original specimens.

These conclusions, however, are only applicable to materials having compositions within the range covered by the table. It is known for instance that the silicon content of the steel is very critical; 0.25 per cent has been found to give coatings more than twice the weight of those picked up by a normal steel under the same galvanizing conditions.

## II. Dross Formation

Dross or hard zinc consists essentially of zinc-iron alloys formed either from direct attack by the molten zinc on the work and on the walls of the galvanizing pot, or from iron salts produced in the pickling and/or fluxing



operations (see below) and carried into the bath on the surface of the work. The zinc-iron alloys are solid at the galvanizing temperature and carry with them a large amount of mechanically entangled zinc when removed from the galvanizing bath. Apart from the economic disadvantages of dross formation, there is also the danger that, with a galvanizing bath high in iron, the quality of the work will be impaired by dross entrapped in the coating.

It is evident from the previous results that provided the temperature of the bath is controlled below  $480^{\circ}\text{C}$ ., the amount of dross formed from direct attack by the zinc on the work and pot is small, since the alloy layers formed on the surface of the steel are strongly adherent.

The more probable sources of dross in practice are the iron salts carried into the bath on the surface of the work since these decompose in the presence of the zinc to form zinc/iron compounds.

By heating small quantities of zinc, zinc chloride and iron chloride together in a closed system at a temperature of  $475^{\circ}\text{C}$ ., it was possible to show by chemical analysis of the products that some of the iron had been displaced from the chloride and alloyed with the zinc. Micro-examination of this alloy revealed the presence of well defined crystals of zinc/iron compounds embedded in a matrix of zinc.

The rapidity of the zinc/iron chloride reaction was demonstrated by an experiment in which molten zinc ammonium chloride  $\text{ZnCl}_2 \cdot 2\text{NH}_4\text{Cl}$  was poured on to the surface of a sheet steel specimen carrying a globule of molten zinc. Under the action of the flux the drop spread out over a wide area with great rapidity and then remained steady. A microsection taken through the specimen after it had been cooled and washed showed, in addition to the normal alloy layers adjacent to the basis steel, an outer layer of comparatively pure zinc containing a large number of zinc/iron crystals. These were attributed to the reduction by metallic zinc of the iron chloride formed in the flux, the large number of crystals produced in such a short time indicating the rapidity of the decomposition.

### Iron Salts formed as Pickling Products (3)

In practice, considerable quantities of iron salts are often carried into the bath as dragout from the pickle tanks. The seriousness of this problem was demonstrated by some simple tests in which sheet specimens were pickled in a typical works pickling tank containing about 85 g./l. of iron and 130 g./l. of free hydrochloric acid, dried, and the adhering iron salts washed off and estimated chemically. The equivalent iron content was found to be sufficient to remove about one part of zinc as dross for every six parts usefully employed in coating the work.

Dross losses of this type may be minimized by washing the work after pickling and the efficiency of different washing treatments has been compared after pickling in hydrochloric acid and sulphuric acid solutions of various iron contents. The main results are summarized in Table II. Washing for 1 minute in running water removed almost all the iron salts remaining after hydrochloric acid pickling but was insufficient to remove more than a small proportion of those carried over from the sulphuric acid pickle, due, no doubt, to the smaller solubility of the sulphate. Thus with sulphuric acid pickling it is essential to wash off in hot water.

The beneficial effect of efficient washing in reducing the weight of iron carried into the galvanizing bath as pickling salts is evident in both cases.

TABLE II

*Iron remaining on Surface as Salts after various Pickling and Washing Treatments*

Pickling Treatment	Washing Treatment	Iron washed off as salts after pickling in acid solutions with following iron contents. gm/in <sup>2</sup> sheet surface			
		0%	5%	10%	15%
15 mins. in 20% HCl plus x% iron as FeCl <sub>2</sub> at 60-70°C.	'None' (Momentary dip in cold water)	0.07	0.13	—	0.43
	'Normal' (1 min. in beaker of running water)	0.02	0.01	—	0.02
	10 mins. boiling water	0.01	0.02	—	0.02
3 mins. in boiling 5% H <sub>2</sub> SO <sub>4</sub> plus x% iron as FeSO <sub>4</sub>	'None'	—	0.90	—	—
	'Normal' 10 mins. boiling water	0.03	0.09	0.13	0.15
	Scrubbed under tap	0.02	—	0.01	—
		—	0.03	—	—

**Dross Formation from the Action of the Flux (3)**

Despite efficient cleansing of the work by pickling, a thin surface oxide film reforms on the work on subsequent exposure to the atmosphere, especially during the short preheating which accompanies immersion into the molten zinc. It is by removing this film, together with the oxide present on the surface of the zinc bath, that the galvanizing flux performs its main function. In practice, the flux may also be required to rectify the results of careless pickling, or to rid the work of surface contamination which has proved insoluble in the acid solution. Hence the flux should be freely molten and also attain its maximum activity at the temperature of galvanizing so that efficient cleansing is achieved at the point where the work enters the bath.

A substantial proportion of the Association's early work on galvanizing was therefore devoted to a study of the reactions occurring between the flux and the metallic components of the system.

*Reactions Occurring in the Molten Flux.* In 'wet' galvanizing the pickled and washed articles are passed into the zinc bath through a layer of molten flux, built up, as a rule, by additions of ammonium chloride. Under galvanizing conditions, however, ammonium chloride is unstable and reacts with the zinc to form a zinc/ammonium chloride compound.

A measure of the efficiency of various molten fluxes was conveniently obtained by determining their solvent action on iron oxide, small quantities of ferric oxide and flux being heated together at 475°C., and the percentage of iron dissolved after various times determined. The reaction products were in some cases partially lost by evaporation.

As ammonium chloride is added to zinc chloride, the solvent power for iron oxide is increased until the composition corresponding to the double chloride ZnCl<sub>2</sub>.2NH<sub>4</sub>Cl is reached. The results are illustrated by Table III in which the superiority of the double chloride is readily apparent. Under the experimental conditions both the double chloride and zinc chloride give rise to free hydrochloric acid, the first by decomposition of the ammonium

TABLE III

*Solution of Ferric Oxide in Flux at 475°C.*

Time of heating (mins.)	Percentage of added Fe converted to chloride		
	ZnCl <sub>2</sub> .2NH <sub>4</sub> Cl	Commercial ZnCl <sub>2</sub>	Dried ZnCl <sub>2</sub> *
5	89.7	—	—
15	88.7	2.3	—
45	95.3	—	—
90	98.2	1.4	—
220	—	3.2	—
7100	—	—	0.05

\* Drying consisted of 70 hours at 150-210°C. in a stream of air dried by passage through CaCl<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>.

chloride, and the second by reaction with the water it contains; much the greater amount is produced by the zinc ammonium chloride. It would appear, therefore, that the activity of the flux depends on the amount of liberated hydrochloric acid, hence, dry zinc chloride and iron oxide would be expected to have little tendency to react together. This view is supported by the results in column three, which indicate that even after prolonged exposure the oxide was almost insoluble in zinc chloride that had been given a preliminary drying treatment at 150° to 210°C.

Apart from dissolving iron oxide, the molten flux also attacks the basis steel at a rate which is much greater for zinc ammonium chloride than for zinc chloride alone. Moreover, increasing the ammonium chloride content of zinc ammonium chloride from approximately 5 to 17 per cent increased the rate of attack on steel at 475°C. from about 3 to 40 times that of zinc at the same temperature.

The reaction products between the molten flux and the iron oxides and steel are chlorides of iron which, as already described, decompose in the zinc bath to form dross.

*Pre-Fluxing.* In the 'dry' galvanizing process there is no flux blanket on the zinc bath, but by a preliminary dipping treatment the work is coated with a thin layer of flux. The pickled and washed work is immersed in an aqueous solution of flux and dried in an oven or over the galvanizing bath. The flux coating so formed is required to fulfil two purposes, firstly to protect the surface of the steel from contact with the atmosphere and further oxidation, secondly to ensure that sufficient active flux is carried over to the galvanizing bath to rid the zinc of oxide at the point of entry into the bath and effect any final cleaning of the work that may be necessary.

The extent to which these objects are achieved with a given flux depends to a considerable extent on the temperature at which the work is dried.

During the drying operation a reaction occurs between the flux and steel base, giving rise to iron chloride or, if the temperature is too high or the treatment sufficiently prolonged, to oxides of iron. The re-formation of oxide is accompanied by a progressive reduction in the amount of flux left to remove it on immersion in the bath. For these reasons there is a maximum temperature at which a given flux may be 'dried off' consistent with a perfect coating.

TABLE IV

*Formation of Iron Salts during drying of Zinc Ammonium Chloride Flux ( $\text{ZnCl}_2 \cdot 2\text{NH}_4\text{Cl}$ )  
(Reported as g. Fe per square metre of sheet surface)*

Time (mins.)	Drying Temperature °C.			
	150	200	250	300
2	—	—	—	1.16
4	—	—	—	3.87
5	0.17	0.65	0.67	—
10	0.25	—	2.15	4.39
20	0.40	0.97	1.31*	—
40	0.44	0.97	0.99*	—

\* Decrease due to increasing formation of iron oxide

The drying temperature is further limited by the necessity to prevent the formation of excessive quantities of iron salts which react to produce dross when the work is subsequently immersed in the galvanizing bath. Table IV shows the amount of iron salts removed from specimens prefluxed in a zinc ammonium chloride solution and dried under various conditions of time and temperature. There is a marked increase in the amount produced when the temperature is increased above approximately 150°C.

### Recommendations to Limit Dross Formation

As described above, dross may be produced in two ways:

- By direct reaction between the molten zinc and the work or galvanizing kettle.
- By decomposition of the iron salts either carried into the bath on the surface of the work from the pickling or flux drying operations, or produced at the moment of galvanizing by direct attack of the molten flux on the work.

Provided that the temperature of the galvanizing bath is maintained below 480°C., the amount of dross produced in the first category is small. In the second category, the production of a certain amount of dross during galvanizing, due to the fluxing reaction, is inherent in both 'wet' and 'dry' galvanizing processes and therefore unavoidable, but it is evident that the dross produced from iron salts carried over from the earlier operations may be reduced to a minimum by suitable pre-treatments. After pickling, the work should be rid of adhering pickling products by washing in water; cold running water is adequate after hydrochloric acid pickling, but hot water is recommended after pickling in sulphuric acid. Where the work is prefluxed, care must be taken in the subsequent drying treatment to prevent excessive reaction between the flux and work with the formation of iron salts; the temperature should be as low as possible consistent with a drying rate fast enough to maintain production.

## III. Corrosion Resistance of Galvanized Coatings

Concurrently with the work on the hot dip galvanizing process, an extensive investigation was made into the behaviour of galvanized steel coatings on exposure to various corrosive environments, with particular reference to the conditions existing in hot and cold water systems.

Since the corrosion of galvanized coatings is to be discussed by Mr. E. F. Pellowe in a separate paper to this conference only a brief summary will be given here of the main results emerging from the work done by the B.N.F.M.R.A.

### Testing of Zinc Coatings

The normal chemical methods for evaluating the quality of galvanized coatings in terms of coating thickness suffer from certain limitations which prompted the Association to develop a new test (4) for the purpose. This was a stripping test to measure the weight of coating by dissolving it off in an electrolytic cell. By suitable adjustment of the test procedure information can also be gained about the proportion of alloy layer in the coating. Subsequently a comprehensive review (5) was made of the existing methods for testing zinc coatings.

### Corrosion of Galvanized Coatings by Water

*Water Containing Free Carbon Dioxide* (6). Corrosion of galvanized steel by hot and cold water is generally increased by increasing the original free carbon dioxide content of the water owing to the formation of corrosion products of increasing solubility. In cold water containing free carbon dioxide the zinc was found to dissolve at a uniform rate. It is recommended that in practice the cold supply water should be maintained with a reasonable degree of hardness and a free carbon dioxide content as low as possible (preferably below 5 parts/million).

In hot water, corrosion is usually of the pitting type, the severity of which is increased by the presence of free carbon dioxide and reaches a maximum at a concentration of approximately 5.5 parts/million.

*Hot Waters* (7). One of the advantages of galvanizing over other types of protective treatment for steel is that under normal conditions of exposure the zinc is anodic to the steel and tends to give sacrificial protection for a time at any discontinuities in the coating. It is known, however, that under certain conditions, e.g. on immersion in hot supply waters, the polarity of the zinc and steel can be reversed; this is usually accompanied by a severe and highly localized pitting type of corrosion.

The electrochemical relationship between the steel and the zinc and alloy layers of the coating was studied for immersion in a number of aqueous media at various temperatures. The results have enabled a general theory for the hot-water corrosion of zinc coatings to be developed.

The change in polarity of the zinc and steel occurred in distilled water and in a number of solutions including a hard supply water, provided that sufficient dissolved oxygen was present. In most cases, it was also necessary for the temperature to be higher than about 60°C., although it was shown that under certain conditions the reversal could occur at lower temperatures. The reversal was attributed more to the ennoblement of the zinc than to any change in the potential of the steel and was associated with a change in the composition of the surface film from zinc hydroxide to zinc oxide.

Pitting corrosion is due to attack being concentrated at small anodic areas present in a relatively large cathodic surface. In soft supply waters this is likely to lead to rapid penetration of the galvanized coating and, because of the change in polarity, to severe attack on the underlying steel

leading to complete penetration. In hard supply waters the attack may be stifled by the deposition of a protective scale from the mineral constituents of the water although continued exposure to high temperatures in the early stages of immersion may cause failure of the galvanized steel before the scale has been built up. It was shown that by moderating the heating conditions at first to allow a scale coating to develop, the corrosion resistance of galvanized coatings is considerably enhanced on subsequent continuous immersion at high temperatures.

The potential of the alloy layer of the coating is intermediate between zinc and steel on initial immersion but becomes more cathodic as time goes on, the change being especially rapid if the water is heated. The alloy layer remains cathodic to steel in aerated supply water whether hot or cold and is also much more cathodic than zinc under similar conditions.

*Water containing Dissolved Copper (8).* Although water systems containing both galvanized steel fittings and copper pipes or cylinders frequently give satisfactory service, a number of cases have been reported from various parts of England in which the galvanized fittings in such systems have failed prematurely; some of the failures have been investigated in detail by the B.N.F.M.R.A.

It was found that the deciding factor in these failures was the cuprosolvency of the water, a minute amount of copper being taken into solution and subsequently deposited on the surface of the galvanized steel, so setting up a number of short circuited electrochemical cells which caused accelerated corrosion of the zinc. As little as 0.1 parts copper/million parts water may be sufficient to cause rapid attack.

Thus the use of systems containing both galvanized steel and copper is only advisable with waters having a low degree of cuprosolvency. The amount of copper dissolved increases with the free carbon dioxide content of the water but decreases with the temporary hardness, and the cuprosolvency of a given water may therefore be considerably reduced where necessary by suitable treatment; e.g. for hard waters aeration is recommended to reduce the free carbon dioxide, while for soft waters lime additions serve the double purpose of increasing the temporary hardness and absorbing the free carbon dioxide.

### Atmospheric Corrosion of Galvanized Coatings

*Effect of Additions to the Galvanizing Bath.* Tests on specimens galvanized in baths containing various addition elements and subsequently exposed to an industrial atmosphere have shown that, under these conditions, the incorporation of one or more of the metals lead, tin, antimony, aluminium and cadmium in the coating, has in general very little effect on the life. Additions of up to 3 per cent Al, 3 per cent Sn, 1 per cent Sb and 10 per cent Cd were investigated, thereby providing a correlation with the work previously described on the effect of these elements on the structure of hot dipped coatings.

*White Rust Formation.* Recent work by the B.N.F.M.R.A. has established the conditions which promote white rusting including the effect of impurities in the environment, and recommendations are made for a simple and cheap dipping treatment to obviate the occurrence of white rusting during storage. Full details of his work will be published in the near future.

#### IV. Current Research

Another paper to be discussed during this conference makes reference to the efforts which the British galvanizing industry is making at the present time to improve the efficiency of its operations. Investigations now in progress at the B.N.F.M.R.A. are largely along lines designed to support this move of the industry. As always, the Association is offering to its members help in the application of existing knowledge and is studying, both in the laboratory and on a production scale, the factors affecting the formation of ash and dross in galvanizing. Methods for the treatment of zinc ash have been studied and as a result of laboratory experiments, supplemented by trials on an industrial scale, a method has been developed by which zinc can be economically reclaimed from galvanizer's ash using a minimum of equipment. About 75 per cent of the metallic zinc in the ash can be recovered and the monetary value of the ash is increased by about 150 per cent\*, excluding the cost of running the process.

As indicated above, a further examination of some of the effects of adding aluminium to the galvanizing bath is in hand. The effect of aluminium and iron on the structure of galvanized coatings is being studied and galvanizing trials under production conditions have been made of techniques by which it is possible to galvanize with up to 0.05 per cent aluminium in the galvanizing bath. The rate of removal of aluminium from the galvanizing bath by oxidation and by fluxing is also being investigated and further work is in hand to develop galvanizing fluxes having improved properties.

In all this work, close contact is maintained with the technical committee of the H.D.G.A. and with investigations on parallel lines in progress in the laboratories of the British Iron and Steel Research Association.

\* Based on prices in June, 1950

## Author's Introduction

MR. M. L. HUGHES, of the British Iron and Steel Research Association, then introduced his paper on the Influence of Aluminium on the Alloying Action in Hot Dip Galvanizing. The literature on hot dip galvanizing, he said, had grown appreciably in recent years, although there were still some obvious gaps, some uncertainty and not a few contradictions in it. He hoped that his short paper would help to fill a gap or to dispel some uncertainty.

As an example of what he meant by a gap he pointed to the small amount of experimental work on galvanizing which had been done with immersion times of less than 30 seconds. There was quite a lot of work at times up to one hour but, in sheet galvanizing at least, it was more important to know what happened during the first 5 to 15 seconds. This was particularly true when aluminium additions were considered, as Table I of the paper showed. This summarized experimental results on the effect of time and temperature.

The amount of aluminium required to eliminate alloy formation was one of the uncertain features referred to above, and was indeed a source of contradiction. The operating conditions were so important that it was difficult to accept a categorical statement that '.2 or .3 per cent aluminium prevents alloying' — or .8 per cent as someone else might recommend. Fig. 3 in the paper showed a coating with no alloy layer after 15 seconds immersion in a bath containing only 0.10 per cent aluminium at a rather favourable temperature, whilst Figs. 4 and 5 showed the bending properties of this coating.

Mr. Hughes then asked whether it was necessary to eliminate the alloy layer completely. Fig. 6 in the paper showed that the presence of a narrow band of alloy, the result of small aluminium additions, was not particularly injurious and had the advantage that it helped to increase the coating thickness which was very low in the absence of an alloy layer. He said he realized that 430°C. was a low temperature for industrial operation, but on the other hand the time of immersion might be much less than 15 seconds in industrial sheet galvanizing.

Turning to the other extreme of aluminium additions, viz. amounts of the order of 0.75 to 1.5 per cent, structures were found which helped to explain the remarkable effect of aluminium additions. After discussing the current explanations for the action of aluminium, his paper showed, in effect, that alloying in the ordinary sense was not so much eliminated as obstructed by the formation of a new type of inwardly-diffusing alloy. There was nothing strange, or even new, in this idea; in view of the known properties of aluminium, such an alloy could be expected, and the existence of an Fe-Al alloy had been suggested before.

In the present paper concrete evidence was given of the formation of such a layer. Its composition was indicated and its exceedingly good adhesion demonstrated. Fig. 10 showed a thick coating with excellent adhesion, a very happy state of affairs, but, alas, there was evidence that the layer was not resistant to hot water. It might, however, be only the outer layer of the coating which was really at fault. The way in which this coating tended to break up, promoted by its expansion during formation, explained the occurrence of loose crystals in coatings high in aluminium, as shown in Figs. 8 and 9; and its composition, given in Table II, obviously explained the enrichment of the coating in aluminium which was always found when the composition of the coating and the bath were compared.



# THE INFLUENCE OF ALUMINIUM ON THE ALLOYING ACTION IN HOT DIP GALVANIZING

by M. L. HUGHES,\* M.Sc., F.R.I.C., F.I.M.

## Introduction

The influence of additions of aluminium to the zinc bath on the results obtained by hot dip galvanizing has been the subject of numerous scientific papers. The literature on this subject is reviewed in the first part of a paper shortly to be published by the Iron and Steel Institute.

The most striking effect of aluminium additions is the change in the structure of the coating which may be produced, with a corresponding change in the bending properties. The usual alloy layers may completely disappear, yielding a coating which is much thinner but which has far superior bending properties. Opinions regarding the amount of aluminium needed to produce this result vary considerably; 0.2 per cent to 0.3 per cent is frequently quoted but recommendations range up to 0.8 per cent or even more.

The explanations offered for this pronounced effect of aluminium in the zinc can only be described as unsatisfactory. These will be discussed later and experiments described which disprove two of them. An alternative explanation for the action of aluminium is put forward, based on the formation of a ternary Fe-Zn-Al phase which has properties quite different from the usual delta and zeta alloy layers. A number of peculiarities associated with the use of aluminium are explained by the formation of this ternary phase.

## Experimental Work

The work described in this paper was undertaken with two main objects in view. These were, first, to determine the minimum amount of aluminium needed to prevent the usual alloying action, and secondly to examine the existing explanations for its action.

The requirements of sheet galvanizing were chiefly in mind and the experimental conditions were chosen accordingly. The influence on bending behaviour is thus of importance and was examined throughout.

Four types of material have been galvanized:

- (a) 'Armco Iron' — an approximation to pure iron.
- (b) Commercial low-carbon, cold-reduced sheet of rimming quality.
- (c) Steel containing 0.10 per cent carbon, killed, i.e. deoxidized but containing only traces of silicon.
- (d) Steel containing 0.22 per cent carbon and 0.10 per cent silicon.

Times of immersion ranged from 5 seconds to 60 seconds, with some supplementary tests at 2 minutes; the temperatures used varied from 430°C. to 490°C. and the aluminium additions from 0.05 per cent to 3 per cent.

## Results

*Baths containing 0.18 per cent and 0.33 per cent aluminium.* Table 1 summarizes some of the results obtained with 0.18 per cent Al. It is clear that with steels (a), (b) and (d), 0.18 per cent Al suffices to produce coatings free from normal alloying at temperatures up to 460°C., and times up to 30 seconds. At 490°C. some alloy formed but an increase in Al to 0.33 per cent

\* British Iron and Steel Research Association

served to counteract this. It would appear that the amount of aluminium recommended is frequently excessive, especially for steels low in carbon and silicon.

TABLE I

*Influence of Steel Base, Temperature and Time of Immersion on Alloying Behaviour in a Bath Containing 0.18% Aluminium*

Steel Base	430°C.		460°C.		490°C.	
	15 secs.	30 secs.	15 secs.	30 secs.	15 secs.	30 secs.
(a) Armco Iron	Generally no alloy; slight local formation	Greater tendency to local alloying	Some local alloying only	Increased local alloying	Uniform, thin, duplex layer of alloy	As for 15 secs.
(b) Cold-reduced steel sheet	No alloy	No alloy	No alloy	Local alloying of abnormal character	As 460°C., 15 secs.	Irregular alloying of an abnormal character
(c) Killed 0.10% C. steel	Little or no alloy. Very little local alloying	Increased alloy formation. Many alloy-free areas	Definite alloy layers. Some alloy-free spots	As 15 secs.	Uniform duplex layer of alloy	As for 15 secs. but occasional local thickening
(d) $\left\{ \begin{array}{l} 0.22\% \text{ C.} \\ 0.10\% \text{ Si.} \end{array} \right.$	No alloy visible	Almost entirely alloy-free	Negligible alloy formation	A few local growths. Elsewhere a few crystals only	Uniform duplex alloy layer, rather thicker than with (a) and (c)	Uniform duplex alloy layer, considerably thicker than with (a) and (c). Local areas free from alloy

A striking result was the discovery that steel (d) formed less alloy at the two lower temperatures despite its higher carbon and the presence of 0.10% Si. It was later discovered that Bablik (9) had observed this property of silicon of apparently enhancing the effect of aluminium. It is known that silicon has a similar modifying action in other coating processes. Figs. 1 and 2 illustrate the remarks made above.

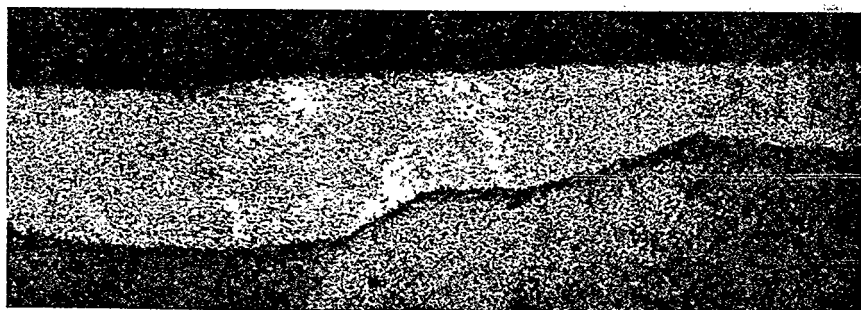
*Baths containing 0.05 per cent and 0.10 per cent aluminium.* Under favourable conditions, viz. using silicon-free steel with a very low carbon content at the surface, a low galvanizing temperature (e.g. 430°C.) and short immersion times, it is possible that smaller amounts of aluminium may suffice. It is not essential to eliminate all alloy in order to obtain adequate bending properties and a relatively small amount of aluminium may then be sufficient.



*Fig. 1. 460°C., 1 minute, 0.33% Al. Cold-reduced steel sheet. (X500).*



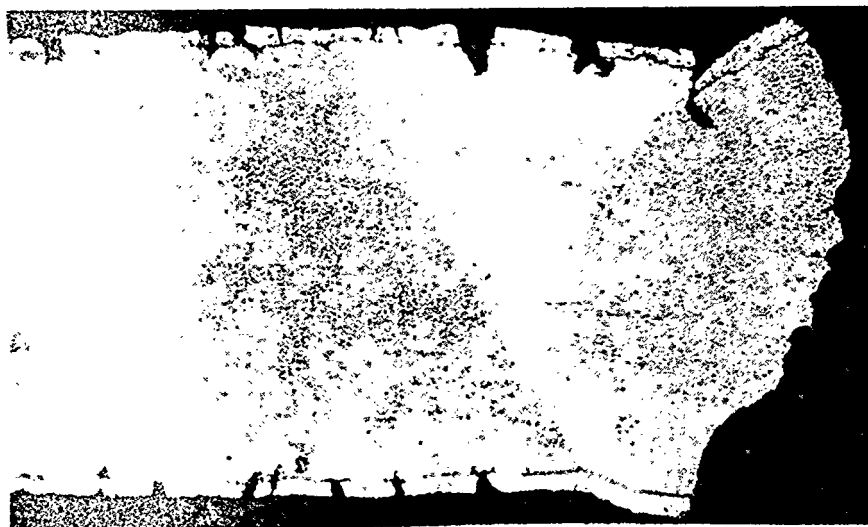
*Fig. 2. 460°C., 15 seconds, 0.18% Al. Steel containing 0.22% C., 0.10% Si. (X500).*



*Fig. 3. 430°C., 15 seconds, 0.10% Al. Pack-rolled steel sheet. (X500).*



Fig 4 15 seconds, 0.10% Al. Cold-reduced steel sheet; after 22 bends in alternating bend tester. (X125).



15 seconds, 0.10% Al. Cold-reduced steel sheet, after 18 bends. Steel fractured. (X125).

It was found that, under these conditions, coatings from a bath containing 0.10 per cent Al showed no alloy after 15 seconds immersion and only a sprinkling of crystals after 30 seconds. When the aluminium content was reduced to 0.05 per cent, alloy was formed but in reduced amount. The bending properties were very good with both cold-reduced and pack-rolled steel base.

Figs. 3 to 6 illustrate the structures of these coatings and the behaviour after bending in a 'Jenkins' Alternating Bend Tester.

*Baths containing 0.75 per cent and 1.5 per cent aluminium.* Heavier additions of aluminium were made in order to investigate a metallographic structure frequently observed with samples galvanized in baths containing aluminium.

Samples apparently free from alloy show under the microscope a peculiarly roughened steel surface below the coating proper. The disruption of the surface generally increased with time of immersion and this zone etched in an abnormal manner.

When the amount of aluminium, the time of immersion and the temperature are raised there is progressive growth of a layer which is quite unlike the normal layer of delta and zeta phases. It is a pale bluish-grey colour, structureless (except for fissures, etc.), and its inner boundary is often difficult to detect, if the metallographic preparation is sufficiently good. It was later found that this occurred with much less aluminium provided the time and temperature were suitable. Its presence may be observed by dark-field illumination. Examples of this appearance are given in Figs. 7a and 7b.

This result has an obvious bearing on the theory of the action of aluminium in galvanizing. The present unsatisfactory explanations for its action will first be reviewed.

### **Current Theories Regarding the Influence of Aluminium on Alloy Formation**

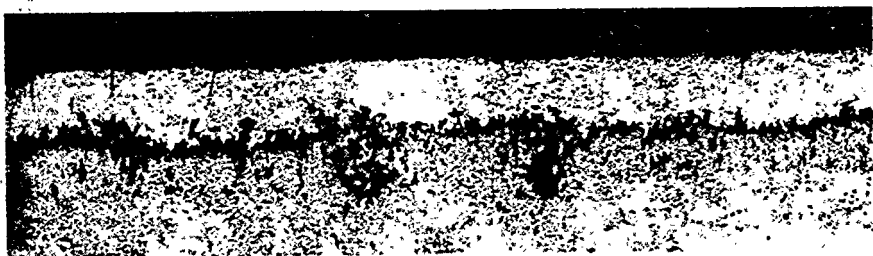
The 'Membrane' theory depends upon the supposed existence of a film or 'membrane' of alumina over the surface of the sample which prevents alloying. The film is said to form by interaction of the aluminium in the bath with a film of oxide, or moisture, on the sample. Its chief attraction is that it serves to explain the formation of isolated nodules of alloy which are supposed to form at breaks in the membrane. On the other hand it is difficult to understand why, by this theory, an increase in time or temperature of immersion can promote alloying; or to understand why such a film does not form in hot-dipping in aluminium.

The theory is contradicted by the following experiments, suggested to the writer by Mr. W. C. F. Hessenberg.

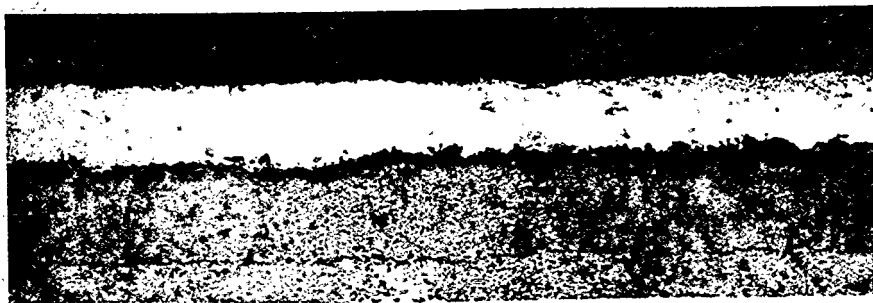
- (a) When a strip of steel was broken under the surface of a zinc bath containing aluminium, no alloy formed on the virgin surface produced by the fracture. It is difficult to see how any membrane could form on this surface.
- (b) The surface of an immersed sample was vigorously scratched by a toothed piece of steel. This should have caused breaks in the 'membrane' with local growth of alloy. These were not found.



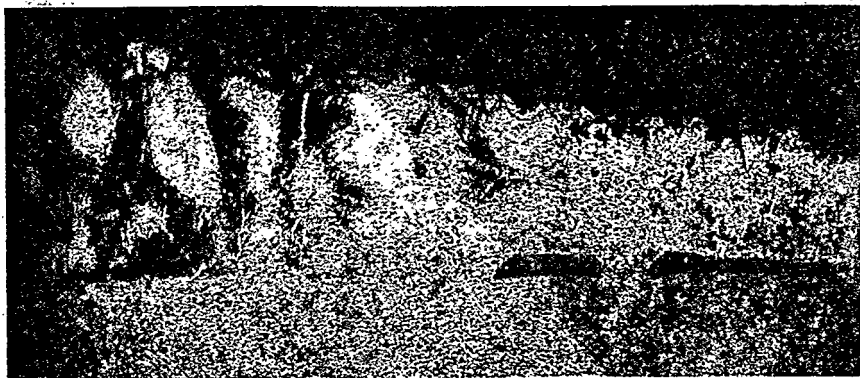
*Fig. 6. 430°C., 15 seconds, 0.05% Al. Pack-rolled steel sheet; after alternating bend test. Steel fractured. (X125).*



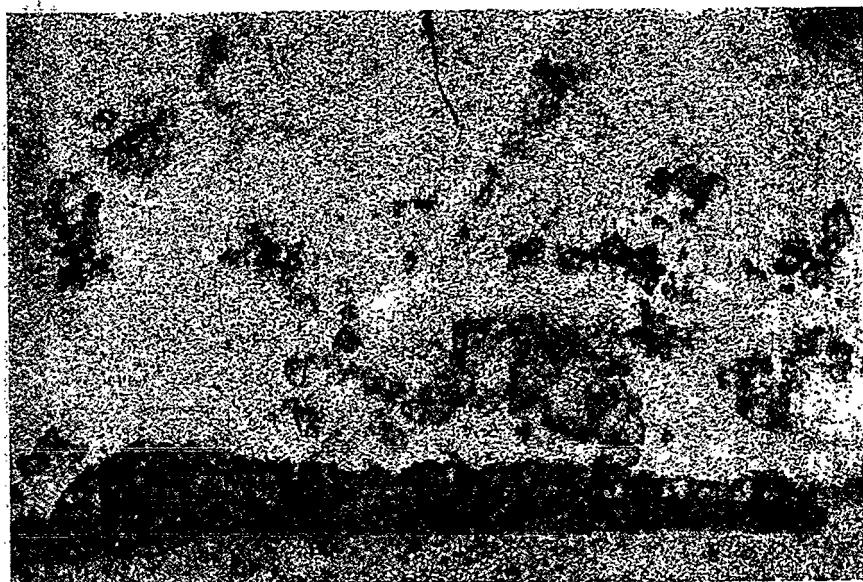
*Fig. 7a. 490°C., 15 seconds, 1½% Al. Penetration of alloy and disruption of steel surface. (X500).*



*Fig. 7b. 490°C., 30 seconds, 1½% Al. As 7a. Uniform penetration. (X500).*



*Fig. 8a. 490°C, 1 minute, 0.33% Al. Local alloying with loose crystals adjacent. (X250).*



*Fig. 8b. 490°C., 1 minute, 0.33% Al. As 8a but at 1000X. Note depth relative to surface elsewhere.*

The '*non-adherent alloy*' theory suggests that aluminium does not prevent alloying but rather makes the alloy extremely non-adherent so that it is lost almost immediately. Unlike the membrane theory, this explanation has the merit that it is based upon experimental observations, such as the frequent presence of trapped, loose crystals in the coating when the zinc contains aluminium. An immediate difficulty with this theory is that the use of aluminium in industrial galvanizing should lead to a considerable increase in dross formation due to the detached alloy. This does not occur and the amount of dross is often appreciably less.

The theory is contradicted by the following experiments:

- (a) A flat steel strip galvanized horizontally in a bath containing 0.3 per cent Al; with no agitation, showed no alloy on either face. An extremely non-adherent alloy might conceivably have fallen away from the under face but could not, under these conditions, have been lost from the upper face.
- (b) If galvanized coatings, made with and without aluminium, are heated *below the melting point of the coating*, the alloy layers in the pure zinc sample can be made to grow considerably thicker. The same treatment with the coating containing aluminium causes little or no alloy formation. This shows that the process of formation of alloy is affected by aluminium and not merely its adhesion.

The loose crystals found in the coating after galvanizing in the presence of aluminium, and thought to be trapped crystals of non-adherent zeta or delta, may be shown by Rowland's reagent (10) to be neither. Furthermore they occur usually in the immediate vicinity of an alloy layer and *not* where alloy is lacking (Figs. 8a and 8b). The true nature of these crystals is discussed later and an explanation is put forward for their detachment and for the presence of the adjacent alloy (dark in Figs. 8).

The '*inhibitor*' explanation, suggested by Bablik (11), likens the effect of aluminium in zinc to that of an 'inhibitor' in an acid solution or to the induction period often observed in the action of acids on metals. This view agrees with the observed effect of increased time and temperature, but is somewhat vague and is not supported by any experimental evidence. It is perhaps descriptive rather than explanatory. The statement that 'Aluminium stops all alloying action' is considered to be erroneous.

### The Alloying Process in the Presence of Aluminium

It has already been stated that galvanizing in baths containing aluminium produced, under suitable conditions, a layer which was quite unlike the ordinary duplex alloy layer. It has no apparent structure and advances into the steel on a comparatively regular front. Its behaviour is thus different from the inward diffusion of alloy in the hot dipping process for aluminium coatings, which proceeds rapidly and on an extremely irregular front.

In order to determine the nature of this layer it was isolated for analysis, by controlled anodic attack on the outer layer. The inner layer was then removed and analysed in the ordinary way. A number of analyses are given in Table II.



**TABLE II**  
*Composition of Alloy Layer Formed in Galvanizing Bath  
 Containing 1.5% Al*

%	490°, 1 min		460°, 1 min					490°, 1 min.			
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Fe	44.6	46.5	44.3	40.0	41.2	43.1	40.5	36.8	41.2	35.0	40.3
Al	29.4	39.8	39.7	37.5	33.5	37.3	39.0	36.9*	33.7	34.8	39.8*
Zn	26.3	11.9	16.9	20.6	26.9	19.6*	21.8	26.3	25.9	30.5	20.9

\*By difference

It is seen that the ratio of Al to Zn fluctuates but that the iron content is comparatively uniform at about 40 per cent.

The layer is thus seen to be a ternary alloy and potential studies indicate the presence of a concentration gradient. It does not seem possible for the whole of the alloy shown in the photomicrographs to be of the above composition; the aluminium content of the whole coating is insufficient for this. Further work is proceeding on this question.

Samples of the ternary alloy have been examined by X-rays by the writer's colleagues in the Physics Section, B.I.S.R.A. Laboratories, Swansea. This work shows that the aluminium in this layer is present as the theta Fe-Al phase (FeAl<sub>3</sub>).

The existence of this alloy layer explains a number of peculiarities associated with the use of aluminium additions.

### The Presence of Loose Crystals in Coatings containing Aluminium

The loose crystals, referred to earlier, were considered to be crystals of the ternary alloy but an explanation was needed for their detachment. It was later found that a second, darker, alloy layer may form beneath the ternary layer. The growth of this new layer, frequently accompanied by a narrow white zone, causes the ternary layer to be pushed upwards and ultimately to break away. Figs. 9 a, b, c and d show four stages in this process.

An explanation is now needed for the formation of a second and even a third layer in this way. Since the initial layer has ruptures or fissures, reaching down through its whole thickness in many places, it is possible that the liquid layer immediately adjacent to the outer alloy surface can penetrate these crevices. This liquid is likely to be depleted in aluminium by the formation of the Al-rich alloy and may be capable of reacting with the underlying steel to form the normal alloys. These grow outwards and by so doing force up the initial alloy layer as shown. A difficulty arises, however, because the secondary alloy layer is so much darker than zeta when etched in 1 per cent nitric acid in amyl alcohol. More evidence is needed to establish the identity of this secondary alloy.

### The Enrichment of the Coating in Aluminium

It is frequently found that a coating from a bath containing aluminium is richer in Al than the bath itself. This is sometimes attributed to the presence of an immiscible layer rich in aluminium which floats on the bath, a film of which is drawn out on the article. However, this enrichment of the coating in aluminium is greater as the time of immersion is increased, which contradicts the above theory.

It is now clear that the enrichment is due to the progressive formation of the Al-rich ternary layer.

It is interesting to recall that Britton, during his work on the controlled anodic dissolution of zinc coatings, concluded that the Al in the coating was preferentially associated in some way with the alloy.

### Bending Properties

Examples have been given of the excellent bending properties of alloy-free coatings and of those containing less alloy than usual as a result of the addition of small amounts of aluminium.

It has been found that with heavier additions of aluminium a thick layer of the ternary alloy may be present without the occurrence of any flaking on bending. Fig. 10 shows that its behaviour on bending is different from that of the usual alloy layers. It should be noted that the thickness of the coating in Fig. 10 is equivalent to about 2.9 oz./sq. ft. of sheet (about 0.0024 in. thickness) which is more than is normally found on galvanized sheet.

Since these coatings are highly lustrous it appears to be possible in this way to produce *thick* coatings of good appearance and with excellent bending properties — a very desirable state of affairs. The disadvantage attached to the use of aluminium, that bending properties are obtained only at the expense of coating thickness due to the absence of alloy, appears at first sight to be overcome.

Unfortunately, some doubt arises concerning the corrosion resistance of such coatings when produced from commercial baths containing the customary amounts of lead.

### Corrosion Resistance of Coatings High in Aluminium

It has been stated (12) that the simultaneous presence of appreciable amounts of aluminium and lead in a zinc coating makes it very liable to attack by hot water and steam.

Laboratory samples prepared at two temperatures from baths containing 0.3 per cent, 0.75 per cent and 1.5 per cent Al, together with 0.5 per cent Pb in each case, were therefore subjected to the action of hot water and water vapour at 84°C.

It was found that the attack was considerable in some cases, particularly at list edges, some of which disintegrated in less than a week. A considerable amount of (red) rust formed within a few weeks although some samples merely darkened. When the test was discontinued after 105 days a marked loss of coating was found to have occurred in most of the samples. Two comparison panels, coated in baths containing 0.3 per cent and 1.5 per cent Al, but without lead, developed no rust though white rust was quite marked, as would be expected.

### The Mode of Growth of the Alloy Containing Aluminium

In some cases, the inward diffusion of the alloy, referred to earlier, occurs very slowly at some points in the steel surface. This fact has made it possible to demonstrate the mode of growth of the alloy in such cases.

Fig. 11a shows the beginning of the process with the original steel surface visible at several points. At Fig. 11b, by further inward and lateral growth of the alloy, the gaps have been closed except at one point. At Fig. 11c is seen what is probably the last stage in the lateral spread of the alloy at that point.

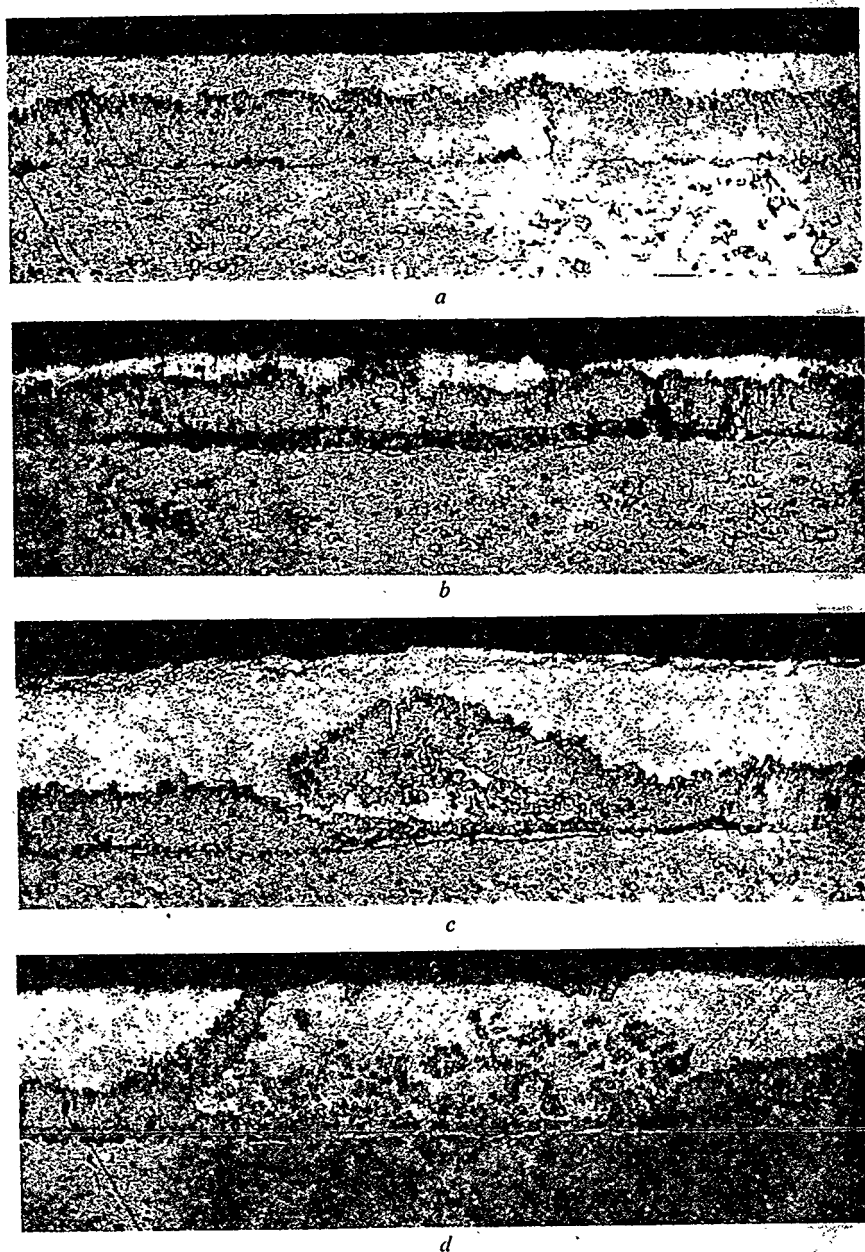


Fig. 9a, b, c, d. 430°C., 1 minute, 1½% Al. Secondary alloying causing detachment of ternary alloy layer and loose crystals. (X500).

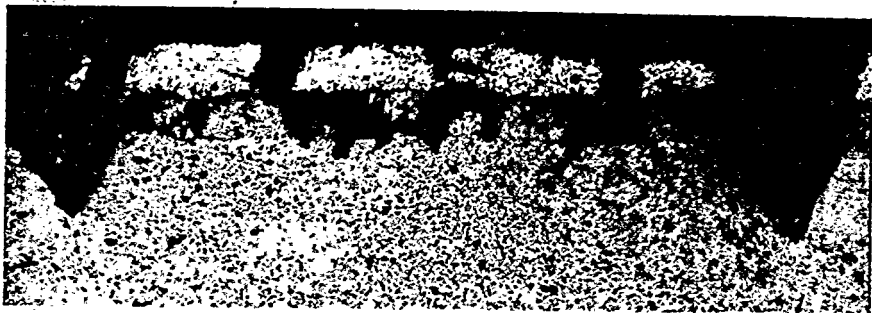


Fig. 10. 490°C., 30 seconds, 1½% Al. Behaviour of alloy in alternating bend test. (X250).



Fig. 11a. 490°C., 15 seconds, 1½% Al. Initial penetration of nodules of alloy. (X500).

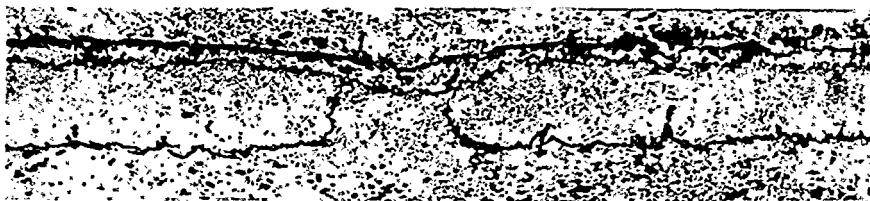


Fig. 11b and c. 490°C., 15 seconds, 1½% Al. Later stages in alloy formation. (X500).

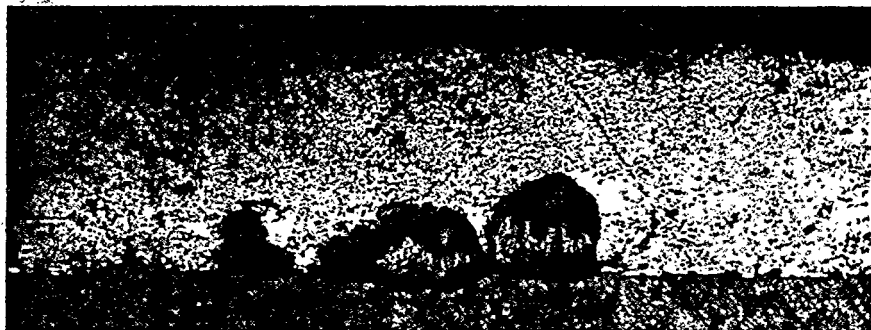


Fig. 12. Outward growth of nodules of alloy. (X500).

The inward growth of the nodules in Fig. 11a should be contrasted with the outward growth of the nodules in Fig. 12.

### Conclusions

- 1 Under favourable conditions, 0.10 per cent Al is sufficient to produce coatings free from the usual alloy layers and 0.05 per cent Al is sufficient to promote good bending properties.
- 2 Under average conditions 0.18 per cent Al prevents normal alloying.
- 3 The presence of silicon in the steel enhances the effect of aluminium.
- 4 Heavier additions of aluminium can cause the formation of appreciable amounts of alloy different from the usual delta and zeta alloys in appearance, composition, properties and mechanism of formation. It is of ternary composition and the aluminium present is in the form of  $\text{FeAl}_3$ .
- 5 The presence of an alloy of this composition explains peculiar results sometimes obtained when aluminium additions are made.
- 6 Evidence has been given to show that the action of small amounts of aluminium, in preventing visible formation of alloy, cannot be explained by the 'membrane' or 'non-adherent alloy' theories. It is concluded that in such cases the aluminium acts by the initial formation of a very thin layer of the alloy referred to in para. 4.
- 7 A secondary alloying process which occurs under the 'ternary' alloy causes the latter to break away and form loose crystals in the coating. The occurrence of this secondary alloying is erratic and more information is needed about it.
- 8 The bending properties of the 'ternary' alloy are excellent, no tendency to flaking having been observed.
- 9 The simultaneous presence of much aluminium and lead in the coatings makes them liable to severe attack by hot water and steam.

## DISCUSSION

## Use of Aluminium

MR. A. H. THOMPSON (General Galvanizers Ltd.) opened the discussion by asking about the black spots which occurred when galvanizing in a bath containing more than .05 per cent aluminium, and whether these were flux inclusions or discontinuities in the coating. MR. FAGG said that these black spots were discontinuities in the coating, and that his Association was working on different flux compositions to overcome this disadvantage of aluminium bearing baths. Of more than 50 different fluxes examined, however, no better flux had been found than zinc ammonium chloride. MR. HUGHES added that one way suggested in the literature for overcoming the black spot difficulty was the use of ammonium chloride *vapour* before galvanizing. This is said to permit the use of 0.10 per cent aluminium (13).

In reply to MR. C. P. H. WEDGE (B. E. Wedge Ltd.) who asked what was the best aluminium content for the general galvanizer, MR. FAGG said that it depended on what the aluminium was intended to do. For enhancing the brightness of the work, .005 per cent was sufficient, but if it was intended to reduce alloy formation, the optimum aluminium was greater than the practical galvanizer could at present use. With the dry process, recent work had shown that about 0.06 per cent Al was the maximum for a rolled window section, and about 0.1 per cent for sheet materials.

MR. M. G. BURROWS (Metaltreat Ltd.) then asked how the galvanizer could measure the aluminium content of his bath. MR. HUGHES agreed that it was important to know how much aluminium was in the bath, but pointed out that if the bath were analysed it would frequently be found that there actually was less aluminium present than was expected. He said that it was difficult to carry out this analysis accurately without a skilled analyst and the right equipment, but suggested that metallographical examination might provide an alternative method which would show whether the quantity of aluminium being added was having the desired effect on alloy formation. He referred to a colorimetric method used in his laboratory for aluminium estimation. This depends upon the separation of other elements in the solution from the Al by means of a mercury cathode electrolysis. The Al remaining is determined, in a suitably buffered solution, by the colour reagent 'Aluminon'. The colour comparison with suitable standards is made in a Hilger 'Spekker'.

MR. FAGG agreed that the analytical technique for aluminium was difficult, but said his Association would be pleased to supply details of the methods (14) used in their laboratories for this purpose. Later in the discussion MR. D. S. BURWOOD (Imperial Smelting Corp. Ltd.) added that some other work his Company had done on the chemical estimation of aluminium in zinc and zinc alloys might prove useful to Members and help them to overcome these very real difficulties. He added that spectrographic methods were more convenient.

MR. BURROWS then asked whether the aluminium concentrated in the surface layers of the bath; and MR. FAGG replied that the segregation of aluminium was not very great. Some tests they had done suggested that the upper layers of the bath did contain somewhat more aluminium than the rest of the bath, as for example in one industrial bath where the top 6 in. contained 20 per cent more aluminium than samples from the rest of the bath.

MR. HUGHES thought there was not much evidence that the aluminium concentrated in the top layers of the bath when the aluminium or aluminium alloy was properly introduced; i.e. by means of a spoon plunged well below the surface.

MR. W. MONTGOMERY (Fredk. Braby & Co. Ltd.) complimented Mr. Hughes on the work he had accomplished, and suggested that the new thoughts put forward would be of the utmost value to the galvanizing industry. Mr. Hughes's theory on the behaviour of aluminium was supported by experimental results and not by theoretical reasoning alone, and he felt sure that the new ground which had been broken would prove very fruitful in leading to further advances. The experiments described were simple and very convincing. Turning to the illustrations in Mr. Hughes's paper, he asked how it was that in Fig. 8 the coating was thinnest when the alloy layer was present, and thickest when there was no alloying.

MR. HUGHES admitted that the illustration was rather misleading. The explanation was really quite simple. It was the normal practice to examine coatings down the length of the specimen and the additional thickness at the points indicated in the photograph was due to drainage.

MR. MONTGOMERY then referred to a major difficulty when using aluminium additions in sheet galvanizing, i.e. the flux sticking to the exit rolls. He asked how this could be overcome. In reply, MR. HUGHES said that sheet galvanizers had tried making simple aluminium additions to the zinc and also the use of the Aplatær process, and had finally given up the use of aluminium in despair. He had a small experimental sheet galvanizing unit in Swansea which should, at a later date, give some information about the problem of suitable fluxes.

Turning to the general problem of obtaining a flexible coating on galvanized steel, Mr. Hughes said that there were at least two ways in which the problem could be approached. Firstly the use of aluminium in the zinc would eliminate or reduce the thickness of the alloy layer and give a flexible coating. This could be operated in conjunction with a doped flux as in the Liban process. The second alternative was to do away with the flux altogether, as when the Sendzimir process was used; and he mentioned some laboratory experiments in which a glass hood had been used at the point of entry. This hood contained a protective atmosphere and was externally heated. Previously 'blued' sheet samples were deoxidized and preheated to various temperatures while suspended over the bath. They were then galvanized for varying lengths of time. In this way the special features of the Sendzimir process were simulated. The glass hood allowed the behaviour of the oxide film to be observed during the reducing and preheating period. As a third alternative there was also the possibility of alloying the steel base so as to reduce the rate of alloy formation.

MR. H. T. EATWELL (G. A. Harvey & Co. (London) Ltd.) thought that sheet galvanizing was very different from general galvanizing with respect to aluminium additions. Sheet galvanizers frequently needed a flexible coating with a thin alloy layer, whereas general galvanizers were less concerned with good bending properties than with uniform, smooth and heavy coatings giving good corrosion resistance. He emphasized that reducing the thickness of the coating curtailed its life.

MR. E. M. WILSON (Henry Hope & Sons Ltd.) said that the mechanism of adding aluminium alloys to galvanizing baths was still not really understood. The makers of aluminium alloys for this purpose recommended an

aluminium addition of .01 to .02 per cent on the zinc as sufficient. He used the dry process of galvanizing, and had tried to follow these instructions, but although analysis of his baths had shown considerable variations through the shift, he had never found as much aluminium as .005 per cent. MR. FAGG thought that it should be possible when using the dry process to maintain aluminium contents of up to .05 per cent fairly easily.

MR. J. ROUFF (Etablissements Schmid) agreed with Mr. Wilson that galvanizers needed a lead in the practical use of aluminium. How should it be added, he asked, and should the quantity of aluminium be considered in relation to the area of the bath? How frequently should the aluminium additions be made?

MR. HUGHES replied that the surface area of the bath must be considered because of oxidation. He was in favour of adding the aluminium frequently, as additions made once a shift were not so good as those made hourly.

MR. BURWOOD then rose to thank the Association's Council for the invitation which they had extended to his Company to be present, and to congratulate Mr. Hughes on the excellence of his photomicrographs. He thought that the amount of aluminium should be related to the speed and type of work passing through the bath, and that the aluminium additions should be related to the amount of zinc consumed, i.e. the zinc additions to the bath.

MR. R. S. BROWN (Rylands Bros. Ltd.) said that in wire galvanizing practice the pots were frequently worked hotter than in ordinary galvanizing, and he had found that, when aluminium additions were made, there was a strong tendency for the dross to rise to the surface and form a semi-solid layer through which it was difficult to work. He would be glad to know more about this effect and whether it had been observed by other operators.

MR. HUGHES said that ternary aluminium-zinc-iron alloys might rise to the surface of the bath as they were a little less dense than zinc. Any free  $\text{FeAl}_3$  crystals would rise to the surface very easily and could be recognized by their dark colour.

### Effect of Tin Additions and Galvanizing Temperature

MR. THOMPSON asked whether the addition of tin to the zinc helped galvanizers to obtain a thinner coating by allowing the use of a lower temperature, and whether the spangle obtained by its use was good or bad. He added that galvanizers usually used higher temperatures when galvanizing light-gauge work, as it was thought this would give a thinner coating, but he wondered whether, in the light of Mr. Fagg's work, the higher temperature would not really give a heavier coating.

In reply MR. FAGG said there was no evidence that tin had a beneficial effect on the life of a zinc coating, and that the presence or not of the well-defined spangle which could be obtained by its use was a matter of personal taste and aesthetics. On the question of galvanizing temperature, he thought that galvanizers were misled in thinking that higher galvanizing temperatures gave thinner coatings because they increased the fluidity of the zinc. Any increase in fluidity would be balanced by the effect of high temperatures in favouring thicker alloy layers. His Association's work had shown that for a given immersion time and rate of withdrawal, thinner coatings were obtained with lower galvanizing temperatures. MR. HUGHES said that additions of tin gave other effects than good appearance, as such coatings often showed small cracks but less flaking than those free from tin.



### The Effect of Lead in Galvanizing

MR. BROWN said he was very interested in the effect of lead, and was disappointed that lead received so little mention in the papers before the Conference. In his opinion, lead was a most important constituent of hot dip galvanizing baths, and in the absence of lead, great difficulty was experienced in obtaining satisfactory finishes. His works, which hot galvanized 400 to 500 tons of wire and wire products each week, had had some rather peculiar experiences with lead additions. In the well-known method of galvanizing nails by tumbling in heated barrels with granulated zinc, it was at one time essential to add 2 per cent of tin to the electrolytic zinc in order to obtain a galvanized coating. Recently it had been discovered that if zinc containing 1 per cent of lead was used, galvanizing was just as effective. In the absence of lead, galvanizing did not occur at all.

Difficulty had also been experienced in galvanizing wire netting when using pure zinc. Rough coatings and scummy deposits seemed to form very readily, and not until lead was added to the extent of about 1 per cent were clean running conditions obtained. He would be interested to know whether other galvanizers had had similar experiences. He thought that more attention should be given to the role of lead in galvanizing, and that an examination of its effects would be worth while.

MR. HUGHES said that sheet galvanizers were familiar with the effect of lead which they described as making the work go more easily. He did not yet know the reason for this. Experiments beginning with 99.99 per cent zinc had shown that the effect of tin on spangle was very much less when lead was absent, and he thought this might indicate something of the way lead worked, viz. by its effect on the freezing range. He stated that lead appeared to improve the distribution of the coating over sheets, possibly by helping the metal to flow over the surface.

MR. W. WALKER (The Whiteinch Galvanizing Co. Ltd.) said that some two months ago he had added 20 tons of lead to two of his baths and had been amazed to find that the amount of dross made in the baths had fallen. He could not explain this, but thought the meeting would be interested in his findings. He added that the lead had been added simply because he had been able to buy it more cheaply than zinc.

MR. FAGG said that he had been very interested to read in Imhoff's paper that the presence of lead had been found to produce a marked effect in reducing the amount of dross formed in galvanizing baths, and the implication that this was because it reduced the rate at which zinc attacked the steel. This view was not supported by the work of E. J. Daniels on 'The Attack on Mild Steel in Hot Galvanizing' (1). In this investigation Daniels had measured the rate at which mild steel was attacked by different brands of zinc and had found very little difference in the rates of attack by the various zinc samples, even though their lead content varied from .002 per cent to 1.35 per cent. In view of the evidence from two separate sources which had been laid before the Conference he now thought that there was scope for further work on this question.

MR. H. CORBETT (Wm. Corbett & Co.) wondered whether zinc coatings containing lead would be sufficiently good to pass Admiralty tests and other specifications.

MR. HUGHES then pointed out that lead was usually present in hot dip galvanized coatings to an extent depending on its solubility in molten zinc. Sometimes galvanized coatings when examined micrographically showed

minute globules of lead. This did not come from mechanical entrainment of the lead but was due to the separating out of lead held in solution in the zinc as the coating cooled and solidified.

MR. H. BUSCH-JENSEN (J. Chr. Jensens Galvaniserings Etablissement) agreed with this view, as in his experience lead never got on to the articles being dipped.

MR. F. C. BRABY (Fredk. Braby & Co. Ltd.) thought that some misunderstanding might have arisen from the survey considered in Bailey's second paper where a number of baths were described as having no lead layer. This applied to some of those in his own factories. Although no special lead additions were made, the degraded zinc used contained 1 per cent of lead, some of which accumulated at the bottom and facilitated drossing.

MR. BAILEY replied that only when galvanizing baths were running on zinc containing 1 per cent of lead or more, did a lead layer remain automatically in the bath. Where electrolytic zinc was used the lead layer would gradually dissolve and disappear. Only when G.O.B. or Prime Western zinc with more lead was used, or when lead was deliberately added, would the lead layer remain in the bottom of the bath.

MR. BURWOOD confirmed this statement and said that, if new baths were run entirely on debased electrolytic zinc with under 1 per cent lead, no lead would settle out at the operating temperature of the galvanizing baths. The use of G.O.B. or P.W. zinc with more than 1 per cent lead would result in the formation of a lead layer.

MR. EATWELL said that in over 20 years' experience of galvanizing he had never emptied a bath which had no lead layer at the bottom.

MR. BURWOOD added that before the war when it was easier for smelting companies to know who bought the different grades of zinc, it was found that a brand with a very low lead content was not much in favour with galvanizers, who preferred zinc with a higher lead content. No very clear explanation of this was available at the time. There was no price difference, thus the reason was technical rather than commercial.

### Steel Compositions

MR. THOMPSON commented on the fact that in Mr. Fagg's paper no significant differences were observed in the rate of attack of zinc on different qualities of steel, provided that the silicon content was normal. In future he did not see that galvanizers could complain to bath manufacturers that the steel from which their baths were made was the cause of their burning out quickly.

MR. FAGG agreed that steel composition was not the main cause of galvanizing baths burning out. In those cases which had been investigated by his Association, it had usually been found that overheating was the cause of the failure. He said that silicon was certainly the most dangerous element, and that it should be kept below 0.07 per cent in the steel used for making galvanizing baths.

MR. HUGHES said that steel composition was also very important in the exit rolls used in sheet galvanizing. These rolls had to remain covered with zinc all the time, and should contain practically no silicon and have a very low carbon content.

MR. BROWN then referred to the composition of the steel being galvanized, and said that the wire industry, owing to the short times of immersion usually involved, was probably more conscious than other galvanizers of the

effects of slight changes in steel composition, particularly with regard to silicon. The effect exercised on 'killing' steel by even a small amount of silicon was most pronounced, and steel of this nature was manipulated in considerable quantities in order to obtain tight, flexible coatings. Where 'silicon-killed' steels could not be used for various reasons, the surface of the wire was treated by immersion in a carburizing salt which produced the same effect, and it was noteworthy that no difficulty whatever was experienced in galvanizing high-carbon steel unless the surface had for some reason become decarburized.

These effects were well known and were an essential part of the technique of wire galvanizing. Abundant evidence was available that the effect of silicon additions was to bring the carbon in the steel to the surface where its effect was similar to that obtained by the treatment in a molten carburizing salt.

MR. HUGHES then mentioned the effect of carbon present as pearlite at the steel surface in silicon-killed steel and referred to experiments carried out after moist hydrogen decarburization. He said that his results showed clearly that the presence of silicon in the steel enhanced the effect of aluminium in preventing normal alloy growth. By eliminating the carbon from the steel it was shown that silicon had a distinct effect on alloying, apart from its effect on carbon distribution.

MR. MONTGOMERY asked whether titanium and other elements of the fourth period chemically related to silicon showed similar effects when present in the steel. MR. BROWN thought that as titanium was, like silicon, a powerful 'killing' agent, it might be expected that its effect would be the same. MR. HUGHES, however, doubted whether titanium would act like silicon, as titanium fixed carbon as titanium carbide. Experimental work in his laboratory had shown that titanium affected alloying; but the industrial application of steels containing titanium was difficult, as it involved a changeover to 'killed' steels, and furthermore, titanium was lost from the surface when the sheets were oxidized.

THE CHAIRMAN then closed the discussion, and in his summing up paid a tribute to the work carried out by Daniels, Britton, Kenworthy, Hall, Gilbert and other members of the staff of the B.N.F.M.R.A., and by Vernon, Hudson, Hughes and their predecessors and colleagues of B.I.S.R.A. This work was the result of research sponsored on a co-operative basis which he believed was unparalleled elsewhere. He thanked the authors for their valuable papers and the members present for their useful contributions to the discussion.

## THE HEATING OF GALVANIZING BATHS AND EQUIPMENT

The heating of galvanizing baths and equipment is a very wide field and the paper presented to the Conference under this heading covered only a small section of it, being confined to fundamental thermal considerations. The discussion, however, was not circumscribed on that account and covered a wide range of heating problems of importance to general galvanizers, including the design and heating of drying ovens. This chapter describes the proceedings at the second Technical Session of the Conference, under the chairmanship of Mr. H. T. Eatwell.

### Author's Introduction

Introducing his paper on Thermal Considerations in Galvanizing Bath Heating, MR. BAILEY said that it should not be read as a blueprint for furnace design, although he hoped it would serve the purpose of helping the practical galvanizer who intended installing new equipment to weigh up the rival merits of the many different heating systems with which his good friends the plant manufacturers would no doubt try to beguile him. The plant manufacturer, he suggested, gave the galvanizer what he asked for, and he hoped that some of the considerations in his paper might lead a galvanizer to modify his demands. For example, since the loss of heat from the surface of a dry process galvanizing bath was some 5000 B.Th.U. per sq. ft. per hour, and it was shown that the average heat input through the pot walls should not exceed this figure, it was important that pots should be made deep enough to allow this heat to be brought in easily with something to spare. In the case of a pot 3 ft. deep and 5 ft. wide, obviously the heating engineer was beaten before he began to design his setting.

He then dealt briefly with the question of costs, and suggested that the saving in zinc lost by dross alone might well cover the installation costs and increased running costs of a modern efficient heating system. He thought that heating costs should be considered in relation to the other costs of galvanizing, nearly all of which were very much greater. It was difficult to assess the economic advantage of the better work which could be obtained from clean baths freer from dross, and the value of the thermostatic control which the newer systems allowed.

Finally, he referred to an even more important advantage and suggested that the new methods of heating had contributed much to a new outlook on galvanizing, stating it as his belief that the introduction of new bath heating systems in a plant had often been the first stage in transforming hot dip galvanizing from a traditional art to a scientifically controlled process. This change in outlook, for which the Hot Dip Galvanizers Association stood, could not be achieved while the old coke fired pots were used. The new systems allowed temperature control—the first step to the control of all the other variables—and clean galvanizing shops which could attract a better type of labour. He thought that it was not too much to say that, thanks to the

pioneer work on bath heating, their industry was now taking its place alongside other industries where controlled metallurgical operations were done.

## SOME THERMAL CONSIDERATIONS IN THE HEATING OF GALVANIZING BATHS

by R. W. BAILEY,\* M.A., B.SC., F.I.M.

Perhaps the main advance in general galvanizing during the last ten or fifteen years has been in improvements in the methods of heating galvanizing baths. The advances have been due to a better understanding of the underlying principles, and a willingness to apply knowledge from other branches of industry to the problem. The new methods of galvanizing bath heating have resulted in economy in fuel and zinc, in longer pot life, in cleaner baths freer from dross and in better coatings.

This paper is an attempt to set down the main principles involved in heating a galvanizing bath, and to evaluate the extent to which different systems fulfil the requirements of galvanizing bath heating. Questions of furnace construction, the design of burners, controlling mechanisms for thermostatic control, temperature measurement and instrumentation are not discussed.

### 1. General Principles

Hot dip galvanizing consists in the dipping of prepared steel into molten zinc. With the exception of some experimental units mentioned later, the molten zinc is always held in steel pots or kettles. Zinc attacks steel to form dross, a suspension of zinc-iron alloys in a matrix of zinc. The pot are therefore steadily attacked by zinc throughout the whole of their working life. No steel completely resistant to molten zinc has been found, although the rate of attack does depend to some extent on the quality of the steel, and those with less than 0.07 per cent silicon have been found to give the best performance.

The rate of attack on the steel is, however, greatly influenced by temperature, and perhaps the first clear statement of this effect was given by Daniels in 1931 (1) when he published a table showing the expected life of a pot wall 1.5 in. thick at various temperatures. The figures given were as follows:

<i>Temperature °C.</i>	<i>Life</i>
432	2,410 years
477	1,487 years
500	28.1 days
540	19.6 days

Daniels attributed the very big change in the expected life between 480° and 500°C. to a marked change in the adherence of the iron-zinc alloy layer. Below 480°C. this layer protected the steel pot walls, but above 500°C. it became non-adherent and flaked away, exposing the steel to further attack. Although these figures may perhaps give an exaggerated picture of the importance of steel temperature, experience since then has shown that temperature is the main factor in controlling the attack of zinc on the steel pot, and that the rate of attack increases very rapidly at temperatures above 480° to 490°C. The normal temperature in general galvanizing for the molten zinc is 450° to 455°C., and since the heat needed to keep the bath up to temperature has to

\* Zinc Development Association

be supplied through the steel walls, it will be seen that there is little margin in the working temperature difference between the steel and the zinc which controls the heat input, if the safe maximum temperature of  $480^{\circ}\text{C}$ . for the steelwork is not to be exceeded. If rapid attack by the zinc on the walls is to be avoided, the maximum heating area must therefore be utilized, and the heat input be very evenly distributed.

When a galvanizing bath is working, the biggest heat loss is from the top surface of the zinc. The other main heat requirement is that necessary to heat up the work as it is immersed through the top layers of the bath. Since the heat in both cases is taken from the top of the bath, the main heat input should be through the top part of the pot walls.

There is another important reason why the heat input should be mainly confined to the upper parts of the pot walls. Imhoff has given in the paper he has presented to this Conference the reasons why it is practically impossible to galvanize without forming dross. The zinc-iron alloys of which dross is formed are solid at the galvanizing temperature, and being somewhat heavier than the zinc, settle if the bath is relatively quiet and undisturbed to a porridge of solid suspended in molten zinc in the lower strata of the bath. Where a lead layer is used this semi-solid dross suspension rests in the layer immediately above it. Good galvanizing can only be obtained if this dross remains undisturbed at the bottom, which is one of the reasons for the deeper galvanizing pots now being installed in many works. It is therefore of the greatest importance that no attempt should be made to heat the bath below the dross line, for any heat below this level will tend to cause convection currents in the bath which will carry the dross upwards to contaminate the bath and the work treated in it.

From the standpoint of bath heating there is another reason for confining the heat input to an area above the dross line. The dross layer is too sluggish to allow efficient heat dissipation, and any attempt to heat the steel walls below the dross line is bound to lead to overheating of the steel in this area and so to early failure of the pot.

These considerations lead to the following conclusions. The pot should rest on a bed of insulating material carried up above the highest probable dross line, so that no heat is introduced through the steelwork below this line. The greatest heat input should be at the top where the heat is mainly needed, but all the available surface area should be used for heating the pot. The heat should be very evenly distributed round the kettle, and no part of the available heating area should be called upon to do more than its fair share of work. No hot spots can be tolerated, as these are bound to lead to premature failure of the pot.

### The Heat Requirements of the Galvanizing Bath

Before discussing individual systems in detail, it will be helpful to set down some figures for the heat requirements of a galvanizing bath so that the various factors involved may be kept in their right perspective. The heat required to maintain the temperature of a galvanizing bath is used in the following ways:

- (a) To make good the heat lost by radiation and convection from the surface of the bath.
- (b) To raise the temperature of the steelwork being dipped to the temperature of the bath.

- (c) To heat and melt the fresh zinc added to the bath.
- (d) To make good insulation losses.
- (e) Through stack losses.

As will be shown below, stack losses are always a heavy item, unless electric heating is used, and should really be placed much higher in the list. Stack losses do, however, depend on all the other heat factors, being directly proportional to them, and they have therefore to be calculated last.

### A Typical Galvanizing Bath

Consideration of these questions will be helped by reference to a typical bath and tabulation of its heat requirements. The bath we will choose will be of medium size, 8 ft. long by 6 ft. wide and 4 ft. 6 in. deep, holding approximately 40 tons of molten zinc. We will assume that it is handling a good tonnage of steel and has a throughput of one ton of steel per hour. This steelwork picks up 10 per cent of its weight of zinc, and allowing for zinc losses at 33 per cent the bath therefore needs 3 cwt. of zinc per hour. Assuming the bath is operating on the dry process, at a molten zinc temperature of 455°C., the surface heat loss will be around 5000 B.Th.U./sq. ft./Hr. The other figures are calculated from the latent heat of zinc and the specific heat of zinc and steel, and the insulation losses are estimated on the assumption that the setting is reasonably well lagged. The heat requirements then appear as in the following table:

<i>Heat Requirements for a Dry Bath 8 ft. × 6 ft. and 4 ft. 6 in. Deep at 455°C.</i>	
Surface losses	240,000 B.Th.U./Hr.
To raise steelwork to galvanizing temperature	220,000 B.Th.U./Hr.
To heat and melt zinc	35,000 B.Th.U./Hr.
To make good insulation losses	60,000 B.Th.U./Hr.
<b>Total</b>	<b>555,000 B.Th.U./Hr.</b>

To find the fuel requirements, the stack losses must be added. The stack loss where a fuel is being burnt is that proportion of the total heat of combustion which is wasted in the hot flue gases going to the stack. Heat may, of course, be recovered from these gases by using them to do other work in the galvanizing department, but this heat must in the first instance be charged against the galvanizing bath heating. To consider a simple example, we will assume that producer gas is being burnt to give a flue gas containing 12 per cent CO<sub>2</sub>. Unless the furnace is of a very special design, it is unlikely that a higher CO<sub>2</sub> figure than this will be achieved. In many instances the use of larger quantities of excess air may actually give rise to a lower CO<sub>2</sub> content and even higher stack losses, for the more air that is heated, the more heat is wasted in the stack. The following table gives the percentage stack losses at 12 and 16 per cent CO<sub>2</sub> as a percentage of the total heat produced by combustion.

<i>Temperature</i>	<i>Stack Losses</i>	
	12% CO <sub>2</sub>	16% CO <sub>2</sub>
600°C.	51%	40%
550°C.	47%	37%
500°C.	43%	33%
450°C.	39%	30%

As the pot walls have to be heated, it is unlikely that the temperature of the flue gas at the point where it leaves the pot walls will be much below

500°C., and an all-round stack loss of 43 per cent may not therefore be considered excessive in a typical galvanizing bath heating furnace. Very similar considerations apply where other types of fuel are being used, and it would therefore seem that the heat requirements for this bath coating one ton of steel per hour will be around one million B.Th.U./Hr.

### Heat Input through Pot Walls

In view of the considerations mentioned earlier, it will be inadvisable to heat the bottom 6 in. of the walls of our imaginary pot 4 ft. 6 in. deep. Practical considerations in constructing the furnace will preclude the heating of the top 6 in. of the pot walls, leaving an available depth of 3.5 ft. for heating. If the sides and ends of the bath are all heated, the available area becomes  $28 \times 3.5$  sq. ft. = 98 sq. ft. In the above table, all the heat with the exception of the insulation losses will have to be transmitted through the steel walls, i.e. 495,000 B.Th.U./Hr. This gives an overall rate of heat input of 5050 B.Th.U./sq. ft./Hr. which is practically the 5000 B.Th.U./sq. ft./Hr. often quoted as the safe limit for the overall heat input for galvanizing baths.

Before discussing whether this figure has been correctly assessed, further consideration must be given to the flow of heat from the pot to the zinc. Assuming the steel walls of the pot to have a thickness of  $1\frac{1}{2}$  in., the calculated temperature gradient between the outer and inner surfaces of the steel is 13°C. No information seems to have been published about the film coefficients for heat transfer between steel and molten zinc, if the term 'film coefficient' can be applied to the transmission of heat through the zinc-iron layer on the inside of a galvanizing pot. Observations made on the temperature difference between the lead jacket and the molten zinc in the special lead-jacketed galvanizing bath recently patented (15, 16) do however give some useful information about the temperature gradients to be expected between the steel and the zinc. In this case a temperature difference of about 20°C. between the lead jacket and the galvanizing bath gave a calculated heat transfer of 3000 B.Th.U./sq. ft./Hr. At this rate of heat transfer the temperature drop through the steel walls would be approximately 7°C., giving say a 10°C. temperature drop between the steel and the zinc, the balance being the drop between the lead and the steel. More definite information on temperature differences between steel and zinc would clearly be of the greatest advantage in fixing firmly the limits of heat input which a pot can safely take, but these figures suggest that the inside of the pot walls will run at a temperature of around 16°C. above the average temperature of the zinc bath for every 5000 B.Th.U./sq. ft./Hr. of heat input. With a galvanizing temperature of 455°C., heat inputs in excess of 10,000 B.Th.U./sq. ft./Hr. will therefore bring the pot walls dangerously near the temperature at which very rapid dissolution of the steel will occur. It will be shown later that, except in very special heating systems, it is difficult to maintain an overall heat input of 5000 B.Th.U./sq. ft./Hr. without rising to 10,000 B.Th.U./sq. ft./Hr. over parts of the bath wall surface, and the indications therefore are that this overall figure of 5000 B.Th.U./sq. ft./Hr. is a reasonable and safe overall maximum for the designer.

### Heat Transfer from Furnace to Pot Walls

The following table gives the results of some calculations which have been made on the expected rate of heat transfer from a furnace to the pot walls at different furnace temperatures. The walls have been taken at 470°C. on



their outer surface, and calculations are made on the basis of published information (17), on the heat transfer by convection from hot gas to steel, and by radiation following the Stefan-Boltzmann law and assuming an emissivity factor of 0.75. In practice a higher figure than this may be achieved, but the figures obtained on these assumptions give a guide to the expected rates of heat transfer which are not far removed from those actually found. The figures are not intended to be used to check up on the performance of existing heating systems, but rather to show the relative effects of different flue temperatures on heat input. Allowances will also have to be made in the case of solid fuel fired furnaces for the build up on the outside of the pot of flue dust which will act as an insulator.

*Expected Heat Transmission, Furnace to Bath Walls at 470°C. in B.Th.U./sq. ft./Hr.*

	570°C.	670°C.	770°C.	870°C.	970°C.
Convection	320	650	950	1250	1550
Radiation	2520	6180	11300	17950	26750
Total	2840	6830	12250	19200	28300

These figures are expressed graphically in Figure 1, from which it will be seen that the calculations lead to an expected heat transfer of 5000 B.Th.U./sq. ft./Hr. at a flue temperature of 630°C., and 10,000 B.Th.U./sq. ft./Hr. at a temperature of 735°C. It should be noted that at higher temperatures the heat input increases more rapidly, reaching 20,000 B.Th.U./sq. ft./Hr. at a flue temperature of approximately 880°C. The graph will be referred to again when the effect of flue temperature on heat input is condensed in connection with special systems of bath heating.

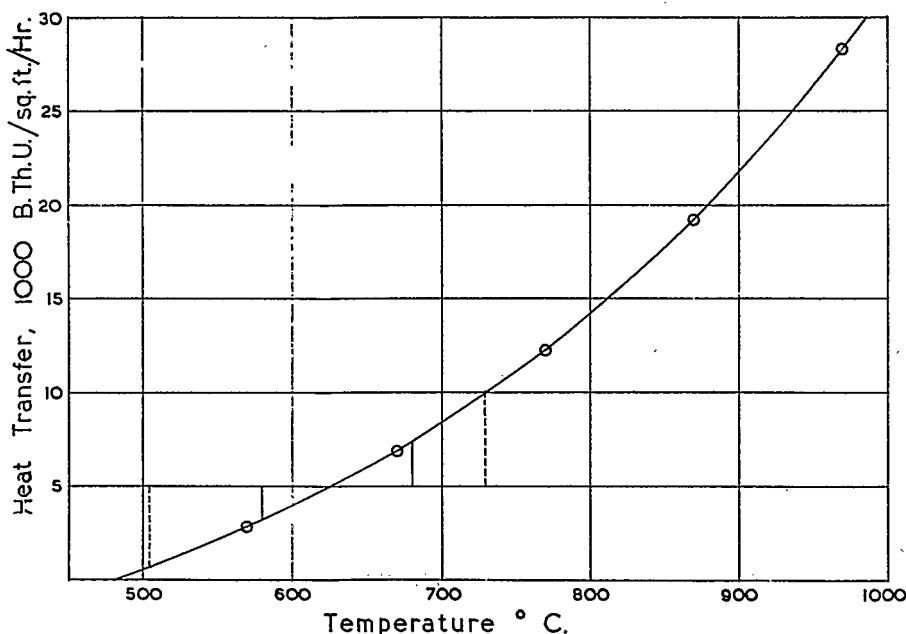


FIG. 1. Expected heat transmission, furnace to bath walls at 470°C.

Before proceeding to examine individual heating systems, the requirements of a heating system for a galvanizing bath may be summarized under the following headings arranged roughly in their order of importance:

- 1 An adequate heat input.
- 2 Even heating over all the available wall surface.
- 3 High thermal efficiency for fuel economy. Where solid fuels are burnt, this necessitates working to a high  $\text{CO}_2$  content in the flue gas, and allowing sufficient time for contact between the hot gases and the galvanizing pot for the gas temperature to be reduced as nearly as possible to the temperature of the molten zinc at the point where the gases leave the furnace. In considering fuel economy, 'soft flames' should be viewed with suspicion if these low-temperature flames are obtained by the introduction of large quantities of air. Where 'soft flames' or their equivalent are obtained by the recirculation of flue gas, there is, of course, no loss in efficiency.
- 4 The system must lend itself to thermostatic control. This is usually arranged on the on/off principle so that, except where solid fuel is in contact with the pot walls, no real difficulty arises with most systems. It is of the greatest importance from the standpoint of fuel efficiency that the air/fuel ratio should remain constant whether the furnace is operating in the maximum (on) position or the minimum (off) position. This requirement has caused difficulties, but unless the fuel/air ratio is kept in step all the time the  $\text{CO}_2$  content of the flue gas will fall sharply in one or other stage of the cycle with a consequent increase in stack losses.
- 5 Simplicity, affecting first cost and maintenance.
- 6 Low heat content of furnace for flexibility. Some calculations later will show the effect of large masses of hot firebrick in preventing a thermostatically controlled bath adjusting itself quickly to considerable changes in load. A furnace of high heat content practically precludes the use of insulating bath covers during standby periods because of the dangers of the zinc temperature rising excessively before the furnace has cooled.

There are also two important points affecting working conditions:

- 7 The heating system should not contaminate the atmosphere in the galvanizing shop.
- 8 When the bath is above floor level, as it always is in the U.K., the setting must be compact enough to allow easy access to the bath.

## II. Heating Systems

### Coke Firing

The traditional method of heating galvanizing baths for well over 100 years in the U.K. has been the simple provision of coke fires built against the walls of the pot itself. This type of furnace was simple to build, used a cheap fuel and gave plenty of heat for galvanizing. But the control of the coke fires to give a steady zinc temperature depended entirely on the skill and attention of the workers, and although very good results have been and are being obtained by the use of coke firing, the fact remains that no real advance in hot dip galvanizing could be made while such a primitive system of firing was in use. Draughts from open doorways could easily cause the fires on one side of the bath to burn fiercely and overheat the kettle on that side, but even when carefully controlled, coke fires still only heat the baths in patches, thereby shortening the pot life. Thermostatic control is, of course, quite out of the question.

Coke fired baths were often overheated, as for example at the end of a shift, when the furnaces would be recharged by the men before leaving the shop. After raking, the fires would tend to burn up and supply more heat to the

bath, although in fact less heat would be needed when the dipping of cold work had stopped, and the ash left on the bath surface would act as an insulating blanket. Coke fired pots therefore had usually but a short life. An important indirect consequence of coke firing was the impossibility of achieving a clean galvanizing shop in keeping with modern ideas of factory layout. Until the process could be closely controlled in good clean shops, no real advance in technique could be expected.

### The Use of a Furnace external to the Galvanizing Bath burning Gas, Oil, or Solid Fuel

The simple settings of this type were usually coal heated and consisted of an external furnace from which the products of combustion passed round and along the sides of the galvanizing bath, sometimes returning through a flue under the bath but insulated from it; or in the double pass type, with two sets of flues placed one above the other, the hot gases travelled first along the top of the bath and then back along the bath walls midway up the sides. The main difficulty with this type of heating is the very high temperature, 1200°C. or more, of the hot gases coming from the furnace. To reduce the temperature of these gases by drawing in excess air only lowers the thermal efficiency of the heating system by greatly increasing the stack loss, and Bablik (18) points out that the heating efficiency of these settings was often as low as 15 or 20 per cent.

To overcome the harmful effect of the high temperature on the bath, a wall was usually built between the flue and the bath through which the heat had to be transmitted, this wall extending round the sides of the bath until a point was reached where the flue gases would no longer overheat the pot walls. This meant that perhaps two-thirds of the total heat input was transmitted through fireclay or refractory, and the high heat content of this furnace work made the heating system very inflexible, for it can be shown that this protective refractory will store as much as one hour's heat supply to the galvanizing bath when operating at maximum load. The system, however, had the advantage that many different sorts of relatively cheap fuel could be used, and was an improvement over coke firing.

### Heating Systems using External Furnaces in which the Flue Gases are recirculated

This method of galvanizing bath heating represented a very big advance on the systems described above. It made use of a principle well established in industrial heating, and was first introduced into this country by a member of the Association under the name of the Williams system. The method consists essentially in reducing the high flame temperature, inevitable where fuels are burnt efficiently, by diluting with flue gas which is recirculated. In practice, an external furnace burning either gas, oil or solid fuel is provided, from which heat can be drawn into the system as it is needed. In a modification of this system (19) the flue gas after circulating round the bath is drawn through a furnace in which producer gas/air mixtures are burnt. The system aims at maintaining as little difference as possible between the maximum and minimum flue temperatures.

The operating conditions may best be illustrated by considering our typical bath and referring to the graph in Figure 1. If it is decided that not more than 100°C. difference is to be allowed between the maximum and minimum

temperatures of the flues, then to give an overall heat input of 5000 B.Th.U./sq. ft./Hr. the mixed gases will have to enter the heating flues at 680°C. and leave them at 580°C. If producer gas is being burnt efficiently at a flame temperature of 1200°C., it will need diluting with five times its volume of returning flue gas at 580°C. in order to re-enter the system at 680°C.

In the case of the bath we are considering, some 7700 cubic feet of producer gas will be needed each hour, and will give at 12 per cent CO<sub>2</sub> in the waste gas some 21,600 cubic feet (at N.T.P.) of gas at 1200°C. for introduction into the system. An equivalent volume of waste gas will, of course, be bled off to the stack from the coolest part of the flue. The recirculation of five times this volume of waste gas to maintain flue temperatures in the range 680° to 580°C. involves therefore the circulation of 130,000 cu. ft./Hr. of gas and demands very generous flues. A further point to be remembered is that the high velocity of the recirculated gas necessary to maintain these temperatures involves the gas leaving the system for the stack at the relatively high temperature of 580°C., with a high stack loss in consequence. This disadvantage may be unimportant if the waste heat can be used elsewhere in the plant.

A further margin might, however, be allowed between the maximum and minimum flue temperatures. If the maximum heat input from the top flue is allowed to rise to 10,000 B.Th.U./sq. ft./Hr. then, from the graph, it can be seen that the temperature of the inlet gas to the kettle heating flue can be allowed to rise to 735°C., and the outlet temperature to fall to 500°C. whilst still maintaining an overall heat input of 5000 B.Th.U./sq. ft./Hr. These conditions only involve the recirculation of two volumes of flue gas for every one volume of freshly burnt producer gas/air mixture, and reduce the speed of recirculation to 63,000 cu. ft./Hr. The decrease in minimum temperature allows the stack loss to drop from 50 to 43 per cent at 12 per cent CO<sub>2</sub>.

Although this system of bath heating has a good reserve of heat, it does not rely on a mass of hot brickwork close to the pot to supply it, but on the external furnace and the large volume of circulating gas. The bath can therefore accommodate itself to rapid changes in load, as the following calculation shows.

Suppose that at the end of a shift, when the bath had been operating at an average overall heat input of 5000 B.Th.U./sq. ft./Hr., insulating covers are placed in position which reduce the total heat requirements to one-third. Then, from the graph and the above figures, it will be seen that the necessary average drop in the temperature of the brickwork setting will be 100°C. Assuming 4 in. of brickwork all round the bath is involved in this temperature change; that the specific gravity of the brick is 1.9; and that its specific heat is 0.2, then the brickwork will carry approximately 20 minutes heat reserve, i.e. it could continue giving heat at 5000 B.Th.U./sq. ft./Hr. for 20 minutes before its temperature had dropped to accommodate the necessary low heat input conditions. On the bath we are considering the 40 tons of zinc might, therefore, rise in temperature by 13 to 14°C. This temperature increase would not, however, be sufficiently great to cause any damage to the bath.

Variations on the Williams system in which the gases are recirculated by a fan are still today among the best methods of heating galvanizing baths. The system can be adapted to different kinds of fuels, and can burn them efficiently. It is very suitable for thermostatic control. Although not low in first cost, the design is straightforward and presents no special difficulties in construction or operation. The system is flexible, and the very even heating

of the pot walls which it achieves leads to long pot life and low dross production.

### Recuperative Types of Setting

The term 'recuperative' is used here to describe those types of galvanizing bath heating in which heat is transferred through firebrick walls both to heat the bath by radiation and to maintain the temperature of the flue gases as they impart heat to the pot. The settings aim at maintaining an even flue temperature without the complication of recirculation in the type of heating considered in the last section.

There are two important modifications of this system which may be termed the vertical and horizontal modifications. In the vertical modification the burners are placed at the bottom and on the outside of a vertical wall spaced away from the bath. The flue system is arranged so that the flames heat this vertical wall as they are drawn up on the outside of it, and then having dropped to a temperature of 600° to 700°C. pass over the wall and down the side of the bath to heat it by direct contact. This design is particularly suitable for multiple gas burners and perhaps for oil burners, and various modifications of it have been proposed.

In the horizontal modification an external furnace is used in which practically any type of fuel may be burnt. Double flues are provided round the bath, the hot flames from the furnace first passing along the outer flue and then returning in contact with the bath walls along the inner flue. A second set of flues below the top flues may also be used. Heat transfer takes place from the flames in the outer flue through a thin firebrick wall to the gases in the inner flue, so that the bath is evenly heated by these gases and by radiation. A fan may be needed to assist the natural draught from the stack if the bath is large and the flues are long.

Both the horizontal and vertical modifications rely on considerable heat transfer through furnace walls, and call for careful furnace construction. The following figures show the extent to which heat will pass through walls made either of fireclay brick or magnesite brick in terms of the necessary temperature gradient for a transmission of 5000 B.Th.U./sq. ft./Hr. Fireclay brick under these conditions needs a temperature gradient of 450°C. per inch, whilst magnesite brick, more suitable for withstanding higher temperatures, has a higher heat conductivity and needs only a temperature gradient of 135°C. per inch for the same heat transmission. Assuming the radiating wall to be 1½ in. thick and to have an internal temperature of 600°C., the outer temperature would need to be 1275°C. in the case of fireclay brick or 800°C. when magnesite brick is used. Good results should therefore be possible with a heating system using this principle in which the materials of construction are carefully chosen.

Either the vertical or horizontal modification of the recuperative system is well adapted to thermostatic control, but where a number of individual burners are used as on the vertical system, it is very important that both the gas and the air supply to all the burners should be regulated together to keep the thermal efficiency high and the stack losses low at each part of the operating cycle.

### Radiant Heating using Gas as the Fuel

Heating systems of this type have attracted designers of galvanizing bath settings as a means of securing very even heat input to the pot, and special

alloy tube radiants have been described for this purpose in the American literature (20). Radiant tubes are well known as a method of industrial heating. They operate by the internal combustion of gas/air mixtures, secondary air being admitted through a concentric inner tube at different points along the tube to control the heat distribution or to keep the whole tube radiating at a steady temperature. Radiant tube heating is particularly valuable for furnaces which have to operate with a clean and controlled atmosphere, but it is doubtful whether the high first cost of the installation can be justified on the grounds of even heat input alone in view of the other satisfactory solutions of this problem. There is also the question of fuel efficiency. To some extent the radiant tubes used for industrial heating in the U.K. are recuperative in that the secondary air can be preheated (21), but the method when applied to galvanizing baths suffers from the disadvantage, fundamental to heating systems other than electric, that where the heat is being supplied at a relatively high temperature the stack losses from the combustion products are likely to be very great.

An alternative type of radiant gas heating has also been proposed, and some trials are being made with a system employing radiants similar to those used in domestic gas fires to provide the source of heat. It is hoped that some information about this application may later be published elsewhere.

### **Radiant Heating using Electric Elements**

The electrical heating of galvanizing baths using ordinary resistance elements is a well-tried and excellent method where electricity can be supplied at a price competitive with other fuels. If the heating can be done economically, there can be no doubt that this method of heating galvanizing baths is ideal. An electrically heated setting is clean, the heat can be very evenly applied exactly where it is wanted, it is simple to design, easy to operate, flexible and suited to thermostatic control. Electric furnaces operate at high efficiency and unless the insulation is poor 80 per cent of the electrical energy should be transmitted through the walls to the zinc.

The electrical heating elements are usually arranged round the bath in layers, one above the other, three layers being commonly chosen. The top bank of heaters will operate most of the time and the lower banks will come into operation when the thermostatic controlling mechanism calls for extra power. Mention should perhaps be made of a special electrical bath setting designed in Australia (22) where the furnace can be wheeled away from the bath in two halves to allow for inspection or replacement of the elements or the pot.

### **Gas Immersion Heaters**

Although engineers have often considered the use of immersion heaters in the molten zinc bath as a simple and straightforward method of heating, this application has not yet been realized because no material which is unattacked by the molten zinc has been found for making the heaters. High rates of heat transfer would be called for, and the use of steel is obviously out of the question. Experiments with ceramic coatings, such as fused enamel, have not yet produced an enamel which will withstand the rigorous conditions demanded by a tube immersion heater. In this connection mention should be made of the small experimental bath carrying a ceramic lining and heated externally which was used by Imhoff with some success. Efforts to extend the

use of this ceramic lining to industrial galvanizing baths resulted, however, in failure, and the steel pot with a ceramic lining which lasts indefinitely is still a dream of the future.

A successful application of immersion heaters to galvanizing bath heating has, however, been described recently (15, 16). Here the tubes are heated with towns' gas and are immersed not in the molten zinc but in molten lead. Lead does not, of course, attack the steel tubes, and methods such as this for heating lead are well-established in other industries. In this new heating system the lead is contained in pockets welded to the walls of the galvanizing pot and covering practically the whole available heating area. Published information shows that at heat transmission rates of around 3000 B.Th.U./sq. ft./Hr., the lead bath may be controlled at 465°C. to give the correct galvanizing temperature. Apart from the disadvantage of high initial cost the method would seem to combine all the main features of an ideal galvanizing bath heating system. The pot walls can never be unevenly heated, and the very low heat content of the lead pockets makes the bath very flexible. In the case of the bath we are considering, some 18 tons of lead would be needed in the pockets. As lead has only about one-third the specific heat of zinc — an advantage overlooked in the author's calculations — covering the bath with a good insulating cover at the end of a working shift can only cause a 2° or 3°C. change in the zinc temperature. The lead in the pockets is never heated to a temperature at which steel would be attacked quickly by zinc, and the pot should therefore have a very long life, and show a correspondingly low dross production from the walls.

### Low Frequency Electrical Induction Heating

Information about an interesting new development in galvanizing bath heating has come recently from America (23). The well-known Ajax metal melting furnace has been adapted to heating a galvanizing bath built entirely of ceramic material, so that the molten zinc never comes in contact with a steel pot at all. The low frequency induction furnace is inclined to the vertical alongside and rather below the centre of the zinc bath, and the currents set up in the zinc cause a circulation of metal from the furnace to the bath and back again. The channels through which the zinc circulates are placed sufficiently above the bottom of the bath to allow the dross to settle undisturbed. The constant circulation of zinc in the bath is said to have no disadvantage, although some adverse effect on ash production might be anticipated.

## III. Relative Costs of Fuels

A straight comparison of the relative cost of coal, towns' gas and electricity, to mention three of the fuels dealt with above, would not alone give a fair picture of the economic considerations determining the choice of the most suitable galvanizing heating system. In the case of coal and gas the efficiency with which these fuels are burnt may be the over-riding consideration. Even with the more costly fuels, other aspects of the heating system, such as the possibility of completely lagging the bath surface at standby periods, or the long bath life and low dross production which it achieves, may offset the extra cost of the fuel. In the case of the bath considered, during working hours the cost of coal at £4 a ton would be 3s. 7d. per hour if it were burnt efficiently to keep the stack loss at not more than 45 per cent and the total heat requirement at one million B.Th.U./Hr. Electricity at  $\frac{1}{8}$  penny per unit

would cost 7s. 8d. per hour as only 555,000 B.Th.U./Hr. would be needed. Gas at 11d. a therm in the case of the lead-jacketed immersion heater type bath would, on the published information of a 32 per cent stack loss, also cost 7s. 8d. per hour during working periods. Against the higher costs for towns' gas and electricity must be set the saving which the use of well-lagged covers can provide during standby periods; such covers could, perhaps, only be safely used elsewhere in the case of the recirculation type of setting described in Section 3 above. The use of covers should cut the fuel requirements to about one-third, i.e. 2s. 6d. per hour for the towns' gas and electrically heated settings. No estimate can be made here of the economic value of long pot life and uninterrupted galvanizing in dross-free zinc, and it is for the galvanizer to decide to what extent such considerations as these justify the higher first cost and high fuel costs of some of the systems described in this paper.

#### IV. Conversion Factors

- 1 *ft.* = .3048 *m.*
- 1 *inch* = 2.54 *cm.*
- 1 *B.Th.U.* = .252 *k.cal.*
- 1 *B.Th.U./sq. ft./Hr.* = 2.71 *k. cal./m<sup>2</sup>/Hr.*
- 1 *Ton* = 1016 *kg.*
- 1 *Cwt.* = 50.8 *kg.*
- 1 *Unit (Electricity)* = 1 *kWh.*
- 1 *Therm (Gas)* = 100,000 *B.Th. U.*
- 440°C. = 824°F.
- 450°C. = 842°F.
- 460°C. = 860°F.
- 470°C. = 878°F.



## DISCUSSION

MR. E. FELLOWS (Thompson Bros. (Bilston) Ltd.) introduced the discussion by referring to the contribution which the modern fuel-fired and temperature-controlled galvanizing bath furnace was making to the advancement of galvanizing technique in replacing the old four-wall coke fired furnace. The dipping or processing of the articles or ware was now the galvanizing operative's only job, and he was therefore free to concentrate his skill and labour upon production. In a correctly designed furnace there was no waiting time for the required amount of heat, neither was it necessary to attend to fires. All this was done by mechanical means operated automatically. With solid fuels the periodical removal of clinker was necessary. The heating unit or furnace had now become a mechanical one, and as such needed regular maintenance and attention, in much the same way as any other production unit.

Although the new galvanizing furnace was quite a complex unit, it was simple to maintain and keep working provided the right type of person was chosen and that he made himself acquainted with the working of it. By the firm or galvanizer who applied wise management to the changeover (and it did mean a considerable change in outlook in the works) the following advantages could be obtained: (a) higher output of processed goods than ever before; (b) less worry about run-outs; (c) cleaner shops; (d) better working conditions for the operatives, and (e) considerable saving in consumable materials and residues. With zinc at its present high price, the design of the furnace became all the more important. Starting up must be correctly done because all the well-known risks were attendant until the metal was molten, with controls and instruments correctly set and balanced. The close range of temperature between the safety and danger limits as well as the high density of the metal had to be borne in mind.

Furnace designers should primarily ascertain: (a) the size of the articles to be treated; (b) the maximum weight of each piece or bundle per immersion; (c) the quantity-rate throughput envisaged per hour. In the design, careful consideration must be given to zinc capacity, design, shape and size of the pot; the provision of adequate stays or supports, and accessibility of flues to facilitate cleaning when solid fuels were used. Other important factors included the available heating surface for heat input, the distance between the inside of the pot and the outside of the casing where hand dipping was in operation, and adequate access to zinc pits.

### Fuels and Fuel Costs

MR. FELLOWS then turned to the choice of the fuel to be employed, and said that this was one of the first considerations when installing a furnace and that the decision was one entirely for the user. Points in this connection were the availability of the fuel for a few years ahead as revealed by geography or mineral yielding capacity, and economic reasons where oil was concerned. For guidance, however, it was necessary to make some comparison, and he would use as a basis the costs ruling in Britain. There was not much appreciable difference in the capital cost of the plant for any of these fuels. Unquestionably coke was the cheapest when burned in the well-known manner against the walls of the pot, but up to the present no satisfactory way had been found of using the temperature of the zinc to control the heat by automatic means, and at the same time obtaining a reasonable life from the

furnace. It was, however, possible to control the burning of coke if this were done in a separate combustion chamber under the same conditions as any other solid fuel. This was uneconomic because coal is cheaper than coke when so burned and has a higher calorific value. For comparisons of fuel costs, the commonly used fuels could be arranged in the following order of increasing costs: coal, coke, oil, gas, electricity. Controlled automatic galvanizing furnaces had been built, balanced and set to work utilizing each one of these fuels, and their behaviour under varying conditions of production was known.

MR. J. J. STORDY (Stordy Engineering Ltd.) thought that Mr. Bailey's paper had not brought out fully the big difference between the cost of coal which was quoted at £4 a ton, and that of electricity where  $\frac{5}{8}$ th penny per unit was mentioned. Coal in the Midlands was less than £4 per ton, and he knew that some members present were paying up to 3d. per unit for their electricity, and that electricity was in any case likely to be over 1d. per unit.

MR. F. C. BRABY (Fredk. Braby & Co. Ltd.) then asked whether anyone had had experience with producer gas. MR. C. H. FREWER (Boulton & Paul Ltd.) said he was fortunate in his works in having cheap fuel available in the form of 8 tons a day of sawdust and shavings. There were three distinct works on the one site, one being woodworking. For flexibility he had installed near the galvanizing department three small producer gas plants to use this sawdust, and obtained gas at a pressure of 26 in. water gauge. As a subsidiary source of fuel he bought town gas, boosting the pressure to 6 in. water gauge before use. Water in the producer gas had made thermostatic control somewhat difficult. In addition to this he was fortunate in having ample supplies of well water for cooling the gas.

MR. J. BRADBURY (Incandescent Heat Co. Ltd.) said there were two types of producer gas — clean and dirty. The hot, raw gas produced from bituminous and other fuels was not so easy to apply or to control as the clean gas. Clean gas was usually obtained from either anthracite or coke, and could be burnt and controlled for temperature and heat input in much the same way as town gas. Gas made from anthracite was the better, the disadvantage of making gas from coke usually being the high and variable sulphur content. Gas could be produced from anthracite at approximately  $7\frac{1}{2}$ d. per therm, but gas could be obtained more cheaply from coke at about  $6\frac{1}{2}$ d. per therm.

MR. J. BOSSCHER (N. V. Plaatwerkerij) then rose to thank the Council on behalf of Mr. van Kempen and other Dutch galvanizers for the invitation they had received to attend the Conference.

He would like to give the meeting some actual figures for the operation of an electrically resistance-heated galvanizing bath of length, 5.5 m., width, 1.1 m., and depth, 1.2 m. It had a zinc content of approximately 50 tons. Electricity cost 0.6d. per kilowatt hour. Operation was in three shifts, covering 120 hours per week, and the wet process was used for galvanizing light 25-22 gauge articles. The total power consumed in six months was 697,000 kWh.

Weight of finished articles produced	.. .. .	2886 tons
Weight of zinc consumed	.. .. .	497 tons
Dross produced per hour of heating (5088 hr.)	..	11 kg.
Dross produced per hour of operation (3120 hr.)	..	18 kg.
No zinc ashes (Liban process)		

MR. BRABY thanked Mr. Bosscher for these figures which would be very useful for reference purposes, and asked the Chairman whether he could have some information about the Ajax low-frequency induction heated system, and how it behaved in practice. Did the dross really settle down when the zinc was circulating all the time?

MR. D. S. BURWOOD (Imperial Smelting Corp. Ltd.) said that although he had not seen a galvanizing bath heated in this way, he had some experience with Ajax induction melting furnaces of 300 kVA. capacity used for zinc alloying. The circulation and metal flow were considerable, and he thought that although dross which reached the bottom of a galvanizing pot heated in this way would not be lifted, he wondered whether the suspended dross would in fact settle easily.

MR. BAILEY said that an induction heated bath was now being installed in the U.K., and that an invitation had been received for the Anglo-American Productivity team to see the bath which was already working in the U.S. He asked whether Mr. Bennerstedt could give the meeting some information.

MR. BENNERSTEDT (A.B. Max Sievert) said his company was now building the first galvanizing bath of this type in Sweden, but of course he had not yet had any experience of its operation. The bath would be built as a 60 kW. induction furnace of the new type with straight melting channels, and the size of the kettle would be 750 mm.  $\times$  750 mm., with a depth of 800 mm. The furnace consisted of a 60 kW. standard twin coil induction unit and a refractory lined pot. It would be used for galvanizing nails. He promised to make a full report available later about its operation.

MR. J. H. GRAHAM (Galvanizers Ltd.) said all the figures quoted so far for the advantages of modern bath heating systems had referred to material and power savings. He would like to add that in his experience a major saving had been the 20 per cent decrease in wages consequent on the installation of modern bath heating plant.

### Fuel Efficiency and Stack Losses

MR. STORDY said that from the standpoint of the general galvanizer, the typical bath described by Mr. Bailey would be more likely to have an output of 5 to 10 cwt. per hour than the 1 ton per hour mentioned in the paper, so that its efficiency would be, under practical working conditions, 10 per cent or even as low as 5 per cent. Dr. Bablik's figures of 15 to 20 per cent, referred to as being low, were not usually attained in practice in the works of jobbing galvanizers.

MR. BAILEY in reply said that Dr. Bablik's figures referred to fuel efficiency defined as the proportion of the total heat of combustion passing into the galvanizing bath, whereas he thought Mr. Stordy's figures of 5 to 10 per cent must refer to the proportion of the total heat supply to the bath which was used in galvanizing. In any case he thought that galvanizers should not be satisfied with a state of affairs which gave a working efficiency as low as 5 per cent.

In his introduction he had addressed a few remarks on stack losses to the practical galvanizer who might not quite understand this important concept — important because much fuel might be lost if stack losses were not kept to a minimum. The stack loss, he said, was that proportion of the heat obtained from the fuel which escaped from the system in the hot flue gases. Its extent depended on the temperature of the gas, and the amount of excess air drawn in, which was measured by the carbon dioxide content of the flue

gas. In keeping stack losses to a minimum the heating engineer was faced with two dilemmas in the case of galvanizing pots. If the maximum amount of heat was to be extracted from the flue gases, a comparatively large heating area needed to be exposed to the gases after they had lost much of their heat. This meant that a relatively smaller heating area was available for the absorption of the main heat input, and defeated the purpose of even bath heating and the avoidance of high rates of heat transfer. The second dilemma referred to the amount of excess air used. If the air was kept to a minimum consistent with complete combustion, the result was a high flame temperature. Increasing the air supply to lower the flame temperature and give 'soft flames' would mean that there would be high heat losses in the excess air which had to be heated.

MR. FELLOWS said that although with solid fuels at least one-third of the heat passed into the outlet flues, some of this could be used for drying, hot wash, and flux tanks on its passage to the chimney. The losses through the furnace walls and other sources were relatively small. It was known that the temperature of the outgoing gases was of the order of 500°C. The only case where stack losses could be ignored was that of the electric furnace where there were no outgoing gases. This had the highest thermal efficiency of all.

MR. BRADBURY called attention to the statement made in the paper that the heat loss from the flue gases tended to be high when the recirculation system was used. He agreed that this was so if the gases were simply discharged to the atmosphere. It was, however, always possible to utilize a good proportion of the sensible heat in the waste gases for the preheating of the air required for combustion, and in this way the stack losses could be reduced to a very low figure. The high-flame temperature obtained by the use of preheated air was not a disadvantage with full recirculation, since the fuel was burnt in a combustion chamber remote from the bath proper and dilution was obtained by the recirculated gases.

### Rate of Heat Input

MR. FELLOWS thought that more should be said about the rate of heat input to galvanizing baths. Much had been written about heat losses and the maximum temperature of the flues, or the number of B.Th.U. per sq. ft. per hour it was permissible to apply to any bath with safety. He feared that many of these figures were of the text-book variety and bore little relation to the actual, and suggested that there was in fact no hard-and-fast rule which would apply to all galvanizing furnaces except that approximately 4000 B.Th.U. per sq. ft. would be lost by radiation from the top of the bath, when the surface was exposed. In some instances this surface loss proved to be 50 per cent of the heat input. Text books and laboratory tests suggested that the heat units per sq. ft. per hour on the outside could be related to the temperature inside, dependent upon the thickness of plate in the pot wall, but this was assuming that constant conditions were prevailing inside, which in practice was not the case. Heat was required: (1) to make up the losses from the surface of the bath, dependent upon its length and width; (2) to heat up work being processed; and (3) for the zinc addition. A bath dipping 2 tons per hour would obviously require a higher temperature in the flues than one of the same size dipping only 1 ton per hour. There was now in the design stage a bath capable of dealing with 7 tons per hour in which it might be necessary to have heat input in the region of 10,000 B.Th.U. per

sq. ft. per hour. This might involve a shorter pot life, but the degree would not be very much.

It was always desirable for the depth of the bath to exceed the width so that adequate heating surface would be available, but even so 8000 B.Th.U. per sq. ft. per hour had been proved necessary for a jobbing galvanizer with a comparatively small output.

MR. STORDY agreed that galvanizing baths should be so designed that the depth exceeded the width, and thought that this was now a generally accepted principle. He wondered whether the bath mentioned in Mr. Bailey's paper was really a typical general galvanizing bath and appealed to those present at the Conference for support. He thought it would be better to consider a typical bath where the top area was a minimum and the depth was a maximum, so that a combination of these two would result in reducing the heat needs whilst increasing the available heating area.

MR. BAILEY replied that this criticism was indeed justified and confessed that the dimensions of the bath in the paper had been specifically chosen to illustrate the main points about heat input with which he was concerned.

MR. BRADBURY said that he was not at all happy about the low figure of 5000 B.Th.U. per sq. ft. mentioned in the paper as being the safe limit for galvanizing baths, as this conflicted with his own experience. On many installations with which he had been connected, the heat input was of the order of 10,000 to 12,000 B.Th.U. per sq. ft., and in one or two exceptional cases as high as 25,000 B.Th.U. was released per sq. ft. Obviously at the latter high rates, pot life was shortened, but in view of the continuous production obtained from the bath, the reduction in pot life was somewhat of a minor factor.

Secondly, the ratio of zinc in the bath to the weight of work at 40:1 was extremely high. In the galvanizing of heavy work, 20:1 was often encountered, and he was surprised that Mr. Stordy should refer to an output of 5 cwt. being a more suitable figure for a bath containing 40 tons of metal.

Various methods of heating were referred to in the paper. His company were concentrating on full recirculation-type furnaces using high rates of circulation and lower temperatures than had hitherto been the case. The rapid convection currents broke down the inert film on the outside surface of the bath and allowed high rates of heat input, viz. up to 15,000 B.Th.U. per sq. ft. The minimum temperature lead was maintained at all times and full automatic temperature and combustion control was applied.

Reference was made several times in the paper to evenness of heating. This was desirable for many installations, but there were continuous hot-dip processes where this principle did not apply. He referred particularly to wire and strip galvanizing, where the cold work entered at one end of the bath and travelled through the molten zinc to the other end before coming again into the atmosphere. Such processing required high rates of heat release at the charging end of the bath and low rates at the discharge end, since it was necessary to maintain temperature where the cold work entered, and to compensate for the effect of the heat carried forward to the discharge end by the moving load.

Reverting to the question of zinc to work ratio, he added that generally in wire galvanizing the figures were 25:1, but he was aware of one installation on another type of work where the ratio was much lower. A bath 25 ft. long, 4 ft. wide and 5 ft. deep containing approximately 120 tons of zinc had a maximum output of 18 tons of work per hour, or approximately 7:1

zinc to work ratio. He knew that such figures were not usually practicable, but he did consider that much higher work throughput figures could be obtained, if, in many cases, handling methods were mechanized and modernized to suit the work being processed.

MR. BAILEY in reply said that Mr. Bradbury's remarks about the high rate of working of galvanizing baths on continuous processes illustrated the difference between general or jobbing galvanizing and the more specialized plants handling large tonnages of repetition work. His other paper to be discussed later in the Conference showed that among the general galvanizers the figure he had chosen was, if anything, a high one. Only one general galvanizer had an hourly output of work as high as 6 per cent of the weight of zinc in the bath, and many of them had an output weight which was less than 1 per cent of the weight of zinc.

MR. STORDY suggested that, in considering the heating of galvanizing baths, most of the points raised could be covered by the concept of 'proportionate' heating. For example, it was not advisable to heat the areas close to the corners at the same rate as the flat side of the bath, and the heat input from top to bottom of a bath, or from end to end of a bath treating wire or strip, should also be varied proportionately.

MR. R. STEWART (Smith & McLean Ltd.) raised the question of provision for bath failure with the newer types of heating apparatus. MR. FELLOWS replied that means were provided in all well-designed plants to prevent zinc coming in contact with gas jets or mechanical stokers. These were kept separate and away from the walls. MR. STEWART then pointed out that unfortunately the metal did not always run just where it was wanted, to which MR. FELLOWS replied that his experience had shown that if the temperature of the zinc were limited by pyrometers and the fuel feed regulated from this, safe working conditions would result.

MR. STORDY thought that to regulate the temperature of the zinc in the pot was not enough. The safe maximum temperature of the steelwork of the pot had been given as 480°C., but it should be realized that this safe steel temperature could be exceeded, even though the bath temperature was below 450°C. This could occur if the rate of heat input became excessive, when high flue temperatures were used in an endeavour to heat the bath contents too rapidly, and he had known of pots failing through frequent overheating in this way. Did this not call for control of rate of heating as well, and should not this be done in the case of baths heated by flue gases by controlling the flue temperature as well? Although this would result in some limitation of the capacity or throughput of the bath, it safeguarded the pot and, in the case of recirculation settings, it had the advantage of protecting the fan as well.

MR. E. J. BARLOW (British Furnaces Ltd.) agreed that this was an important point. In addition to the gas and oil heated bath settings which his Company had installed, he had built several settings utilizing the re-circulating system of heating. At the moment he was building two such settings having baths 12 ft. long  $\times$  5 ft. 6 in. wide  $\times$  9 ft. deep, each of which would have an output of 4 tons of work per hour. The temperature of the zinc would be automatically controlled and so would the temperature of the flue gases.

MR. BAILEY added that the remarks about the importance of flue temperature control reminded him of an interesting Swiss galvanizing bath heated electrically where the thermostat was linked to a thermocouple on the outside of the kettle wall.

MR. FELLOWS said that the galvanizers' difficulties were not only those of excessive heat input, as some galvanizers had found the greatest difficulty with too slow a rate of heating. This had become particularly apparent in these days of output incentive bonuses when the operatives had sometimes found their output restricted on this account. He then referred to pot covers which could be used to conserve a large amount of fuel during standby periods. He said that care should be exercised in their use because, if a good amount of heat had been built up in the flues and they were applied suddenly for a lunchtime break, or at finishing time, there was a grave danger that the built-up heat in the flues would carry the zinc temperature higher, even though the fuel supply was restricted, as Mr. Bailey had already mentioned in his paper.

MR. STORDY agreed that covers on control-fired settings should be used with discretion and with due regard to the problems they presented. No galvanizing bath firing could be correctly balanced until it was determined that the heat supply with 'covers on' was less than the heat needs of the system, and that the heat supply on maximum production was adequate for the heat needs. These were very wide limits which, in his opinion, presented a genuine problem to the furnace designer who had to bring them within automatic control, including control of *rate of heating*.

### Pot Life

MR. BOSSCHER raised the question of pot life by referring to his bath 42 ft. long carrying 100 tons of zinc and made of steel  $1\frac{1}{2}$  in. thick. This bath was coal fired and had a life of between four and five years doing general work on three shifts a day. A very varied range of products was handled, and the production rate varied from  $\frac{1}{2}$  ton per hour to 6 tons per hour. These baths had formerly been bought in Germany, but a British manufacturer whom he had approached seemed only to expect a two-year life. He wondered what reason there was for this. MR. BRADBURY said he was also interested in pot life and particularly in the life of a pot operating at a heat input of 5000 B.Th.U. per sq. ft., and although he appreciated that it was somewhat difficult to give a figure for this, he would be interested in any information Mr. Bailey could supply.

MR. BAILEY replied that he would expect a minimum life of five years from a well-designed bath heating system operated correctly, and that if the heat input were really limited to 5000 B.Th.U. per sq. ft. per hour, the life would be very much longer. He knew of many baths which had lives of more than seven years. The two-year period Mr. Bosscher had mentioned probably referred to guarantee.

MR. FREWER said he wondered whether galvanizing pots were really as good today as before the war. He used to get three or four years life from his pots but now, although his conditions were similar, he only got two years from the modern pots. Was there perhaps some fault in the steel, and what were the precautions the pot manufacturers took to control the quality of their steel?

DR. R. HAARMANN (Rheinische Röhrenwerke) then rose to thank the Association's Council for inviting him to the Conference, and said that he did not think it sufficient just to state the life of a pot in years. Surely the throughput per hour must also be specified when considering pot life. He had operated baths of comparable size to those handling 1 ton per hour of steel in general galvanizing at throughputs of as much as 10 tons per hour,

and although shorter lives were inevitable with these higher throughputs, it did not mean that the operation of these baths was any less economic.

MR. H. T. EATWELL (G. A. Harvey & Co. (London) Ltd.) said that Dr. Haarmann had gone to the root of the problem in considering pot life in terms of output. The rate of heat input through the pot walls was the real criterion in deciding pot life. High rates of heat input introduced the danger of heating the walls above  $480^{\circ}\text{C}$ ., a point at which the rates of solution of mild steel in zinc became rapid.

### Drying Ovens

With the wider introduction of prefluxing techniques, galvanizers have been giving more attention to the question of drying ovens. The importance of controlling the temperature of these had been stressed by Mr. Fagg in introducing his paper at an earlier session when he pointed out that considerable quantities of iron salts could be re-formed on the surface of the work if it was dried at too high a temperature.

MR. BRABY called attention to the importance of this closely related subject by inquiring about the best methods of heating drying ovens. He asked whether it was best to have a closed oven, or whether a hot plate on the floor did not provide an easier means of drying; and whether the waste heat from the galvanizing baths should be used. The old practice of drying work on the sides of galvanizing baths, although perhaps inevitable in some plants, caused loss of time and efficiency.

MR. EATWELL said that in the past the general practice at his works had been to dry over the bath, and that in his experience this method was still widely used. He now had gas heated ovens with high speed air circulation and these saved both time and accidents. In his plant the waste heat from the galvanizing baths was only sufficient to heat his ovens when the baths were working under full load, and he had therefore installed ovens which were independently gas heated. Frequently his ovens were needed to prepare work for galvanizing before the baths were in use, and at such times the waste heat was insufficient.

MR. BARLOW said that in those plants with recirculation settings which he had installed, all the necessary drying of the work was accomplished in specially constructed drying ovens heated by the spillage gases from the settings without the use of any additional heat.

MR. BRABY said that the problem in general galvanizing was the wide variety of work which had to be treated, and that an oven large enough to take the biggest jobs would not be economical for small work. For this reason it was quite common, even in modern plants, to see some jobs dried over the baths, and many firms used hot plates. He thought the Conference would be interested in some experiments which Mr. Stordy had been carrying out for his company, and he asked whether he could describe them.

MR. STORDY observed that the problem of drying was twofold: (1) the drying of articles which had been prefluxed, and (2) the drying of articles straight from hydrochloric acid pickle. With the former, air-circulated drying ovens were quite satisfactory, whereas with the latter, where there might be a lot of acid present even after draining, a simple robust drying plant was best without employing recirculation, as the hydrochloric acid fumes would naturally attack the steel work. Experiments had been carried out employing an old galvanizing pot sunk into the floor in the usual way and surrounded by flues leading from the true galvanizing pot so that the hot gases



flowed around and underneath this 'drying pit'. Using the same handling means as that provided for the bath, it had been found that the capacity of the drying pit, which in the experiment was somewhat less in dimensions than the galvanizing pot, was more than adequate for drying all the articles that could be galvanized. Such a plant was simple and effective and no auxiliary heating was required. As a development of this drying pit, another drier was now being installed, which had open ends and an open top leaving two sides and a bottom around which the flue gases passed. The work was handled on a conveyor, the platform of which was level with the floor. This conveyor served to carry the work from the pickling area to the galvanizing baths. It only moved when required to do so by the leading hand on the pot, and the picklers could only load it as the conveyor became vacant at their end. A large unwieldy part could be handled by a crane and unusual shapes could be accommodated because the drier was open-topped and open-ended. In size it could be the same dimensions as the pot, because what could be galvanized in the pot could be dried in the drier.

MR. EATWELL said that his drying problem was overcome by using two ovens, one for small work and one for larger work. There were, he said, two ways of drying, either by using a high temperature or by using a large volume of warm air. Mr. Fagg's paper had shown that a temperature of 300°F. should not be exceeded, and his ovens operated at a maximum temperature of 250°F., or well below this maximum. When his ovens were first started up he had used higher temperatures, but had found that this practice spoiled the flux and prevented good galvanizing from being obtained. These troubles disappeared at the lower temperatures. He too had found conveyors necessary in handling the work through the ovens. When drying prefluxed work he had found that the dried fluxed work should be dipped within one hour of leaving the drying oven, as otherwise the flux seemed to 'go stale'. If the work was left in the oven, it did not seem to deteriorate in this way.

MR. A. H. THOMPSON (General Galvanizers Ltd.) said that old galvanizing works usually lacked the space for large ovens. Many of them, however, had standby baths, and he would like to ask whether Mr. Stordy thought these could be used as ovens by a suitable by-pass flue arrangement.

MR. STORDY said he would not like to answer Mr. Thompson's question without first working out the possibilities on the drawing board. He was afraid that leading the heat round the second bath might well be found to double the cost of the installation, and that a fan might have to be installed to overcome the additional resistance.

MR. G. R. FAULKS (John Williams & Sons (Cardiff) Ltd.) said he had adapted part of an old plant as a drying oven for work straight from the hydrochloric acid pickling tank. This oven was made of sheet steel and although he realized that it would eventually rust, it had been in use now for two years without giving trouble, despite the acid fumes.

MR. E. W. MULCAHY (John Thompson (Dudley) Ltd.) referred to the advantage of the hot fluxing which he had installed in connection with a sulphuric acid pickling plant for treating small fittings, bolts and screws. After immersion in hot flux at 80°C., all but 5 per cent of the work dried itself without the need for special drying equipment at all. He thought that when drying ovens were used, the velocity of the drying air was more important than its quantity or temperature.

MR. EATWELL thought that insufficient attention was often given to the humidity of drying ovens and asked for some advice.

MR. BAILEY said that drying ovens needed rapidly repeated changes of air if quick drying was to be achieved at low temperatures. Drying could, of course, be done at temperatures high enough to drive the water vapour off at high humidity, but Mr. Fagg's paper showed that under these conditions iron salts were formed which it was the very purpose of prefluxing to prevent. He thought it should be emphasized that no drying oven could use the waste gases directly for drying work, as these were contaminated with sulphur and would spoil the galvanizing. He thought that an open hot-plate type of drying oven was very good because it provided the large volume of air at low humidity without the necessity of mechanically circulating it.

MR. M. G. BURROWS (Metaltreat Ltd.) pointed out that Mr. Stordy's theory about the size of drying oven necessary was only true if the drying could be accomplished in as short a time as that needed for dipping. Otherwise the drying equipment would have to be bigger than the bath. He agreed that the introduction of large awkwardly shaped articles into the oven and their subsequent removal caused very real handling difficulties; and said he was experimenting with a pipe built under the flue of his bath furnace through which hot air was blown on to the articles so as to dry them before dipping.

MR. EATWELL thought that Mr. Burrows's system would work well if the temperature were carefully regulated. In his ovens, drying time was quite short, and at temperatures not exceeding 250°F. it only took ten minutes to dry tanks so that they could be dipped without undue spitting.

MR. STORDY replied that in practice with the open-topped heater even large tanks dried quite as quickly as they could be galvanized, and that the system he had proposed introduced no difficulties on this account. He agreed that Mr. Burrows's system could work well, but thought that this would depend on how it was applied. He added that many times, to his knowledge, designs for galvanizing equipment, intrinsically good, had failed because they had been badly applied. For example, it was important, when designing these indirectly heated drying ovens, to allow a sufficiently large heat exchange area.

MR. EATWELL said he had handled some large work which took twenty minutes to galvanize in a bath 15 ft. by 4 ft. by 5 ft., but which could be dried in ten minutes.

### Closure

MR. EATWELL then closed the session by paying tribute to the high quality of the paper and discussion, and thanked all the speakers. He emphasized that the problems which they had discussed were of acute interest to all galvanizers and had been prominent for 100 years. These problems were not yet completely solved, but the fact that they had been under study so long was a measure of their depth. With improved bath heating, reductions could be effected in fuel costs, pot replacements, zinc loss in dross and ash, spoiled work, and time lost in firing. There was no doubt that the new heating systems were an important factor in raising the standard of working conditions in general galvanizing shops.

## THE RELATIVE MERITS OF FLUX GALVANIZING AND DRY GALVANIZING

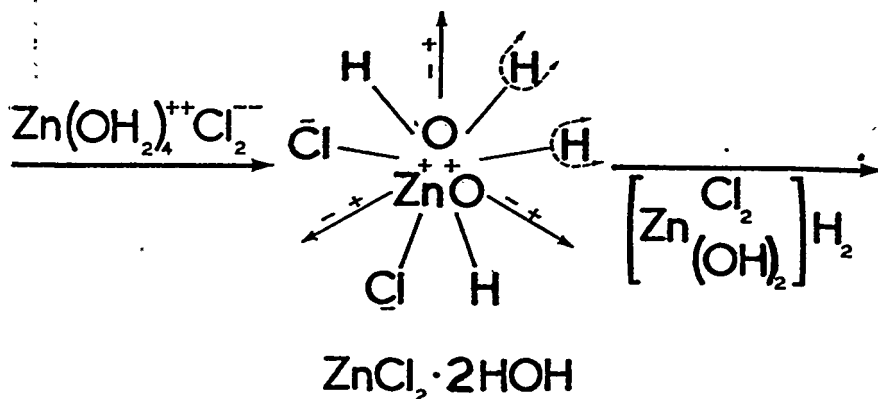
The two processes most widely used in general galvanizing are wet, or flux, galvanizing on the one hand and the dry process on the other. In the former the pickled articles, which may have been washed, are dipped whilst still wet through a substantial flux blanket into the molten zinc bath; whilst in the dry process the work is washed after pickling, prefluxed, and then dried before dipping into the molten zinc, the surface of which is kept relatively clear of flux.

The first part of the third Technical Session at the Conference was devoted to a comparison of these two galvanizing processes and was held under the chairmanship of Mr. H. Busch-Jensen (J. Chr. Jensens Galvaniserings Etablissement). The following chapter discusses the mechanism of fluxing and considers practical aspects of the two processes.

### Author's Introduction

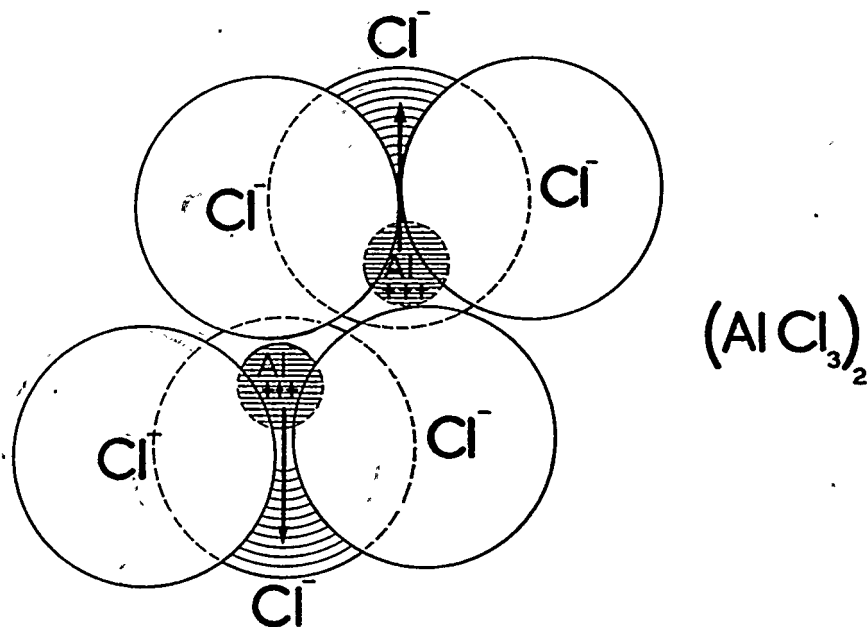
Introducing his paper 'Wet Galvanizing versus Dry Galvanizing', DR. BABLIK thanked the Council for the opportunity of adding some remarks to his paper, and turned to the characteristics of a good flux described on page 77. He explained that the flux discussed there was, of course, the one used in wet galvanizing on the surface of the zinc bath, and emphasized that a good flux was one which had a low basicity, whilst a bad flux was one with a high basicity. A simple measure of this basicity was the relative zinc and chlorine content of the flux. If these were equal, the flux was good, whereas if the chlorine content was much lower than the zinc content — to give an example perhaps only 70 per cent of the zinc — then the flux had a high basicity and must be classified as a bad one.

Dr. Bablik then turned to the flux reaction itself, and the importance of the special configuration of the salts used in fluxing. The term 'ansolvo-acid' as applied to zinc chloride fluxes in his paper on page 79 might not, he said, be familiar to some of those present, and he would like to explain how zinc chloride developed the character of an 'ansolvo-acid'. In an aqueous solution of  $\text{ZnCl}_2$  of low concentration, it could be assumed that the compound was broken up in the ordinary way into  $\text{Zn}^{++}$  and  $\text{Cl}^-$  ions. The metallic ion would, of course, be surrounded by an envelope of water so that the compound would be  $\text{Zn}(\text{OH}_2)_4^{++} \text{Cl}_2^-$  with a hydrated Zn ion. In German this was called Salz-Hydrat-Einlagerungs Verbindung. As the  $\text{ZnCl}_2$  solution became more and more concentrated, the influence of the Cl ion was observed in that the affinity of the oxygen for the proton became lowered, as also did the binding forces of the OH group. Expressed diagrammatically, these changes were:



It was compounds of this class, which had an acidic character in concentrated solution, which were termed 'ansolvo-acids'.

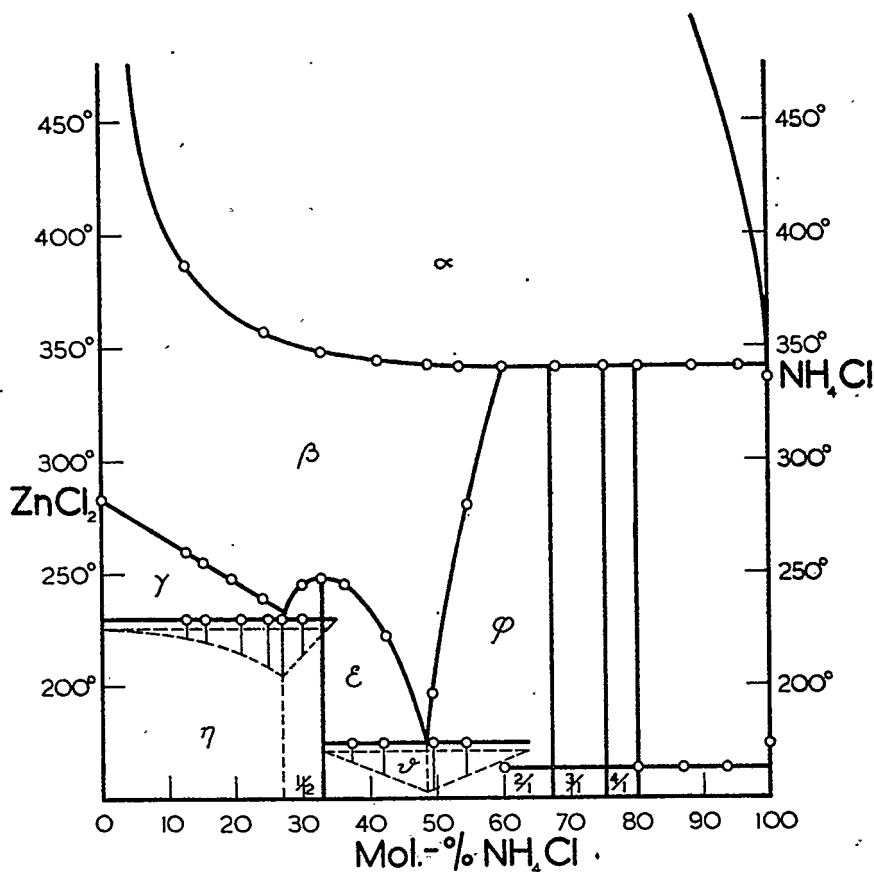
In his paper on page 78 he had referred to the high volatility of aluminium chloride being due to its nature as a fully screened compound. Aluminium chloride was really a double molecule of formula  $\text{Al}_2\text{Cl}_6$ , with the chlorine atoms completely enveloping the compound as shown in the diagram below. The high volatility was explained in this way.



DR. BABLIK then turned to the products used in Austria for fluxing. The Badische Anilin-und-Sodafabrik in Ludwigshafen supplied products for fluxes, and he would mention first those used for wet galvanizing. To form the mother cover, i.e. the first flux layer to be built up on a clean zinc surface, a salt mixture called Inkrustin Zn 14 was recommended. This had the composition 13-14%  $\text{ZnO}$ , 42-43%  $\text{ZnCl}_2$ , and 42-43%  $\text{NH}_4\text{Cl}$ . An explanation of this composition was given at the beginning of his paper. To correct

the flux cover as it became more basic during use, ammonium chloride was added to increase its HCl content. The preference for  $\text{NH}_4\text{Cl}$  in the form of 'dog teeth' was probably due to the inclusion of mother liquor in this salt, the water in this having the effect of accelerating the reaction. The salts recommended for rejuvenating the flux cover were  $\text{ZnCl}_2 \cdot 2\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl}$ , but as the concentration of ammonium chloride in these was lower (only 44% and 54% respectively) their use for this purpose was less effective.  $\text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl}$  was also used as a flux wash.

Turning to dry galvanizing,  $\text{ZnCl}_2$  as a powder of 98-100 per cent purity was used for making up the aqueous flux. Proprietary fluxes were Inkrustin Flux 11 with a content of 87-88%  $\text{ZnCl}_2$  and 11-12%  $\text{NH}_4\text{Cl}$ ; and Inkrustin Flux 26 with 73-74%  $\text{ZnCl}_2$  and 26-27%  $\text{NH}_4\text{Cl}$ . Hachmeister's composition melting point diagram explained their composition (24).



Phase diagram for zinc chloride—ammonium chloride mixtures, after Hachmeister

At 27 mol. %  $\text{NH}_4\text{Cl}$ , equal to 12% by weight, there was a eutectic at 232° C.; and a second one occurred at a concentration of 48 mol.%, equivalent to 28% by weight. The addition of ammonium chloride was, of course, designed to lower the melting range of the salt so that it would melt easily and quickly. This property was of the greatest importance since the fluxing reaction could only take place when molten salt was present on the iron and zinc surface. Of the two proprietary salts mentioned, that with the lower content of

$\text{NH}_4\text{Cl}$  (11-12%) was preferable to the salt of higher  $\text{NH}_4\text{Cl}$  content (26%), although the latter had a still lower melting range. The reason for this was that with the  $\text{NH}_4\text{Cl}$  content as high as 26%, the flux ran off the work too easily. It had also been suggested that the wetting effect of these salts decreased as the  $\text{NH}_4\text{Cl}$  content increased, and to make up for this lost wetting power, special wetting agents were sometimes also added to the flux solution.

Zinc ammonium chloride salts were used for prefluxing at a concentration of 40-43%, since only in such concentrations did the character of an 'ansolvo-acid' become effective. The salt mixture melted at  $230^\circ\text{C}$ . and the best drying temperature was  $180\text{--}200^\circ\text{C}$ . At drying temperatures below  $150^\circ\text{C}$ ., there was danger of too much water remaining in the flux cover and causing excessive oxidation of the zinc and aluminium in the bath, giving too high an ash production. Excessive drying temperatures would cause the flux to decompose in the drying oven and increase the attack on the steel so that it might even happen that there would be insufficient active flux left on the surface of the product.

Summarizing the advantages of the two processes, Dr. Bablik said that dry galvanizing was the more modern way of fluxing, although naturally it could not be employed for all types of article. The most modern way of fluxing was, however, to dispense with the use of fluxes altogether, as in the case of the wonderful Sendzimir process.

## WET GALVANIZING VERSUS DRY GALVANIZING

by H. BABLIK\*, DR.-ING.

### Introduction

The reaction of solid iron with liquid zinc in hot dip galvanizing requires the two reactants to have clean, metallic surfaces. The iron base can be wetted by liquid zinc only if there is no layer of oxides on the zinc surface approaching the iron base, nor any deposit of metallic compounds or residues on the iron base. In fact a reaction between the two metals can take place only if the liquid zinc is enabled to wet the iron surface.

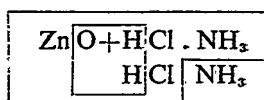
This final cleaning of the two reacting surfaces immediately before they meet is carried out by means of a flux, except in the case where a special galvanizing process is employed which obviates this necessity. In principle, the flux may be applied in one of two ways, called, according to an external, readily seen characteristic, *the wet process* and *the dry process* respectively. This distinguishing nomenclature has been chosen in view of the fact that in the wet process the article is immersed in the zinc bath with its surface wet and in the dry process with its surface apparently dry.

In actual practice the question is often asked — which of these two processes is more advantageous? However, there is no generally acceptable answer to the question in this form; the question should be asked more specifically, namely 'more advantageous to what?' and 'more advantageous in respect of what?' The qualification 'to what' may mean something like 'to what kind of galvanizing process, to what kind of article?' and 'in respect of what' may be used to refer to economy in the consumption of zinc or flux, the quality of the coat produced, the appearance of the galvanized article, and the like.

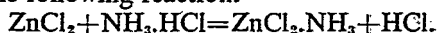
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### The Flux Reaction

To make the answers about to be given more readily acceptable, we crave permission in this connection to throw some more light on the flux reaction proper. The surface is cleaned by the action of molten salts, partly physically by foam formation (similar to soap lather), partly as a result of chemical reactions. The molten salts employed are nearly always zinc chloride melts, prepared either direct from  $\text{ZnCl}_2$  or by reacting  $\text{NH}_4\text{Cl}$  with molten zinc.  $\text{NH}_4\text{Cl}$  must be considered as a molecular compound of the two dipoles  $\text{NH}_3$  and  $\text{HCl}$ . The conventional flux cover is formed according to the following reaction



If there is already some surplus  $\text{ZnCl}_2$  present, it combines with  $\text{NH}_3$  — which would otherwise escape — to form  $\text{ZnCl}_2 \cdot \text{NH}_3$ .  $\text{NH}_4\text{Cl}$  gives with  $\text{ZnCl}_2$  at  $380^\circ\text{C}$ . the following reaction:



On being heated  $\text{ZnCl}_2 \cdot \text{NH}_3$  decomposes to yield  $\text{ZnCl}_2$  and  $\text{NH}_3$ . Thus the fluxing agent proper, i.e. the active molten salt, is also  $\text{ZnCl}_2$  in the case of a 'sal ammoniac flux'. In this instance  $\text{NH}_4\text{Cl}$  is merely the regenerating agent which continually adds chlorine ions to the flux — which is turning basic through use — and thereby restores its reactivity. The compositions of a flux that is still sufficiently active and of an exhausted one, respectively, are shown in the following table:

	Zn		Cl		$\text{NH}_3$		insoluble in acid %	acid sol- uble $\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ %	$\text{O}_2$ %	water (at $105^\circ$ ) %
	%	mol.	%	mol.	%	mol.				
good flux	37.18	0.568	39.6	1.115	5.23	0.307	6.67	0.28	0.17	5.14
exhausted flux	50.81	0.777	31.9	0.898	6.51	0.381	5.26	0.60	5.25	

The quality of a flux may therefore be determined, and the flux graded, by its basicity.

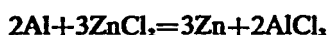
Likewise, it is of importance to the progress of the flux reaction for a melt to be present in accordance with the dictum of the ancients 'non agunt nisi fluida'. There is only a very poor reaction when powders of  $\text{FeO}$  and  $\text{NH}_4\text{Cl}$  are mixed together, whereas a very vigorous reaction takes place between them if they are both added to a melt of  $\text{ZnCl}_2 \cdot \text{NH}_3$ . Fused  $\text{ZnCl}_2$  is likewise able to dissolve and hold  $\text{FeO}$ , and this reaction takes place with greater vigour if  $\text{NH}_4\text{Cl}$  is added at the same time.

### Reaction of Aluminium with the Flux

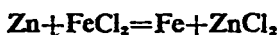
The question 'wet or dry?' is answered by what follows. Dry galvanizing must be used if baths are employed that are alloyed with  $\text{Al}$  to a higher

degree. As is known, such baths are used if the coats to be produced are required to have good flexibility. The Al-content of the zinc bath retards the beginning of the reaction between solid iron and liquid zinc, so that with a short immersion time and the usual immersion temperature only a very light Fe/Zn alloy layer, if any, is formed; but the fact that no alloy layer (which is brittle and consists of inter-metallic phases) is formed enhances considerably the working properties of the zinc coating which is thus not encumbered with an alloy layer. Al-alloyed baths have proved their worth also when it is required to galvanize grades of iron that react very readily with liquid zinc. Sometimes a structure requires the use of steels of superior strength, which is imparted by alloying them with other elements, such as, for example, Si, C or Mn. Steels of this nature react very rapidly with zinc so that extremely heavy alloy layers, rendering zinc consumption prohibitive, would be obtained. It is possible to reduce the velocity of this reaction by alloying the zinc bath with Al. In this case, however, it becomes necessary as a further consequence to resort to dry galvanizing. But the Al-content of a zinc bath is the reason why no flux melt containing a chloride can exist on the surface of such a bath.

According to their behaviour as salts in aqueous solutions metals may, as is known, be arranged in a so-called electrochemical series, leading from the base metals to the noble. This series is so arranged that in it a lower metal will precipitate a higher metal than itself from an aqueous solution of a metal salt, and take its place. In this way one expresses the fact that the linkage of the valency electrons varies with the individual metals. In the same way we must assume for salt melts that in them essentially the same heteropolar linking forces are active as in aqueous solutions, with the exception that in this case there are none of the phenomena associated with the hydration of ions. There is thus a potential series for salt melts, too, and in a similar manner the baser metal displaces a nobler metal from a salt. In this consideration the metals Al, Zn and Fe are of importance, and they appear in the electrochemical series of melts in that order. Thus, the reactions taking place are



and



respectively.

$\text{AlCl}_3$ , as a typical representative of a fully screened compound, is highly volatile; it boils at as low a temperature as  $123^\circ\text{C}$ . Similarly the addition compound  $\text{AlCl}_3\cdot\text{NH}_3$ , with the remarkably high heat of formation of 40 cal./mole, boils at the relatively low temperature of  $400^\circ\text{C}$ . Thus, by reacting Al with  $\text{ZnCl}_2$ , Al would be removed from the bath itself and, at the same time,  $\text{ZnCl}_2$  is removed from the surface of the bath. It is thus impossible for Al in the bath to co-exist with  $\text{ZnCl}_2$  on the surface of the bath, and this is the reason why, if Al is to be retained in the bath, flux is applied to the surface of the article to be galvanized.

### The Dry Process

This is generally performed by first pickling and thoroughly rinsing the articles and then taking them through an aqueous solution of  $\text{ZnCl}_2$  of about 50 per cent strength. As, however, in this manner only 50 per cent of the active flux and 50 per cent of water are deposited on the surface of the article,



it is necessary to dry the article immediately after immersion, which is done by exposing it for about 100 seconds to an oven temperature of 120-200°C. In this manner some 10 g. of  $\text{ZnCl}_2$  per sq. m. of surface is deposited on the article. However, the drying process proper must not be regarded as consisting merely in the evaporation of the water; in fact, it is already part of the flux reaction process. The removal of the water is in its initial stage a concentration of the zinc chloride solution on the surface of the article, whereby the  $\text{ZnCl}_2$  solution assumes the character of an anhydro acid. As soon as the initially 6 mol. solution turns by evaporation into a 9-11 mol. solution, the displacement in the proton affinity of oxygen causes the addition of the polar compound  $\text{H}_2\text{O}$  in such a manner that compounds of the form  $[\text{ZnCl}_2 \cdot \text{OH}]\text{H}$ ,  $[\text{ZnCl}_2 \cdot (\text{OH})_2]\text{H}_2$  or  $[(\text{ZnCl}_2)_2 \cdot \text{OH}]\text{H}$  are formed which have marked acid characteristics. The velocity constant of the sugar inversion of an 11.2 mol. zinc chloride solution, and consequently its acidity, is of the same order as that of a 1.0/mol. hydrochloric acid. Alcoholates of these compounds, such for example as  $[\text{ZnCl}_2 \cdot (\text{C}_2\text{H}_5\text{O})_2]\text{H}_2$ , are known, and it may be justly assumed that glycerin (as a trihydric alcohol,  $\text{CH}_2\text{OH} \cdot \text{CHOH} \cdot \text{CH}_2\text{OH}$ ) or glycol (as a dihydric alcohol,  $\text{CH}_2\text{OH} \cdot \text{CH}_2\text{OH}$ ) added to the sal ammoniac flux are linked in a similar way. In the highly diluted state this acid character is lost, since in this state the zinc chloride is completely ionised and cannot form acidic addition compounds as in concentrated solutions. It seems to be important for the action of the flux that during the drying process the  $\text{ZnCl}_2$  solution acts in the manner of an unsolvated acid. If a drop of an 11 mol. solution of  $\text{ZnCl}_2$  is allowed to dry on a pickled sheet of metal which is then rinsed, it is found that the underlying area has metallic brightness. The effect of an 11 mol. solution of  $\text{ZnCl}_2$  at 170°C acting for 1 hour on a pickled sheet is to cause an iron loss of 0.5 g./100 sq. cm. of surface. In this connection it may be pointed out that all of the organic fluxing agents used in tinplating, such as palm oil, resins, etc., contain considerable quantities of free organic acids, and the effect of the popular metal polishes is attributable to the oxide-dissolving action of free organic acids, such for example as oleic acid  $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ . Consequently, an essential portion of the cleaning action of the flux will take place during drying in the oven. The quantity of flux deposited on the surface seems to depend on the concentration of the solution, whereas the drying temperature and drying time determine the progress of the flux reaction proper. It is necessary for as much of the flux to be used up as appears appropriate for the removal of the superficial impurities, and the flux reaction must not be carried by temperature and duration to a point where the flux is exhausted completely. On entering the zinc bath there must be a sufficient quantity of fresh flux left for the cleaning of the zinc bath surface, and the flux must, at the moment of immersion, be of such a nature that it is readily detached from the article at the bath surface. In the wet process there is a salt melt present on the zinc bath from the start. In the dry process the flux cover must have, on leaving the drying oven, such a composition that its rapid melting is ensured. The addition of  $\text{NH}_4\text{Cl}$  to the solution, as is sometimes practised, promotes the flux reaction as such, and must be so regulated that it does not impede the desirable rapid melting off of the flux cover. E. J. Daniels has published the most satisfactory working methods appropriate to different sets of conditions. (3)

Even though the article leaving the drying oven may appear to have a perfectly dry surface, the salt coat still contains so much absorbed water that it causes oxidation of the zinc, and to an even higher degree the oxidation of

the Al contained in the bath, at the place where the articles enter the zinc bath. Oxidation at the feed-in end thus causes a diminution of the Al-content of the bath, the Al freed from it going into the ashes collecting at that end. Such ashes may contain, for example, 15.2 per cent  $\text{Al}_2\text{O}_3$  and in addition 1.2 per cent Pb and 1.4 per cent Fe. The ashes have been found to have a content of matter insoluble in acids of 24.3 per cent, of which 61.5 per cent was  $\text{Al}_2\text{O}_3$  and 34.2 per cent ZnO. This Al-oxidation — which is quite considerable in some cases — and the formation of  $\text{Al}_2\text{O}_3$ , require on the other hand further additions of flux, because the presence of  $\text{Al}_2\text{O}_3$  on the surface of the zinc bath would impede the wetting of iron by liquid zinc. These ashes are characterized by their high contents of Fe; on 5 consecutive working days it was found to be 1.55, 1.81, 1.75, 2.03 and 1.11 per cent respectively and once, when the Al-content of the zinc bath were particularly high, even 2.5 per cent Fe. By contrast, the Fe-content of a 'sal ammoniac flux cover' as used in wet galvanizing is never in excess of a few tenths of 1 per cent. This striking difference is due to the fact that the removal of iron from the flux cover takes place only by way of the reaction  $\text{Zn} + \text{FeCl}_2 = \text{Fe} + \text{ZnCl}_2$ , which does not occur unless there is a salt melt present. That is the case in wet galvanizing, whereas in dry galvanizing there is no such salt melt present. In the dry process, too, the Fe-salt carried on the surface of the article does pass, mainly during drying, into the flux. However, in this case it is not converted into metallic iron before entering the zinc bath, because there is no chance of the formation of a salt melt that can stay on the zinc bath surface. In view of the fact that the bulk of the dross formed is attributable to the residues of iron salts on the iron surface, dross formation can be materially reduced not only by thoroughly washing the iron surface and thus removing the bulk of iron salt residues from it, but also, in dry galvanizing, by preventing the formation of a salt melt in which the reaction  $\text{Zn} + \text{FeCl}_2 = \text{ZnCl}_2 + \text{Fe}$  might take place.

### Comparison of Wet and Dry Processes

Zinc consumption in the dry process is thus lower, but this is not due primarily to this particular way of flux application, but rather to the fact that this process can be worked with Al-alloyed baths. Likewise, dross formation in the dry process is less than that in the wet process. Another characteristic of the dry process, welcome in most cases, is that its application does not as a rule leave quite so much flux residue on the article. In the wet process it is necessary for each article to be taken through the flux melt, and in this operation it is possible for some solid residue of flux, that cannot be melted off, to remain behind in angles, corners or fillets. Such residues subsequently deliquesce in moist air, and give the article an unsightly appearance. For this reason galvanized articles such as pails, tanks, etc., are generally dry-galvanized, to obviate this shortcoming. Strictly speaking, the dry process has only one disadvantage — it is more troublesome than the wet process. It requires the article to be immersed in  $\text{ZnCl}_2$  solution and subsequently dried, and in addition the  $\text{ZnCl}_2$  solution must be watched all the time. The  $\text{ZnCl}_2$  solution may be prepared from zinc ashes and hydrochloric acid, which is quite simple, but the troublesome part is the necessity of periodically removing the iron from the solution. As drying must be performed in an oven especially designed for this purpose, dry galvanizing can be carried out economically only if a considerable number of uniformly shaped articles are to be galvanized for which one, not too large, type of

### PERFORMANCE OF GALVANIZING BATHS OVER THREE MONTHS' PERIOD

**TABLE 1**

Code No. of Bath	Type of Work Galvanized (a) 1		Weight (a) 3 Galv. Steel	Weight of Zinc Consumed (a) 4		Weight of Ash (a) 5			Weight of Dross (a) 6			Weight of Flux Skimmings (a) 7			Size of Bath (b) 1		Dry or Flux covered (b) 2	Method of Heating (b) 3	Temperature		Allaying Additions (b) 6	Lead Layer (b) 7	Type of Pickling (b) 8	Pretluxing or Pickling Det's (b) 9	If Pretluxed (b) 10		Withdrawal speed (b) 12	Time Factors (b) 11		Standby Procedure (b) 15	Bath surface disturbance (b) 14	Zinc Efficiency (c)	Oxidation. lb./sq. ft. area/working hour		Tons work/hour/ tons zinc in bath (f)	Tons work/hour/ .66 bath wall sq. ft. (g)	Tons work/hour/ sq. ft. bath area (h)
	Description	Classification		Total Zinc in tons	% on steel	Actual tons	Zinc Content	% total Zn	Actual tons	Zinc content	% total Zn	Actual tons	Zinc content	% total Zn	Length Width Depth	Area Sq. ft.			Average (b) 4	Control and check (b) 5					Whether washed	Drying details		Working weeks	Shifts worked				Ash (d)	Oxide (e)			
1	Fabricated steel sheet, rolled steel sections and miscellaneous pressed steel	100% M.S.	1136	110	5.85%	32	88%	25.6%	21	96.5%	18.4%	Nil	—	—	12' 6' 5' 6"	72	Dry	Coal fired with automatic stoker	463°C.	Thermocouple in bath controlling stoker. Checked	Nil	Yes	HCl	Not pretluxed, acid changed 3-4 weekly, mod. well drained	No	65°C. 20 mins.	To suit work	1 11	3 shifts 2 shifts (90 hrs.)	—	Hand skimming	56.0%	0.89	0.05	0.015	0.0077	0.014
2	Fabricated steel sheet and rolled steel window sections	100% M.S.	958.5	55	3.7%	3.5	84%	5.4%	12.5	96.5%	21.9%	Nil	—	—	10' 5' 9"	50	Dry	Gas with motorised valve	463°C.	Thermocouple in bath controlling valve. Checked	Yes. Al as Zn 2.5% Al alloy .001 Al	Yes	HCl	Pretluxed. ZnAmCl with Permanol COL wetting agent	Yes	82°C. 20 mins.	7 1/2 ft/min.	3 9	1 shift 2 shifts (90 hrs.)	—	Special skimming. Entry speed 15 ft/min.	72.6%	0.17	0.04	0.013	0.0056	0.021
3	Mild steel tanks, small sheet work, wirework, angles and plates	100% M.S.	180.42	27.3	10.3%	2.75	89%	8.9%	7.31	95.4%	25.4%	2.16	48.6%	3.9%	10' 6 1/2" 4' 4" 4' 6"	46	Partly f.c. AmCl + comm. glycerine	Coke fired	452°C.	Recorded and checked	Al added	None	HCl	Not pretluxed, acid changed when 6% acid + 120g. Fe/litre by sp. gr. test	No	Dried 4-5 hrs. at 80°C.	Not controlled	12 1/2	2 shifts (90 hrs.)	—	In through flux, out through clear	61.8%	0.12	0.004	0.0044	0.0018	0.0036
4	Dustbins, buckets, baths. 20-31 gauge	100% M.S.	101.62	19.75	19.5%	0.29	81%	1.2%	2.28	96.3%	11.1%	1.7	47.8%	4.1%	6' 4' 3'	24	F.c. AmCl added continually	Coke fired	450°C.	Hand operated pyrometer used	No	Yes	HCl	Pretluxed Ayrton's No. 20	Yes	11 mins. at 160°C.	Not controlled	12	1 shift (50 hrs.)	—	—	83.6%	0.045	—	0.016	0.0043	—
5	Tanks, cisterns, cylinders. 20 gauge — 1/4" plate	100% M.S.	373.7	46.3	8.7%	5.88	75%	9.5%	7.42	94.5%	15.1%	10.04	50%	10.9%	12' 6' 5'	72	Partly f.c. No heavy bath flux	Hot gases from solid fuel	454°C.	Controlled, recorded and checked	5 cwts. 23% Al 77% Zn. .125 Al on Zn	Yes	HCl	Not pretluxed, renewed at 44°F, well drained	No	30 mins. at 52-66°C.	Manual control	11	2 shifts (90 hrs.)	—	Continual skimming	64.5%	0.185	0.006	0.0058	0.0031	0.0054
6	Miscellaneous sheet, tanks, bins, angles, plates	100% M.S.	69.11	26.7	23%	4.14	84%	13.0%	10.60	94.4%	37.4%	0.48	50%	0.9%	12' 3' 4"	36	Flux one end. AmCl and tallow	Coke fired	443°C.	Hand pyrometers, checked	Nominal Al	None	HCl	Not pretluxed, pickle changed every 2 months	No	—	Manual control	13	2 shifts (90 hrs.)	—	Some withdrawn through flux and quenched	48.7%	0.22	0.04	0.0023	0.00073	0.0017
7	Grey iron castings, some sheet work	90% Grey 10% M.S.	172.8	50.0	13.7%	14.49	84%	24.3%	18.1	94.4%	34.1%	Nil	Nil	Nil	10' 5' 4' 6"	50	Dry	Hot gas from external coal furnace	443°C.	Hand pyrometers, checked	Nominal Al	None	HCl	No pretluxing, pickle changed every 2 months	No	—	Manual control	13	2 shifts (90 hrs.)	—	—	41.6%	0.50	0.1	0.0037	0.0016	0.0027
8	Mild steel	100% M.S.	514.3	46.27	6.7%	9.02	75%	14.3%	7.62	95%	15.7%	Nil	Nil	Nil	14' 6' 6" 5'	91	Dry	Gas heating	450°C.	Controlled, recorded and checked	No	None	HCl	No pretluxing, acid changed when necessary, thoroughly drained	No	—	Manual control	13	3 shifts (120 hrs.)	430°C.	—	70%	0.14	—	0.0041	0.0024	—
9	Steel window frames	100% M.S.	5220	420.3	6.5%	56.4	86%	11.5%	53.2	97%	12.3%	—	—	—	8' 5' 9"	40	Dry	Producer gas, remote combustion, re-circulation	454°C.	Dual thermostatic control, periodic check	.02% Al on Zn as 2% alloy	Yes	H <sub>2</sub> SO <sub>4</sub>	No. 20 flux 30%	Yes	Below 180°F.	Controlled	52	2 shifts (100 hrs.)	Covered	Normal skimming	76.2%	0.61	0.1	0.015	0.0064	0.0025
10	Steel window frames	100% M.S.	1496.5	145.8	6.0%	39.85	86%	23.5%	27.35	97%	18.2%	—	—	—	11' 7' 6" 6' 7"	82	Dry	Producer gas, remote combustion, re-circulation	454°C.	Dual thermostatic control, periodic check	.02% Al on Zn as 2% alloy	Yes	H <sub>2</sub> SO <sub>4</sub>	No. 20 flux 30%	Yes	Below 180°F.	Controlled	52	2 shifts (100 hrs.)	Covered	Normal skimming	58.3%	0.21	0.04	0.0031	0.0018	0.0036

## PERFORMANCE OF GALVANIZING BATHS OVER THREE MONTHS' PERIOD

Baths 11-20

Baths 11-20

Baths 11-20

Baths 11-20

Code No. of Bath	Type of Work Galvanized (a) 1		Weight (a) 3 Galv. Steel	Weight of Zinc Consumed (a) 4		Weight of Ash (a) 5			Weight of Dross (a) 6			Weight of Flux Skimmings (a) 7			Size of Bath (b) 1		Dry or Flux covered (b) 2	Method of Heating (b) 3	Temperature		Alloying Additions (b) 6	Lead Layer (b) 7	Type of Pickling (b) 8	Prefluxing or Pickling Det's (b) 9	If Prefluxed (b) 10		Withdrawal speed (b) 12	Time Factors (b) 11		Standby Procedure (b) 15	Bath surface disturbance (b) 14	Zinc Efficiency (e)	Oxidation. lbs./sq. ft. area/working hour		Tons work/hour/tons zinc in bath (f)	Tons work/hour/.66 bath wall sq. ft. (g)	Tons work/hour/sq. ft. bath area (h)
	Description	Classification		Total Zinc in tons	% on steel	Actual tons	Zinc Content	% total Zn	Actual tons	Zinc content	% total Zn	Actual tons	Zinc content	% total Zn	Length Width Depth	Area Sq. ft.			Average (b) 4	Control and check (b) 5					Whether washed	Drying details		Working weeks	Shifts worked				Ash (d)	Oxide (e)			
11	Tubes, fittings, etc. 60%, fabricated sheet material 38%	0.5% Grey 99.5% M.S.	1046	127	5.8%	45.8	88%	31.7%	30.45	95.7%	23%	0.25	(50%)	0.1%	23' 4' 6" 4' 11"	102.6	Dry. Occasional ZnAmCl+saw-dust	Temperature controlled, mechanical stoker	443-454°C.	Hg-in-steel pyrometer, recorder and controller, no check	Nil	None	HCl (HF for sandy castings)	Not prefluxed, .7 lb./gallon Fe max. drain and dry	—	—	Not controlled	26	2 shifts (90 hrs.)	430°C. at standby	5-30 times per hour	45.2%	0.42	0.07	0.0049	0.0025	0.0045
12	Fabricated sheet material 35%, nails 25%, tubes, fittings and pipes 25%	3% Grey 97% M.S.	417	74.6	10.7%	15.75	87%	18.3%	21.1	96.1%	27.2%	0.75	(50%)	0.5%	10' 3' 6" 3' 6"	34.52	Dry. Occasional ZnAmCl+saw-dust	Temperature controlled, mechanical stoker	443-454°C.	Hg-in-steel pyrometer, recorder and controller, no check	Some Cindal Z 25 occasionally	None	HCl (HF for sandy casings)	Not prefluxed, .7 lb./gallon Fe Max. drain and dry	—	—	Not controlled	26	2 shifts (90 hrs.)	430°C. at standby	5-30 times per hour	54%	0.44	0.07	0.0085	0.0028	0.0054
13	Fabricated steelwork, screws, nuts, bolts, wirework, conduit fittings and castings	10% Grey 25% Malleable 65% M.S.	622	82	7.4%	10.5	70%	9.0%	32.5	(96%)	38%	1.5	(50%)	0.9%	7' 2' 6" 3'	17.5	Generally f.c. AmCl rough	Coke fired	465°C.	Recording instruments, checked	Nil	None	HCl	No. 20 flux	Not washed	No special oven	Not controlled	12	2 shifts (88 hrs.)	440°C. at standby	Much disturbance	52.1%	1.3	0.09	0.066	0.015	0.034
14	24 gauge to 1" plate steel, wirework, expanded metal, some tubes and fittings, chains	6% Grey 94% M.S.	178.2	28.95	11.1%	3.17	(85%)	9.3%	7.3	(96%)	24.2%	2.8	(50%)	4.8%	12' 4' 6" 4'	54	Sometimes AmCl used	Coke fired	448°C.	Judged by operators	Nil	None	HCl (HF for castings)	Not prefluxed, pickle not changed, only added to. Work well drained	No	—	Not controlled	12 (1 holiday)	2 shifts (90 hrs.)	—	Much disturbance	61.7%	0.13	0.015	0.0049	0.0020	0.0031
15	General sheet metal work, 24-16 gauge	100% M.S.	136.3	23.4	7.3%	7.3	(85%)	27.7%	7.3	96%	31.3%	In ash	—	—	6' 4' 4'	24	Dry	Coke fired. 12.8 tons coke used	450°C.	—	Nil	No lead added	HCl	Not prefluxed	No	Dried	Not controlled	12	3 shifts (112 hrs.)	—	—	41%	0.51	0.02	0.006	0.0019	0.0040
16	Castings, wrought iron and sheet iron work	20% Grey 40% Malleable 40% M.S.	103.8	7.87	4.8%	0.26	(80%)	2.7%	2.8	(96%)	34%	Flux	thrown away	—	5' 3' 3'	15	Flux covered	Coke fired	430-470°C.	—	Very little	None	HCl 102 carboys used	Not prefluxed	—	—	Not controlled	13	2 shifts (90 hrs.)	—	Frequent disturbance	63%	0.033	0.005	0.012	0.0028	0.0058
17	Fabricated mild steel, tanks and cylinders, 18 gauge to 1" plate	100% M.S.	772	79.2	6.6%	1.74 (of which .63 during standby)	92%	2.0%	10.55 + 4.35 = 14.9	89%	18.8%	13.0	55%	9%	14' 6" 7' 6" 6"	109	Mostly dry, but some in through fl. out clear	Coke fired	450°C. Light Products 460°C.	Pyrometer periodically checked	.001% Al on Zn added as Cindal Z 25	6"	HCl	Pickle changed every 5 weeks. Work well drained and dried	—	—	Not controlled	12 (1 holiday)	2 shifts (100 hrs.)	435-440°C. at standby	Minimum disturbance	60.2%	0.033	—	0.0068	0.0040	—
18	Fabricated sheet 50%, angles, channels and flats 30%, some wirework, rods and tubes	100% M.S.	66.7	9.45	9.7%	3.43	87%	31.6%	0.6 Estimated	95.6%	6.0% Estimated	—	—	—	10' 4' 4' 6"	40	Dry	Special gas heating system	440-450°C.	Pyrometer controlling gas supply, weekly check	Some Al added	Lead from zinc	HCl	Prefluxed 4 1/2 lb./gal. 54% AmCl 46% ZnCl <sub>2</sub>	Yes	No special oven	Not controlled	8	2 shifts (100 hrs.)	Insulating cover at standby	Normal skimming	62.4%	0.24	0.02	0.0026	0.00099	0.0022
19	Sheet work 75%, angles, channels and flats 20%	100% M.S.	206.8	31.38	8.7%	11.88	87%	33%	4.52	95.6%	13.8%	—	—	—	15' 4' 4' 4'	60	Dry	Coke fired	440-450°C.	Pyrometer, weekly check	Some Al added	Lead from zinc	HCl	Prefluxed 4 1/2 lb./gal. 54% AmCl 46% ZnCl <sub>2</sub>	Yes	No special oven	Not controlled	13	2 shifts (100 hrs.)	Not covered	Normal skimming	53.2%	0.34	0.015	0.0038	0.0016	0.0027
20	Cisterns, cylinders and tanks	100% M.S.	330.7	43.4	8.8%	13.8	92%	29.2%	4.1	94.5%	8.9%	—	—	—	9' 5' 4'	45	Dry	External coal furnace, regenerative setting	450°C.	Controlled	.05% Al on Zn	None	HCl	Prefluxed No. 20 flux	Yes	—	Controlled	12	2 shifts (90 hrs.)	—	Continual skimming	61.9%	0.63	0.055	0.0063	0.0027	0.0067

oven suffices. Where articles of a great variety of sizes and shapes are to be galvanized the wet process is preferable by virtue of its great simplicity.

In comparing the respective costs the following factors have to be taken into consideration: the relatively inexpensive preparation of  $\text{ZnCl}_2$  from the comparatively cheap zinc ashes, and the cost of sal ammoniac; the cost of the removal of iron and, if required, the cost of concentrating the  $\text{ZnCl}_2$  bath; the cost of heating the drying oven. Since the articles already have a somewhat raised temperature when they enter the zinc bath, a lesser quantity of heat need be supplied to the bath. Considering the low efficiency factor of galvanizing pots this saving will not amount to much, though; a very considerable saving is effected, on the other hand, by the lesser quantity of zinc consumed in the dry process, a much lighter coating being deposited and less dross produced. It must further be considered that, according to the reaction  $\text{ZnO} + 2(\text{NH}_3 \cdot \text{HCl}) = \text{ZnCl}_2 \cdot \text{NH}_3 + \text{H}_2\text{O} + \text{NH}_3$ , some 65 kg. of zinc are withdrawn from the zinc bath for every 108 kg. of sal ammoniac used up. It is true that this zinc remains inside the sal ammoniac layer but it then has a form in which it is of almost no use at all, so that in this way the quantitative consumption of zinc as such is about 0.5 per cent higher in the wet process.

Another advantage of the dry process, of which not many galvanizers seem to be conscious yet, is — more especially in the galvanizing of sheet — this: It is important for the formation of a zinc coat of uniform weight and pleasing crystalline appearance that the iron base be thoroughly wetted without the interference of not readily wettable solid particles, or of occluded gas bubbles or gas bubbles just detaching themselves from the surface. In the manufacture of tinplate it is usual to heat the sheets for some length of time in a palm oil bath after pickling and before immersing them in the tin bath. Likewise, it is customary in the mechanized wet-galvanizing process to keep the sheets immersed in clean water for some length of time. Both operations serve to remove any hydrogen that may have been absorbed in pickling, before the sheets enter the molten metal. The underlying purpose is to ensure that the hydrogen is removed before the sheets enter the metal bath, as otherwise the escape of hydrogen inside the bath would disturb the formation of the zinc coat and produce what is called the 'grey sheet' appearance. In the dry process this removal of hydrogen is not only carried out at a greater speed as a result of the higher temperature in the drying oven, but it is also made easier by the  $\text{ZnCl}_2$  cover produced. It is obvious that the  $\text{ZnCl}_2$  present on the iron surface facilitates both the penetration of hydrogen into, and its escape from, the iron. Little as the role played by hydrogen in the formation of the zinc coat may be appreciated as yet, it is of highly decisive importance in the assessment of the respective merits of the wet and the dry processes. In point of fact it would appear that an increased hydrogen content leads to a deterioration of the alloy layer formed and, at the same time, to increased zinc uptake.

### Conclusion

In conclusion it may be said that the dry process, as a more recent development, has many advantages over galvanizing by the wet process, insofar as zinc consumption and the quality of the coat are concerned. It is, however, cumbersome, less uniform in its progress, requires certain basic plant and is, above all, practicable only where articles of uniform shape and size are to be galvanized and the coats produced need not be particularly heavy. For the galvanizing of articles of a great variety of shape and size and of complicated contour, on the other hand, the wet process is superior to the dry process.

## Introduction

In the unavoidable absence of Mr. Liban, the Chairman then asked Mr. R. Stewart (Smith & McLean Ltd.) to introduce the short paper from Mr. Liban on the Relative Merits of Flux Galvanizing and Dry Galvanizing.

MR. STEWART said that he knew members of the Conference would be disappointed that Mr. Liban had been prevented from attending the Conference at the last minute, as he was sure that many of those present would like to have asked him questions about flux galvanizing. He was, however, happy to introduce the paper, as he was closely associated with the Liban process, which had been used in his works with every success for many years. Although he was not free to give detailed information about the process, he would be happy to answer such questions arising from the paper as he could.

## SOME NOTES ON THE RELATIVE MERITS OF FLUX GALVANIZING AND DRY GALVANIZING

by T. LIBAN,\* DIPL. ING.

### Galvanizing with Flux on the Zinc Bath Surface

The molten flux on the surface of a zinc bath during hot dip galvanizing is superheated and is therefore strongly reactive. A good flux should contain at least 8 per cent of ammonia, for although it is largely the hydrochloric acid in the flux which makes it possible for the zinc to cover the dipped article, the ammonium chloride is itself important, as it can absorb metal oxides such as zinc oxide with the formation of oxychloride, metal chloride and ammonia. By the addition of small amounts of glycerine, tallow or similar substances, a foam is produced in the flux which facilitates covering. The extent to which the bath surface is covered with flux depends on the size and form of the articles being zinc coated. The covered part of the bath surface is protected from oxidation, and the zinc ash formation with this method of working averages about 6 per cent of the total zinc used. Where the article to be galvanized requires the whole surface of the bath for its immersion, the flux covers the whole surface, and is skimmed back for the article to be withdrawn from the bath.

The functions of the flux are as follows:

- (1) It allows wet articles to be introduced into the bath without danger.
- (2) It preheats the articles.
- (3) It completely dries the articles, and so prevents liquid zinc being sprayed from the bath by trapped moisture.
- (4) It takes up and dissolves residues and iron salts from the surface of the articles, and so prepares a metallically clean surface for galvanizing.

A flux prepared from ammonium chloride performs these duties perfectly, provided that it is sufficiently liquid and of sufficient depth. Massive heavy gauge articles do, of course, require a deeper layer of flux; for otherwise either the flux will solidify on them and prevent perfect galvanizing being attained; or the rate of immersion of the article into the liquid zinc will have

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to be slowed up to such an extent that production is reduced. A flux layer of sufficient depth will allow the article to be plunged quickly into the liquid zinc. The molten flux also has the advantage that it can usually deal with small pickling faults which have been overlooked.

All the types of articles which are normally hot dip galvanized can be successfully treated by the use of a flux on the zinc bath surface. Where only part of the surface of an article is to be galvanized, the remaining surface is covered with a protective coating before dipping through the flux which protects it against the attack of flux and zinc. For this protective coating, slurries of water glass solution with porcelain earth, clay and similar materials are preferred. The protective coating is dried hard on to the surface of the article before dipping.

As a result of the reactions occurring during fluxing, basic zinc salts are formed which may swim on the surface of the flux as solid bodies, but mainly collect under the fluid flux on the bath surface, together with graphite particles, sand, etc. taken up by the flux from the surface of the work. These deposits make up the flux skimmings which form to the extent of 1.5 parts for every one part of ammonium chloride used. The flux skimmings are ladled off at short intervals by perforated ladles, and contain on an average about 50 per cent of zinc. About half of this will be metallic zinc, according to the care with which the flux skimmings are removed. This metallic zinc is in the form of shot-like particles containing about 2 per cent iron. The remainder of the zinc will be present as chlorides. When ammonium chloride is used to produce the flux, the zinc content of the flux skimmings removed from the bath amounts on the average to about 3 per cent of the total zinc used.

In producing the flux, it is an advantage to use zinc ammonium chloride double salt of 22 to 24 per cent zinc content, as the zinc in the flux is then obtained without removing it from the bath. Some ammonium chloride has still to be used, however. The main argument against using the double salt is that its price is too high.

Since flux skimmings sell at a very low price, it would appear to be more economic, even though the zinc chloride were lost altogether, to extract the metallic iron-containing zinc from them. This can be done in a primitive fashion and at small cost. More profitable, however, is the simultaneous recovery of zinc chloride solutions for prefluxing the articles before dipping in the zinc bath. It is not recommended that the entire zinc content of the flux skimmings be recovered as zinc ammonium chloride, as the galvanizing process can use only a part of this, and for the remainder the possibility of disposal is limited. The author recommends the more economic procedure of producing from the flux skimmings metallic zinc, zinc ash and solid zinc ammonium chloride in such quantities as the plant can itself consume. After the iron has been removed from the metallic zinc, this and the zinc ash are re-introduced into the galvanizing process. The apparatus for this treatment is inexpensive and requires little factory space or expenditure on labour. In works of average size, the treatment is well worth adopting.

The iron content of the zinc in the flux skimmings arises from the reaction with the molten zinc, of the iron chlorides on the surface of the articles, and it should be noted that this metallic zinc, a shot-like material, is embedded in the flux skimmings and therefore mostly removed from the bath when the flux skimmings are ladled out, so that the formation of hard zinc cannot be increased by this iron-containing zinc to any important degree.

**Galvanizing with Dry Flux on the Surface of the Article**

In this process, the articles are dipped in concentrated zinc chloride solution (about 40-45° Bé) mixed with ammonium chloride solution, and dried in a special oven at about 100-150°C. The dried articles are then dipped into the molten zinc, the surface of which is uncovered. The flux dried on to the surface of the articles melts away and mingles with the zinc ash which is formed, so that this therefore contains large amounts of chloride. On the average 20-35 per cent of the total zinc used is converted to zinc ash in dry galvanizing.

Articles which owing to their size and shape cannot be treated in the drying oven are dried over the surface of the zinc bath, whereby a part or even the whole of the working space of the pot is put out of action for a time. Furthermore, dry galvanizing is not without its dangers. Only smooth articles having no rolled edges or borders can be galvanized without zinc splashing, as traces of moisture are always present in the interstices of the seams and edges.

It has been contended that less heat is taken from the bath by the introduction of heated articles than is the case in wet galvanizing, but a more important factor is the loss of heat by radiation from the surface of the bath which will be much less in wet galvanizing owing to the covering of part of the bath surface with flux.

Under the heading of Dry Galvanizing, mention should also be made of the primitive method of sprinkling with sal ammoniac. Sometimes wet articles from the pickling tank are sprinkled with sal ammoniac powder and dried over the bath, or alternatively the sal ammoniac powder is sprinkled on the zinc surface as the articles emerge from the zinc bath. So many disadvantages are involved in this method of galvanizing that it is carried out only in rare cases.

**Summary**

The relative merits of flux galvanizing and dry galvanizing may be summarized under the following four headings:

*Zinc Loss in Ash and Flux Skimmings*

- a) In flux galvanizing. The zinc in the flux skimmings averages about 3 per cent of the total zinc used, that in the ash being about 3.9 per cent of the total zinc. The flux skimmings and zinc ash together account for a 6.9 per cent zinc loss.
- (b) In dry galvanizing. The average zinc loss in the zinc ash is 27 per cent of the total zinc used. Owing to its chloride content, the ash is much depreciated in value, and even after the metallic zinc has been removed from this ash at considerable expense, there still remains in it about 11 per cent of the total zinc used.

*Hard Zinc Formation* is the same in both flux and dry galvanizing, under similar conditions of work.

*Drying Oven.* Maintenance and service of the drying oven is an expensive item in dry galvanizing.

*Production Rate.* Flux galvanizing allows higher throughput than dry galvanizing.



## DISCUSSION

### Mechanism of Fluxing

MR. M. L. HUGHES (British Iron and Steel Research Association) opened the discussion by commenting on the theoretical explanation for the mechanism of fluxing given in Dr. Bablik's paper. Was not the proposed mechanism of fluxing perhaps needlessly elaborate? Surely fluxing could be explained on the assumption that zinc chloride and ammonium chloride both contributed to fluxing by forming hydrochloric acid, the former by hydrolysis and the latter by dissociation under heat. The gaseous hydrochloric acid acted on the surface of the steel in the same way as it did in gas pickling. He agreed that zinc chloride and ammonium chloride assisted one another, the zinc chloride allowing the ammonium chloride to be retained at the temperature of galvanizing. He said that the diagram of Hachmeister for zinc and ammonium chloride might need modification. Evidence from hot tinning supported this simple theory of hydrolysis, i.e. the action of water in releasing hydrochloric acid during fluxing. The tin coating was only one-tenth as thick as the galvanized zinc coating, and unless the fluxing were perfect, the tin retracted leaving uncoated spots. Zinc chloride was used as the flux in tinning and to ensure hydrolysis the sheets were sprayed with water.

Referring to Dr. Bablik's parallel between zinc chloride and palm oil as a flux, he said that palm oil as a tinning flux was fifty years out of date except for certain special orders. Its slow action had delayed the growth of the tinsplate industry by holding up mechanization. Equivalent fluxing times were 20 to 30 min. with palm oil, and half-a-second with zinc chloride. He suggested that the organic acids were not, therefore, very active fluxes. He asked Dr. Bablik why sugar inversion was suggested for the measurement of acidity instead of, say, a pH meter using a glass electrode. Measurement in that way was both more accurate and needed less skill.

DR. BABLIK in reply said he was glad to know about possible modifications in the flux phase diagram. Being somewhat isolated from Western sources of information, he was not aware of them. Referring to palm oil, he agreed that it was not a good flux, but still suggested that it owed its properties to its acid character. Glycerol and other similar addition substances were used not so much to improve the activity of the flux as to make it more frothy and deeper. On the method of measuring acidity he said the method of sugar inversion was not his but that of Professor Merwin.

MR. R. S. BROWN (Rylands Bros. Ltd.) then asked for information about the use of lactic acid in fluxes, to which DR. BABLIK replied that this acid was used to replace glycerine and the other more usual addition agents when these were in short supply. He thought lactic acid had no special virtue.

MR. D. N. FAGG (British Non-Ferrous Metals Research Association) then questioned Dr. Bablik's statement that in wet galvanizing with fluxes of the zinc ammonium chloride type, zinc chloride was the 'fluxing agent proper', and supported Mr. Hughes's remarks that the fluxing action was best attributed to the hydrochloric acid liberated by the flux. Evidence of this was obtained by E. J. Daniels (3) who showed that, when the formation of hydrochloric acid from zinc chloride by hydrolysis was prevented by a previous heat treatment to remove all the water, the solvent power of zinc chloride for iron oxide at 475°C. was almost negligible.

Dr. Bablik, he said, had also stated in his paper on page 80 that the removal of iron from the flux by zinc could only occur in the presence of a salt melt; hence under the conditions existing in the dry process, this reaction would not be expected to occur. In contrast to this, however, Daniels found that even with the dry process the iron salts formed on the surface of the work during the drying of the flux coat were definitely reduced by the zinc during subsequent immersion in the bath, the iron going to form dross. In reply, DR. BABLIK agreed that the work of Daniels was important, but said that he thought it could be reconciled with his own.

MR. W. MONTGOMERY (Fredk. Braby & Co. Ltd.) said it was a privilege to be able to question Dr. Bablik in person after studying his work for so many years. He would like to ask at what aluminium content of the bath would ordinary flux cease to be effective in dry galvanizing, and whether Dr. Bablik would recommend any special flux for use on baths of higher aluminium content.

DR. BABLIK said he thought 0.02 per cent aluminium was the limit for zinc-chloride type fluxes, but that the aluminium content of the zinc could only be determined spectrographically. On the question of special fluxes, he said that Liban claimed to have a flux for use on baths of higher aluminium content, but what it was he did not know.

### The Liban Process

MR. F. C. BRABY (Fredk. Braby & Co. Ltd.) also expressed his appreciation of Dr. Bablik's presence, and welcomed the opportunity of thanking him for his invaluable book and his articles which had provided guidance for ordinary galvanizers for many years. He had seen the Liban process operating many years ago when a thick frothy flux had been used, but more recently a very fluid flux seemed to be preferred. He knew that much research was being done to find the best flux for wet galvanizing, but he did not think that this had yet been found.

In response to the Chairman's request, MR. STEWART then said a few words about his firm's experience with the Liban process. It had been adopted many years ago and he considered it better than their previous method. The Liban flux was very fast flowing, and he was most satisfied with it. Although he could not say how much aluminium was used, more was added to his baths than had so far been referred to by anyone at the Conference. Although considerable amounts of tubes and hollow-ware were galvanized, no troubles with flux adhering had been experienced.

MR. HUGHES asked about flux inclusions which were, he suggested, most troublesome when the flux was 'out of condition'. He asked whether flux inclusions were lessened when using the Liban flux, to which MR. STEWART replied that they had less trouble with flux inclusions than before, although the human element must always be taken into account. In reply to further questions, Mr. Stewart said that all types of work were galvanized by this process, and that no special after-treatment was needed other than that which had previously been used.

MR. MONTGOMERY said he was sorry that he could not ask Mr. Liban personally more about the treatment of flux skimmings referred to on page 83. He failed to see why anyone should want to make zinc ash from flux skimmings. He doubted whether good zinc could be recovered from the small particles of iron-contaminated shot.

### Relative Merits of the Two Processes

MR. HUGHES said that among the sheet galvanizers in South Wales the choice between wet and dry galvanizing had already been made. The dry galvanizing process had at one time attracted them because of its promise of providing sheet with a flexible coating. It had, however, been rejected as unsatisfactory even when run by continental operatives. The reasons for this were the very large output, 20 to 30 tons per shift being usual from a pot, and the high zinc efficiency of 85 per cent which was obtained with the present process. When dry sheet galvanizing was used, there was a high loss due to ash formation. In the normal sheet process, the baths remained covered and so very little ash was formed.

MR. H. T. EATWELL (G. A. Harvey & Co. (London) Ltd.) questioned Dr. Bablik's conclusion that dry galvanizing was best for uniform shapes and wet galvanizing for more complicated articles, and asked about the difficulty with flux staining from trapped flux with the latter class of articles.

DR. BABLIK agreed that this could be a difficulty and gave examples of his preferences. For the galvanizing of a hollow mast he would recommend the wet process, but for buckets and such articles where flux could be trapped in rolled edges and corners, he preferred the dry process. In Austria, where zinc was scarce, dry galvanizing was also used to save zinc in sheet galvanizing, as a thinner coating was obtained in this way.

In response to the Chairman's request, MR. BRODBECK-KELLER (Verzinkerei Pratteln A.-G.) gave his experience with the wet process of galvanizing. He said that no dry galvanizing was done in Switzerland. Although Swiss galvanizers treated the widest range of articles, only the wet galvanizing process was used, as they believed that dry galvanizing would only be economic for long runs of similar material. Referring to a well-known flux galvanizing process, he said that he had been one of the first to use it. In practice, however, not all the claims made for the process appeared to him to be justified. The process had certain advantages, and he had found that when galvanizing structural steelwork, the pick-up of zinc by the steel had been reduced from 3 per cent when using the old process to  $1\frac{1}{2}$  per cent with the new. Similarly in galvanizing hollow-ware, between 20 and 25 per cent zinc saving had been achieved. The disadvantages of the process were that it was not really suitable for all types of articles. He thought it good for tubes, but not so generally satisfactory for light hollow-ware. He had found that the zinc ash saving had not been as great as had been promised, because the zinc ash was returned to the flux with the result that this was more quickly spoiled. In his experience the changeover had not fulfilled the claim that dross production would fall by 20 per cent, as he made more dross with the new process than before he had adopted it.

At the request of the Chairman, MR. EATWELL then commented on the dry process as used in his plant. Conditions there were now very different from the old days when there was little scientific control of the process. His works galvanized materials varying from small parts to individual pieces weighing up to 4 tons, and he had found the dry process very satisfactory for them all. The dry process fulfilled the two basic functions of producing an article satisfactory to the customer at a profit to the galvanizer. The improvements in his works had been first in pickling control, keeping the iron content of the liquor under control so that the iron carried over to the baths was reduced. This had resulted in less dross formation, savings of from 20 to 25 per cent having been obtained. Then washing and prefluxing were

introduced and the dross formation had fallen still lower. The subsequent introduction of drying had saved time once the initial difficulties had been overcome, and had made the process safer for the operators. The difficulties had been due to drying at too high a temperature. Difficulties still occurred with prefluxed work if it was left too long after removal from the oven, and this was leading them to co-ordinate more closely their pickling and dipping programmes. Concluding, Mr. Eatwell said he was a little apprehensive about the effectiveness of flux galvanizing in treating closed vessels. Many of those he galvanized had only small pipe connections, and they were satisfactorily coated by dry galvanizing. He did not see how this result could have been achieved so successfully had the wet process been used.

## GALVANIZING RESIDUALS AND THEIR TREATMENT

Increases in the price of zinc during recent years have turned the galvanizer's attention more and more to the importance of keeping the amount of zinc lost in galvanizing residuals to a minimum. The primary task in combating these losses is so to control the process that less ash, dross and flux skimmings are made; but attention is also being given to the development of economical methods of recovering useful zinc from these residuals.

The interest of the industry in these questions is reflected in the three papers presented to the Conference under the general heading of 'Galvanizing Residuals and their Treatment' and in the discussions which took place during the second half of the third Technical Session when these papers were considered under the chairmanship of Mr. H. Busch-Jensen.

### Author's Introduction

MR. BAILEY introduced his survey of the formation of residuals from general galvanizing baths by referring to the considerable amount of tabulated data which it presented. The extent of this was, he said, a measure of the work which had been put into this paper, not his work alone, but that of all his colleagues on the Association's Technical Committee, whose labours had made the survey possible. The paper was the first of its kind ever to be published, and typified the pioneer work which the Association was doing in making available factual information about galvanizing for the benefit of the whole industry.

Questions had been asked (by those who did not quite understand the open-handed way in which the Hot Dip Galvanizers Association worked) as to why this paper had been published when it revealed certain shortcomings in the industry. In reply, it could be said that, apart from the new outlook which the Association was bringing to the galvanizing industry, an answer to this objection might be found in a parallel case drawn from military tactics, where today speed was more important than secrecy. By the time the enemy had picked up and acted on the information contained in a military dispatch, the operation had often been completed. So in the galvanizing industry they were building on their experience and moving forward, and the Association need not, he thought, be ashamed of publishing information about conditions in the industry when the Association started. It was for this reason that the paper referred in its title to a survey made in 1949.

MR. BAILEY then referred to three important conclusions arising from the survey: (1) the big variations in the relative efficiency of different plants, which pointed the way to the possibilities of widespread improvement; (2) the very variable nature of zinc ash and its high metallic zinc content which indicated the possibility of large scale zinc recovery from the present ash and the need for further work to reduce the metallic zinc content of ash in the future; and (3) the important effect on dross production of washing work

after pickling, the figures for dross production from those plants which were washing being on the average almost 50 per cent lower than those from plants where iron salts from the pickling were brought forward to the galvanizing bath. He referred in this connection to the paper by Hall and Fagg, where figures were given for the quantity of iron salts present on the surface of work dried after pickling in hydrochloric acid liquor containing 75 grammes of iron per litre. The iron salts were equivalent to the loss, as dross, of 14 per cent of the zinc used for galvanizing the steel. In view of the big savings when the work was washed, and particularly Mr. Eatwell's remarks that he had reduced dross formation by careful control of the iron content of his pickling baths, he suggested that the Association should give more consideration to the possibilities of reducing dross formation by careful control of the pickling acid in members' works where washing and prefluxing were not used.

## A SURVEY OF THE FORMATION OF ZINC ASH, DROSS AND FLUX SKIMMINGS FROM GALVANIZING BATHS DURING 1949

by R. W. BAILEY\*, M.A., B.SC., F.I.M.

This paper describes a survey made by the Technical Committee of the Hot Dip Galvanizers Association on a cross section of galvanizing baths typical of those operating in different branches of the general galvanizing industry during 1949.

Among the primary objects of the Hot Dip Galvanizers Association founded at the end of 1948 is, to quote from its Constitution, the undertaking of work 'to improve technique and working conditions in the industry'. It early became apparent that before any comprehensive programme of work to improve galvanizing technique could be undertaken, factual information would be necessary about current works' practice and bath performance. This was particularly true in the field of secondary or residual formation, where very little definite information was available about the extent to which zinc ash, flux skimmings and zinc dross were being made, the figures quoted by the different firms represented on the Committee varying between wide limits. It was therefore decided to make a survey of the position by keeping accurate records of the performance of a number of galvanizing baths operating on different classes of work with the objects of finding the extent to which secondary formation was a serious problem in the industry and, if possible, the variations in the amount of secondary material formed when different classes of articles were galvanized and when different galvanizing techniques were used.

At the time this work was being considered, the British Non-Ferrous Metals Research Association had set up a Committee to control a research, which had been asked for by a number of galvanizers who were Members of that body, on zinc losses in general galvanizing. The Research Association soon reached the same conclusion as the Hot Dip Galvanizers Association, namely, that before real progress could be made, factual information must be obtained about the extent to which zinc losses were occurring in a representative cross-

\* Zinc Development Association

section of galvanizing plants. To avoid any unnecessary duplication of effort, steps were therefore taken to co-ordinate the two programmes of work, and it was mutually agreed that the H.D.G.A. with its wide membership should undertake this industrial survey.

A comprehensive statement of the information needed about the performance of each bath was therefore drawn up by the two Associations and sent in the form of a concise questionnaire to each of the firms who had agreed to participate in the work. In all, 20 baths were kept under observation for this test. The baths were chosen to cover all the more important types of work, and wherever possible were baths dealing mainly with one particular class of galvanizing. No effort was made to choose baths which were known to be particularly efficient, although it must be remembered that the firms who offered to help with this work were naturally those most anxious to adopt progressive techniques, and that many of them were already using improved methods of galvanizing.

The classes of material covered by the survey included nuts and bolts, malleable castings, grey iron castings, hollow-ware made from 31 to 20 gauge sheet steel, fabricated sheet steel material varying from 20 gauge to  $\frac{1}{4}$  in. plate, and certain specialized classes of work such as steel window frames. Where baths galvanizing a very mixed variety of work were included, a rough record was kept of the proportion of work done in the various classes. The survey covered flux and dry galvanizing; prefluxed work and work dipped straight from hydrochloric acid pickling without washing; some baths operating with and some without aluminium additions; and galvanizing baths heated in many different ways, only some of which were thermostatically controlled.

The questionnaire sent to each of the participating firms is reproduced below, and it will be seen that it is divided into two main sections. The first section (a) covered the type of work being galvanized and the quantitative data required about the bath in which it was being done. The second section (b) was a general questionnaire on the galvanizing technique employed, and the physical dimensions and heating methods of the bath.

### Summary of Information Needed about the Performance of a Galvanizing Bath over a test period of three months.

#### (a) General Information

1 Type of material being galvanized. The important divisions under this heading are (a) grey iron castings, (b) malleable iron castings and (c) mild steel material including fabricated ware, tubes, sheet and angles. Any further details will, however, be helpful in analysing the results.

2 Depth of zinc in bath:

(a) At the beginning of the period.

(b) At end of period.

*Note:* The bath should be drossed before the beginning of the period and at the end of the period before the final readings are taken. The depth should be measured down to the lead layer when this is present.

3 Weight of galvanized steel coated in bath during 3-months' period.

4 Weight of zinc added to bath during 3-months' period.

5 Weight of zinc ash removed from bath during 3-months' period.

- 6 Weight of dross taken from bath during 3-months' period.
- 7 Weight of flux skimmings produced.
- 8 Relevant information about zinc content of the secondaries. If this is not available arrangements will be made for the sampling and analysis of secondaries. *Note:* The weight of secondaries should be given as removed from the bath before any treatment for zinc recovery if this is employed.

*(b) Galvanizing Technique*

- 1 Size of bath, including depth and surface dimensions of exposed zinc.
- 2 Whether dry or flux covered.
- 3 Method of heating employed.
- 4 Average operating temperature of the zinc.
- 5 How is the temperature controlled, and is there any check on the accuracy of the temperature instruments?
- 6 Are aluminium or other alloying additions made to the zinc?
- 7 Is a lead layer maintained in the bottom of the bath?
- 8 Type of pickling. Whether hydrochloric or sulphuric acid.
- 9 Is the work washed and prefluxed before dipping? If so, give composition of prefluxing solution or name of proprietary salt used. If not, how frequently is the pickle changed and how well is the work drained?
- 10 Is special drying equipment used? If so, give temperature and time of drying.
- 11 If a flux is maintained on the surface of the bath, some information about the materials added to the flux to maintain it should be given.
- 12 Is speed of withdrawing work from zinc controlled?
- 13 The number of shifts worked and the procedure adopted at weekends and during standby periods.
- 14 Extent of disturbance of bath surface, and frequency of skimming.

In drawing up this schedule a minimum period of three months was decided on for the record keeping, as a shorter time would have introduced serious errors and invalidated the test. Some of the figures did, however, cover a longer period than this required minimum. As an example of the kind of error which short periods of test can introduce, we may cite the effect of changes in the level of the zinc on the actual quantity of zinc used during the test compared with the weight of zinc added to the bath during the period. In one of the baths investigated there was a change in the depth of the zinc of 3 in. between the beginning and end of the test. From the bath dimensions this was calculated as equivalent to over  $2\frac{1}{2}$  tons of zinc, or 10 per cent of the zinc used during the three months. This change in the depth of the zinc bath was measured and allowed for, but had a shorter period of test been chosen an error of an inch in measuring the depth, which could very easily have been made in practice, would seriously have affected the recorded weight of zinc consumed. Over a period of three months, however, such an error could not affect the results appreciably.



## I. Correlation of Results

The results obtained from each of the 20 baths for which records were kept are gathered together in the two large sheets of Table IV, where, in order to conceal as far as possible the identity of the firms providing the information, each bath is referred to solely by a code number. The information in the following columns corresponds closely to the actual questions asked, and each of the sets of columns referring to a particular aspect of the process is headed with the serial number of the question from which the information is derived. The columns (a) 1 describe in general terms the type of work done, and break it down into percentages of mild steel, grey iron castings and malleable iron castings. Column (a) 3 gives the total weight of steel after galvanizing, i.e. the galvanized weight, while the total weight of zinc used, including losses, is shown in the first of the columns (a) 4. This is the weight of zinc in tons added to the bath during the period, with an allowance for any increase or decrease in the total zinc content of the bath as revealed by the depth measurements. The second of the columns (a) 4 expresses the zinc on the galvanized steel as a percentage of the steel by weight, the figures here being calculated from the previous figures after deducting the zinc lost in the dross, the ash and the flux skimmings.

The next three sets of columns deal with the residual losses. Under each of the headings ash, dross and flux skimmings the first column gives the weight in tons, the second the average percentage of zinc in the secondary material, and the third the zinc loss expressed as a percentage of the total zinc used during the test.

The following columns (b) 1 to (b) 15 are self-explanatory. Here are grouped details about the size and surface area of the bath, whether the dry or flux galvanizing technique is used, the method of heating, the operating temperature and whether the bath is thermostatically controlled, the presence of a lead layer in the bath, and the use of alloying additions. Here also are recorded details of the pretreatment of the work before galvanizing, covering pickling, washing, prefluxing and drying; and finally the technique of immersion and withdrawal, the duration of the test, and the number of hours worked.

The last 6 columns of the table (c, d, e, f, g and h) give figures calculated from the preceding data. The first of these columns (c) is the most important, as it shows the overall zinc efficiency of the bath, expressed as the percentage of the total zinc consumed, which appears on the surface of the finished work. The next two columns (d and e) show zinc ash and zinc oxide formation per unit area of the bath surface, the second of these columns (e) being an estimate of the rate of oxidation after allowance has been made for the considerable quantities of metallic zinc which are always found in zinc ash. The figures are taken from Table I in the next section. The figures in columns (f) and (g) show the throughput of the bath during working hours expressed as a ratio of steel per hour to zinc content of bath (column f), and steel per hour in relationship to the effective heating area of the bath walls (column g). The final column (h) expresses the throughput of work as a function of the bath surface area.

### Ash and Flux Skimmings

The figures for ash production are given in the columns headed (a) 5. The first column gives the total weight in tons, the second the average percentage

of zinc in the ash, and the third that proportion of the total zinc added to the bath which was lost in the zinc ash. The figures refer to the actual weight and zinc content of the ash taken from the bath, and make no allowance for any zinc recovery process which may be operated.

*Extent of Losses.* The first conclusion which emerges from these results is that the proportion of zinc removed from the bath in the ash varies between very wide limits from one plant to another; and as a corollary to this that in some cases as much as one-third of the total zinc added to the bath may be skimmed off as zinc ash—a loss of zinc as ash which can be a most serious one to the galvanizer.

*Effect of Flux Cover.* The figures also show the importance of the condition of the surface of the bath in determining the extent of zinc ash formation. Ten of the baths were operating on the dry process (viz: Baths Nos. 1, 2, 7, 8, 9, 10, 15, 18, 19 and 20). The average proportion of the total zinc removed as ash from these baths was 23 per cent. This figure *excludes* the flux skimmings which in most cases were relatively unimportant. Turning to the baths which were either generally flux covered or partly flux covered during operation, five such baths are included in the table, and these showed an average zinc loss of 12 per cent. Naturally in this case the zinc lost in flux skimmings is an important factor, and the average figure of 12 per cent *includes* both the zinc lost in ash and that lost in flux skimmings. Four baths were reported as operating occasionally or sometimes as flux covered or partly flux covered baths, and for these baths—again including the flux skimmings—the average zinc loss was 19 per cent of the total zinc. The figures of 23 per cent loss from dry baths, 12 per cent loss from flux-covered baths and 19 per cent for the borderline cases, show very clearly the reduction in zinc losses in the residuals skimmed from the surface of the bath which resulted from the use of flux galvanizing as opposed to dry galvanizing under the average techniques in use at the time this test was made.

*Effect of Bath Surface Disturbance.* In order to estimate the importance of bath surface disturbance in ash formation, some tests were made by the Technical Committee to find the rate at which ash formed on the quiescent surface of a galvanizing bath during standby periods. Aluminium-containing and aluminium-free baths were used for this test, the baths being skimmed after different periods of time varying from 1 to 48 hours during weekends when no dipping was being done. It was found that the rate of ash formation dropped from around  $\frac{1}{2}$  oz. per sq. ft. per hour during the first hour to about 0.5 oz. for periods of 24 hours or longer, the figures being a little lower for baths which contained traces of aluminium. If the figures in column (d) are expressed as ounces, it will be seen that during working hours the rate of zinc ash formation per sq. ft. of bath area per hour varies between 3 and 13 oz. These figures are so vastly in excess of those obtained during standby periods that we are justified in considering only the working periods as important in ash formation.

*Effects of Aluminium Additions, Bath Area and Throughput of Work.* The laboratory work of Gebhardt (25) has shown that small quantities of aluminium in zinc have a big effect in retarding the rate of oxidation, and some indication of this effect was found during the tests on zinc ash formation

during standby periods. The figures for ash formation in the two parts of Table I have therefore been examined to see whether there are any indications that those baths with aluminium additions made less ash than those baths without aluminium. No such relationships can, however, be found. Attempts have also been made to explain the amount of ash formed on the basis of the area of the bath surface and the number of working hours (column *d*). These figures are certainly more consistent than those for the percentage of total zinc lost as zinc ash, and show that the number of hours worked and the area of the bath are, as would be expected, basic factors in determining zinc ash formation. But any attempt to draw more detailed conclusions from the figures, e.g. by comparing them with the figures for throughput of work (column *h*), breaks down completely. The reason for these failures to find more consistent correlation between zinc ash formation and the other bath variables is almost certainly due to the very indefinite and variable composition of the material known as zinc ash.

*The Nature of Zinc Ash.* The following table gives the results of a number of analyses made by the British Non-Ferrous Metals Research Association on zinc ash samples from some of the baths investigated. Many of the samples were not taken at the same time as the three months' tests were done and this, together with difficulties of sampling, prevents any direct comparison being made between these figures and those in the second column (*a*) 5 of Table I. The figures do, however, show the variations in the composition of zinc ash, its high metallic zinc content, and the relatively unimportant part played by zinc oxide as such in its make-up.

TABLE I  
*Analysis of Zinc Ash*

Code Number of Bath	Weight of Sample/lb.	Metallic Zinc%	Total Zinc%
1	16	83	88
2	17	61	84
3	1	88	91
5	10	92	95
11	2	67	83
13	6	67	74
14	15	78	89
15	4	88	92
16	1	61	77
18	5	80	89
19	6	86	90
20	12	80	89
21	$\frac{3}{4}$	96	97

*Oxidation Rates.* The analyses in the above table were made at the suggestion of the Research Association to see whether there was any correlation between the rates of oxidation of the baths as distinct from the rates of ash formation. In column (*e*) the rate of oxidation of the bath surface per square foot per working hour has been calculated on the over-simplified assumption that the difference between the metallic zinc and total zinc represents zinc oxide. No attempt will be made to analyse the figures further except in the interesting case of baths 1 and 2, which show clearly the over-riding effect of skimming techniques and bath surface disturbance in determining the

formation of zinc ash as distinct from zinc oxide. Baths 1V and 2 dealt with similar quantities of similar work (columns (a) 1 and h), but different handling and skimming techniques were used, bath 2 employing a special skimming device whereby the bath surface was little disturbed, and the entry and removal speeds of the work were very carefully controlled. The percentages of zinc lost in the ash were 26 per cent for bath 1 and 6 per cent for bath 2. Analysis of the ash, however, revealed that the amount of metallic zinc was very much greater in the case of the first bath than with the second, and if the oxide content of the ash is taken as the difference between the metallic zinc and total zinc in each sample, the rates of oxide formation (column e) are practically the same in the two cases.

These results are of the greatest importance as they indicate that, in dry galvanizing, dipping and skimming techniques can be developed which will drastically reduce the rate of ash formation. The earlier generalization about the higher zinc losses in dry galvanizing revealed by these tests must therefore be qualified by this observation about dipping and skimming techniques.

### Dross Production

The figures in the 3 columns headed (a) 6 in the two sheets of Table IV give the amounts of dross formed in the baths during the test period. In each case the bath was drossed immediately before the beginning of the test, so that dross accumulated beforehand was not included. A final drossing was also made at the end of the test period. The first of the three columns gives the weight of dross removed at the weekly drossings throughout the test, the second its zinc content, and the third the percentage of zinc lost in the dross on the basis of the total zinc added to the bath during the period. In a few cases an allowance has been made for dross accumulated in the bath during the test.

The figures for the percentage zinc lost in the dross vary very widely from a minimum of 6 per cent to a maximum of 38 per cent, and although it is not possible with the limited data available to explain all the differences which occur, certain general trends are apparent. In the following Table III the baths have been regrouped to show the effect of some of the more important factors likely to influence dross production.

The first 17 baths in this table were mainly galvanizing mild steel as opposed to castings, while the last 3 were working to a considerable extent on castings. Of the 17 baths treating mild steel articles, the first 7 were fed with work which had been washed and prefluxed, the remaining 10 baths receiving work straight from the pickling tank without the intermediate washing of acid and iron salts from the surface.

The average dross production expressed as a percentage loss on the total zinc was 13 for those baths receiving washed work and 24 for those baths where iron was brought forward from the pickling tanks. Before drawing any conclusion from this important difference, it is necessary to examine the figures a little more closely, so as to see to what extent newer methods of bath heating (which may also have been installed in those works where washing and prefluxing have been introduced) may be influencing the dross production. A further sub-division has therefore been made to show whether these very considerable differences in dross production are in fact caused by washing or are due to improved methods of bath heating. The average figures based on these four groups answer this question.

## FORMATION OF ZINC ASH, DROSS AND FLUX SKIMMINGS

TABLE II  
Dross Production

Bath No.	Type of work	Washing or Pickling details	Firing	Temperature C.	Work/Heating area lb./sq. ft./hr.	Dross	
						% total Zn	oz./sq. ft. bath heating surface/working hour
18	M.S.	Washed	Temperature controlled	445	2.2	6	0.3
20	M.S.	Washed	Temperature controlled	450	6.0	9	1.8
10	M.S.	Washed	Temperature controlled	455	4.0	18	1.2
9	M.S.	Washed	Temperature controlled	455	14.5	12	2.4
2	M.S.	Washed	Temperature controlled	465	12.5	22	2.1
19	M.S.	Washed	Coke	445	3.6	14	1.2
4	M.S.	Washed	Coke	450	9.6	11	3.5
11	M.S.	Direct, acid changed 70g.Fe/l.	Temperature controlled	445-455	5.6	23	2.6
12	M.S.	Direct, acid changed 70g.Fe/l.	Temperature controlled	445-455	6.3	27	5.2
8	M.S.	Direct	Temperature controlled	450	5.4	16	1.4
5	M.S.	Direct, acid changed 120g.Fe/l.	Temperature controlled	455	7.0	15	2.3
1	M.S.	Direct, acid changed monthly	Temperature controlled	465	17.5	18	5.1
6	M.S.	Direct, acid changed 2-monthly	Coke	445	1.6	37	4.1
3	M.S.	Direct, acid changed 120g.Fe/l.	Coke	450	4.0	25	2.6
15	M.S.	Direct	Coke	450	4.3	31	3.7
14	M.S.	Direct, much iron	Coke	450	4.5	24	2.6
17	M.S.	Direct, acid changed monthly	Coke	455	9.0	19	2.4
13	35% castings	Flux dip	Coke	465	34.0	38	29
16	60% castings	Direct	Coke	430-470	6.3	34	2.7
7	90% castings	Direct, acid changed 2-monthly	External furnace	445	3.6	34	6.2

The 5 temperature-controlled baths where the work was washed showed an average zinc loss in dross of 13 per cent, whilst the only two coke-fired baths treating washed work gave an average of 12 per cent. Where the work was taken direct from the pickling tank to the molten zinc without washing, the temperature-controlled baths gave an average figure of 20 per cent, whilst the coke-fired baths gave an average dross figure of 27 per cent. According to these figures, the major factor in reducing dross formation is, therefore, washing and prefluxing before dipping, and the figures suggest that an average saving of 50 per cent in the zinc lost in the dross may be expected where this system is employed.

It must be emphasized that the results of the survey can only be interpreted as giving broad indications of the importance of some of the major factors controlling residual formation. The figures which have been obtained are too few in number for any strict statistical analysis to be made from them. For example, the figures cannot be broken down further to show the advantages in lower dross formation of carefully controlling the iron content of the pickle, although some such effect is probably hidden among them. Another important factor should be the operating temperature of the different baths which varied over a range of 20°C., and there is perhaps some indication that the higher operating temperatures tended to give higher dross figures.

The rate at which a galvanizing bath is being worked cannot be disregarded in considering its performance, and the figures in the sixth column of Table II show the weight of steel being galvanized per working hour per square foot of bath wall heating surface. In the case of a pair of baths such as 9 and 10 from the same factory and working under very similar conditions, it will be seen that, where a bath is handling a reasonable amount of work, the percentage of the zinc lost as dross falls as the rate of working increases. This is presumably because the zinc lost as dross is being expressed as a percentage of the total zinc added to the bath, and thus when the throughput of work and zinc is greater, the effect of the iron dissolved from the bath walls becomes less apparent. In bath 6 with a very low throughput of work, the iron from the walls locked up a greater proportion of the relatively static zinc, and hence the dross figure expressed as a percentage of the total zinc is high, at 37 per cent.

To overcome the disadvantage of this method of expressing the dross loss, some figures are quoted in the last column of Table II for the weight of dross formed per working hour as a function of the bath wall heating area. When the dross is expressed in this way, the figures for baths 9 and 10 are reversed, and it is seen that the bath doing most work makes most dross.

The effects of washing the iron salts from the work, and controlling the temperature of the baths, may now be examined again using these more fundamental figures for the total dross production in relation to bath size and working hours. This is done in the following Table III.

TABLE III  
Oz. dross/working hour/sq. ft. bath heating surface

		Minimum	Maximum	Average
Temperature controlled—washed	(5 baths)	0.3	2.4	1.6
Coke Fired —washed	(2 only)	1.2	3.5	(2.4)
Temperature controlled—not washed	(5 baths)	1.4	5.2	3.3
Coke Fired —not washed	(5 baths)	2.4	4.1	3.1

Although the inter-relation between the dross figures from individual baths is very different when expressed in this way, the conclusions which emerge from the four main groups are the same as those arrived at on the simpler analysis made earlier, and emphasize the importance of washing in reducing dross formation.

Turning now to the last three baths in Table II, which are those baths dealing with castings in more or less considerable amounts, the percentage zinc lost as dross would suggest that high dross figures are associated with the galvanizing of castings. Further examination of the figures, however, makes this conclusion more doubtful. In the case of bath 13, the very high rate of working — 34 lb. of steel/sq. ft. heating area/hour — will require a heat input of over 4500 B.Th.U./sq. ft./Hr. to deal with the steel and zinc melting alone. Unless the work was very evenly distributed throughout the working hours, this figure would frequently have been exceeded, and in any case the additional heat to make good surface losses has to be transmitted. In the case of this bath with a throughput of work more than twice as great as that of any of the other baths investigated, it is therefore not altogether surprising that the percentage dross figure is high, and that the dross figure per unit area of bath walls is excessive. The 35 per cent of castings dipped in this bath may not, therefore, have been the controlling factor.

Bath 7, treating mostly castings, shows well above average dross production whichever way this figure is expressed; but bath 16, with more than half its throughput castings, is not an unusually heavy dross producer on a bath wall area basis. As far as these records go the case against castings as high dross producers is therefore 'not proven'.

### Zinc Efficiency

The figures in column (c) of the two sheets of Table IV give the zinc efficiency of the bath. The zinc efficiency figure is that percentage of the total zinc added to the bath which appears on the surface of the galvanized work. The figures range from 41 to 84 per cent, showing that of the 20 baths investigated, the worst lost nearly 60 per cent of their total zinc in their residuals, whereas the best lost only 16 per cent of the zinc in this way.

From what has been said in the previous sections it will be clear that considerations of zinc efficiency cannot be divorced from the rate of working or throughput of the zinc bath. The truth of this statement is immediately seen in the case of a bath galvanizing a negligibly small amount of work, as the ash and dross which would still be formed in this bath would cause the zinc efficiency to fall to zero, i.e. all the added zinc would be removed as residuals. The other main factors affecting efficiency have already been dealt with in the previous sections on the individual losses through dross, ash and flux skimmings, but it is instructive to consider briefly the main reasons for the good results obtained from the three most efficient baths.

The first of these, bath 4, had an overall zinc efficiency of practically 84 per cent. From column (f) of Table IV it will be seen that it also had the second highest throughput. The bath was treating comparatively light-gauge fabricated hollow-ware, and was completely covered with a flux blanket, the washed work being immersed through this and withdrawn through it as well. The bath was, however, coke-fired. That the most efficient of the baths examined was heated in the old way shows how much can be achieved by careful and conscientious workers. Where special systems of bath heating are used, thermostatic control takes the place of personal factors, but this result

shows that careful workers can obtain very good results from comparatively primitive equipment.

The two baths with the next highest efficiencies were bath 9 (75 per cent efficiency) and bath 2 (73 per cent efficiency). These two baths had the third and fifth highest outputs respectively (column *f*) and were thermostatically controlled dry baths receiving washed and prefluxed window frames. In these two cases the advantage of treating only one type of work was probably the most important single factor in achieving high zinc efficiencies.

## II. Conclusions

Although the intention of this survey was rather to obtain information about the extent to which zinc losses were occurring than to discover the underlying reasons for these zinc losses, the foregoing analysis of the figures does allow certain tentative conclusions to be drawn. These conclusions may be summarized as follows:

### Losses from Ash Formation and Flux Skimmings

The two important factors are:

- (a) the extent to which the surface of the bath is flux covered,
- (b) the extent to which the bath surface is disturbed both during operation and during removal of the zinc ash. Careful skimming, and controlled speed immersion and withdrawal of the work are probably more important with dry baths than any other single factor, both in determining the extent to which oxidation occurs, and the amount of metallic zinc entrained in the ash.

### Zinc Loss through Dross Formation

The most important factors in controlling dross formation are:

- (a) the washing of iron salts from the work after pickling and before dipping,
- (b) bath heating. Thermostatically controlled baths seem on average to give lower dross figures than coke-fired baths, although the results suggest that the different bath heating systems vary considerably in effectiveness, and that coke-fired baths can still hold their own if properly tended,
- (c) the throughput of work. Although when a bath is overworked it is bound to produce an excessive amount of dross, the results show that the highest efficiencies are obtained by maintaining a high throughput of work so long as the safe maximum is not exceeded.

## Acknowledgments

The figures included in this paper reveal for the first time factual information about the practice and performance of an important zinc consuming industry, and the Zinc Development Association is indebted to the Council of the Hot Dip Galvanizers Association for their farsightedness in agreeing to the publication of the results. This survey is in the true spirit of the pioneer work which the Association is doing to improve the technical efficiency of the general galvanizing industry. The results are published not as a proud record of achievement, for clearly much still remains to be done if general galvanizing is to become a truly efficient and progressive industry, but rather as a



guide to those firms who have not yet reached the standard of the more efficient and to show them how greater efficiency can be obtained.

In conclusion, the author wishes to express his thanks to his colleagues on the Technical Committee who so willingly agreed to undertake the considerable extra work which the keeping of the detailed records entailed. Without their help, the work could never have been attempted, and this corporate investigation is a unique example of what can be done by a group of firms when they decide to work together and pool their technical information for the benefit, not only of themselves, but of their whole industry.

# CAN DROSS BE ELIMINATED IN HOT DIP GALVANIZING?

by W. G. IMHOFF\*

## Foreword

Any intelligent discussion of the important question of whether dross can be eliminated in the hot dip galvanizing process must be based on a complete understanding of what dross is, how it is formed, and what methods have already been adopted to reduce and eliminate its formation. Many articles have been published on dross production, as it is the most costly angle of hot dip galvanizing. The real significance of its importance is emphasized most vividly in the field of malleable iron pipe fittings' galvanizing, where a low dross formation is 40 per cent, the average is 45 to 55 per cent, and during the war the high reached 70 to 80 per cent dross based on the metal charged into the pot.

This discussion will be from three distinct viewpoints, namely, first, what is dross; second, what are the sources of dross production; and third, what has already been done to reduce dross production, and is it possible to eliminate dross entirely when hot dip galvanizing.

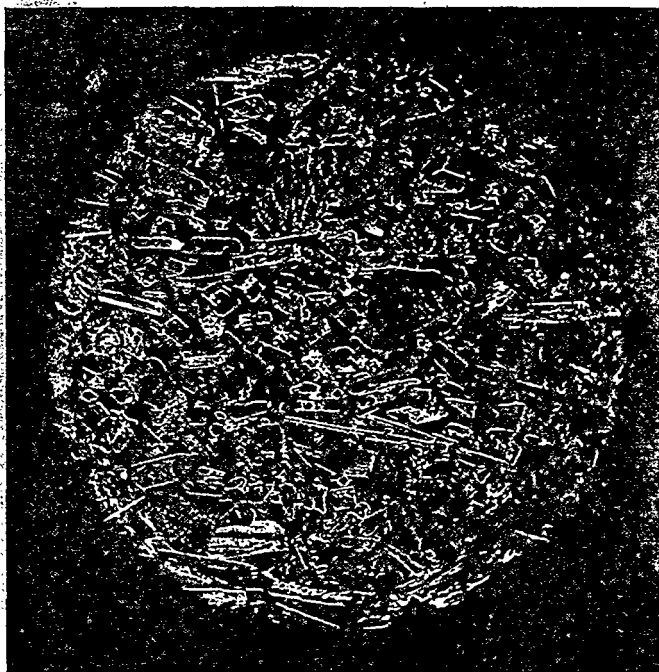
## What is Dross?

In the very narrow sense, dross is the zinc-iron alloy that accumulates in the bottom of the galvanizing pot. In the broad sense as understood by practical galvanizers and smelters and those interested in galvanizing, it is the 'metal sludge' or deposit that is removed periodically from the bottom of the pot by the operation called 'drossing'. Out of the pot, the dross consists of zinc-iron alloy crystals embedded in the frozen galvanizing bath left after the 'metal sludge' has been drained, 'cut and sliced' and 'vibrated' in the dross spoon immediately after the spoon has been filled and raised out of the bath. The 'metal residue' after draining, cutting and slicing, and vibrating, is the commercial material called 'galvanizer's dross', and sold back to the smelters for recovery of the good zinc in this by-product. This is the narrow meaning of 'dross', but in the larger sense it has to be considered as not only this direct by-product, but also in the form of the zinc-iron alloys that form in, and eventually destroy, the pot itself; and also as the zinc-iron alloy that forms on articles lost in the galvanizing bath during operations, and the zinc-iron alloys that form as 'the alloy bond' to hold the upper zinc coating to the base metal. It is impossible to give an intelligent discussion of 'dross' without also taking into consideration all of the angles of its formation, including these zinc-iron alloys that destroy the pot, and are a part of the zinc coating.

## I. Sources of Dross

To eliminate dross it is necessary to know what the sources of dross production are. The main sources of dross are therefore listed below, with a brief comment about each particular item:

\* Wallace G. Imhoff, Co., Los Angeles



*Fig. 1. Ordinary plant dross from a metal ware galvanizing plant. Iron content 3.54 per cent. (X36).*

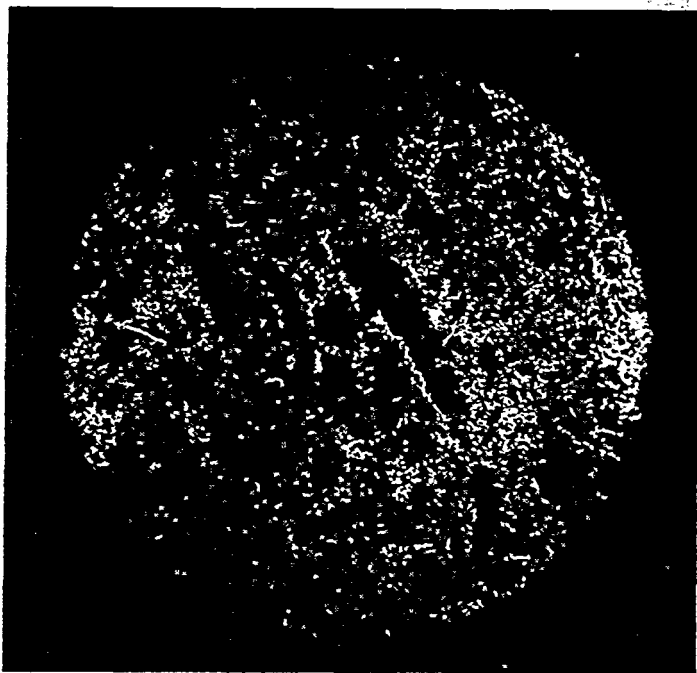
### **From Production**

- (a) Malleable iron, cast iron, grey iron.
- (b) Steel, in the form of sheets, pipe, angles, pole-line hardware, metalware and miscellaneous articles.
- (c) Wrought iron in the form of pipe, etc.

Dross production is in direct proportion to the production passing through the galvanizing bath, but varies through a wide range according to the kind of base metal and the surface area. Other features such as rolling, forging, casting, etc., i.e. the mechanical treatment, also are of importance; soft cast metals, in the form of malleable iron fittings, give a very much higher dross production than rolled steel articles, as for example in the metalware field of galvanizing. But the production itself is a basic factor of dross production, and especially from the standpoint of surface area exposed to the molten zinc for coating, as well as the softness and grain structure of the base metal, which is a factor of penetration. Therefore dross production is a direct function of production; the greater the production, the more dross produced.

### **From Corrosion of the Surface of Production**

Very careful research investigations have definitely established the fact that any corrosion that is permitted to form on the surface of the production between the pickling and galvanizing operations is a source of creating iron in the form of iron oxides that, upon entering the molten zinc bath, are immediately attacked and reduced by the molten zinc, creating both the oxide skimmings from the oxygen released, and dross from the iron in the corrosion product. The same investigations also definitely established the fact that the



*Fig. 2. Iron oxide on the surface of the work being changed into dross as a result of attack by molten zinc. The black areas are iron oxide. (X36).*

iron salts in the pickling bath, the ferrous sulphate and ferrous chloride when carried out of these baths on the surface of the production, also are a large source of dross from the iron content of the iron salts in the pickling solutions. The iron salts are first in the above forms as pickle bath salts, but if the work is allowed to stand in the air, these iron salts slowly oxidize and change over into 'sullrust', limonite iron oxide, or if permitted to be in contact with the air for a very long period of time, they will eventually change over to the ferric oxide form of rust, which at first may be red, but finally turns to the familiar brown rust, iron oxide. Iron that is permitted to enter the galvanizing bath in any form, either as the base metal of production, or the iron corrosion after pickling, or the iron salts carried over from the pickling baths, eventually finds its way into the zinc-iron alloy dross which settles to the bottom of the pot. Corrosion after pickling, and due to drying, is one of the most prolific sources of iron to form dross. A perfectly clean surface may be ruined by drying, or due to long intervals before galvanizing.

#### **From the Pot**

Years ago the galvanizing pot itself could be a very prolific source of dross. The heat application with coke fuel created 'hot spots', and especially at night when the bath often became 'red hot', dross accumulated in excessive amounts due to overheating of both the metal and the pot. How much dross comes from the pot is a function of the kind of steel in the pot, and the heat application. As a general thing the steel is of the best quality, Firebox Steel, which so far is the best and most practical base metal for making galvanizing pots. On the other hand, even Firebox Steel will dissolve very rapidly when badly overheated, or simply from general overheating due to faulty heat application from a poor galvanizing furnace design. Pots have failed in an

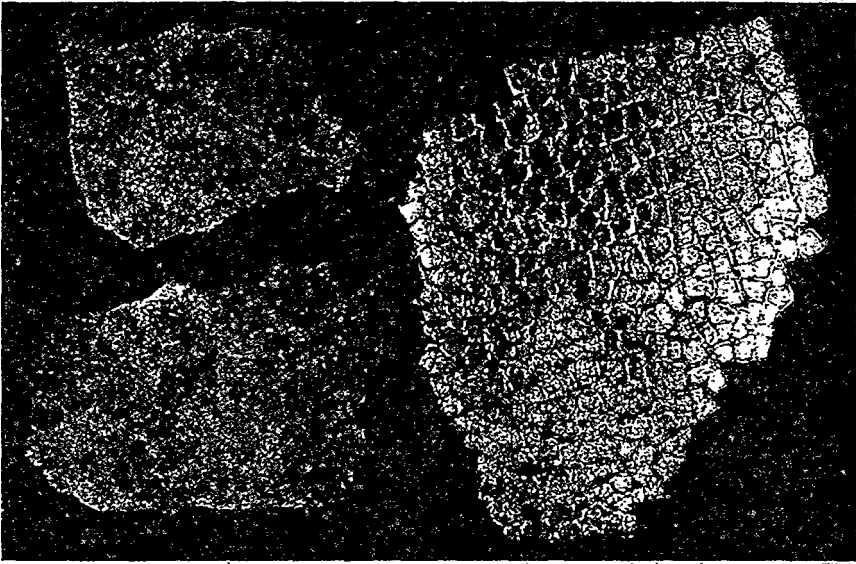


Fig. 3. Zinc-iron alloys removed from the top and middle portions of the walls of a hot dip galvanizing pot.

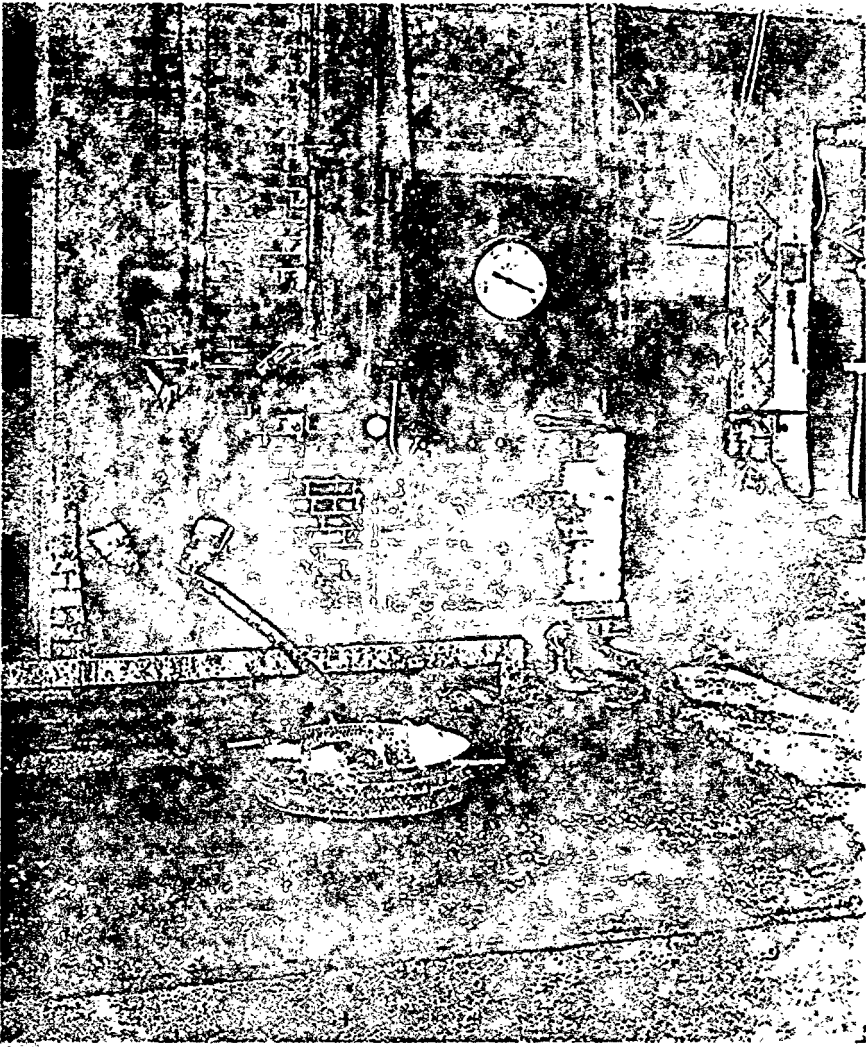
extremely short period of time, and in such cases they may be a large source of dross formation. On the other hand, today, most galvanizing pots and furnaces are of good design so that dross from this source has been minimized.

#### **Overproduction, too high Operating Temperature and Overheating the Bath at Night**

It is surprising how many galvanizing pots when checked for correct production requirements, show overloading. Cases have actually been found where pots have been overloaded 100 per cent, and most pots are being operated at some overproduction. If checked carefully from the standpoint of heat input balance based on metal capacity and side heating area, it will be found that there is an overproduction. Calculations for correct production requirements should be based on the side heating area if the heat application is made on two sides, and the total heating area, if the pot is heated all around. Overproduction will naturally greatly increase dross production, as will a pot where the heat application is badly out of balance.

As a direct result of overproduction, the operating temperature will always be too high, and this also is a direct cause of excessive dross production. All galvanizing installations have a correct rated production capacity, and when production is carried in excess of this rated capacity, overheating results, and this in turn creates excessive dross.

In early installations it was practically impossible to have much control at night. Coke fuel would not permit of automatic control of the fires, and a night watchman often had too much ground to cover, and therefore could not give the fires the close attention they required to maintain a low, even bath temperature. It was not at all uncommon to have a bath so badly overheated that the zinc became red hot. This not only ruined the metal for galvanizing purposes, but in addition it created excessive dross from both the metal and the iron derived from the pot due to overheating.

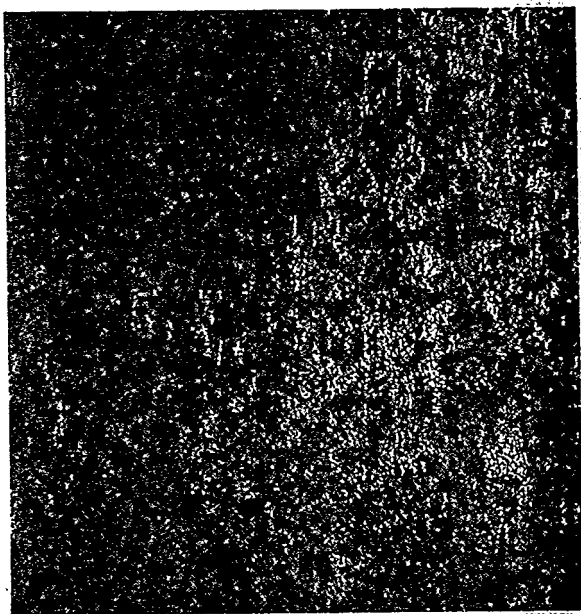


*Fig. 4. Basket work; the articles sometimes float out, or are poked out of the baskets, and go to the bottom of the pot to form dross.*

(Courtesy Leeds & Northrup Co., Philadelphia)

#### **From Work lost in the Pot**

There are some fields of galvanizing, as for example malleable iron pipe fittings and pole-line hardware, in which, due to the method of handling when galvanizing, the pieces either float out of the baskets, or are 'poked' out in the operation of working the pieces around in the baskets to expose all parts to the molten zinc bath for coating purposes. In one actual case under observation it was found that a ton or more of pieces were lost in the pot every week, and were removed in the dross. Malleable iron pipe fittings make more dross than steel articles, but either, on a large scale, when lost to the bottom of the pot, create dross rapidly if left down in the dross until the next dross period.



*Fig. 5. The zinc coating is disintegrating, forming the zinc-iron alloy, because the bath temperature (920°F.) is too high, and the submersion time (1 min.) too long for such a light base metal (28 gauge).*

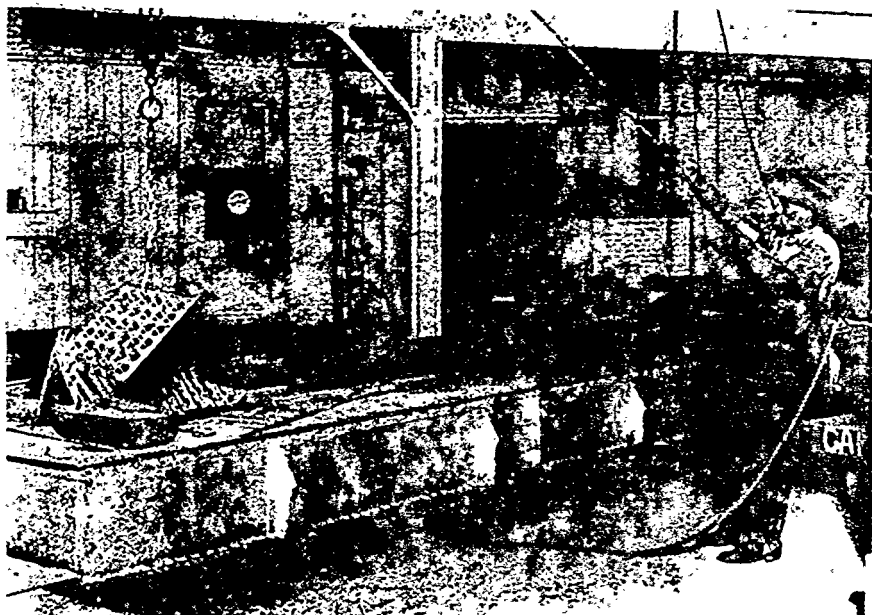
### **From too long a Submersion Time**

As an excessively long submersion time is similar in effect to work lost in the pot, dross formation is a function of too long submersion time in the molten zinc. There is a correct submersion time for every article, and prolonged submersion in the molten zinc tends to form more and more zinc-iron alloy, thereby increasing dross production. This is especially true of a soft base metal like malleable iron.

Poor, ineffective cleaning and pickling, too severe heat in drying, or too long a time between pickling and galvanizing, may be the reason for raising the bath temperature and increasing the submersion time in the molten zinc to obtain a perfect coating. However, raising the bath temperature and increasing the length of submersion time both tend to increase dross production.

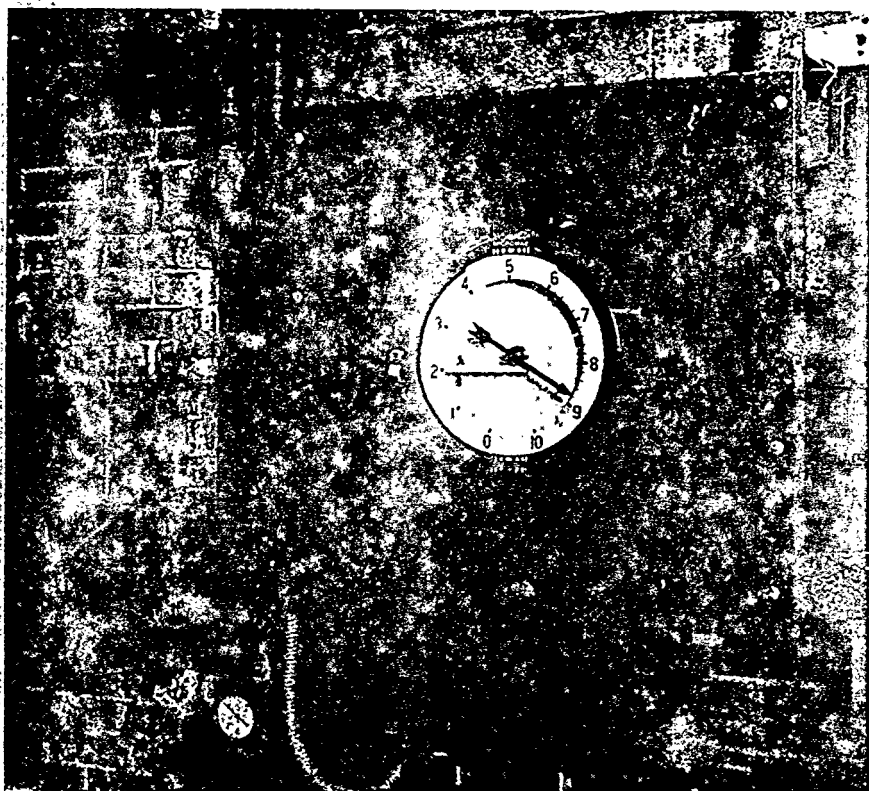
### **From poor Galvanizing Furnace Design, and improper Heat Application**

Regardless of what kind of fuel is used in the galvanizing furnace to heat the pot, if the furnace design is not correct there may be a heavy dross production. Poor galvanizing furnace design may be considered from at least three different angles, namely, first, improper heat application which may cause general overheating, or concentration of high heat intensity on some particular spot or part of the pot; second, improper location of the flues, which may draw the heat down into the dross area of the pot, thereby greatly exaggerating and intensifying the dross forming conditions; and finally, third, excessive dross production due to unbalanced heat input in the relation between production, metal capacity of the pot and side heating area.



*Fig. 6. Large modern hot dip galvanizing furnace. Note the pyrometer on the wall in the background.*

(Courtesy Leeds & Northrup Co., Philadelphia)



*Fig. 7. Dial-type of Electric Recording Pyrometer. Latest equipment for bath heating control.*

(Courtesy Leeds & Northrup Co., Philadelphia)



### From the Kind of Zinc used

It was formerly believed that the mere fact that the zinc used was of Prime Western Grade was enough of a guarantee that the quality of the metal was high enough for hot dip galvanizing purposes. However, after World War I a paradox developed commercially. Prime Western Grade metal was zinc that could carry up to 1.60 per cent lead, or Prime Western zinc could be metal with little or no lead at all in it. Because of excessive dross production, when the metal zinc was scarce during World War II, careful investigations proved conclusively that zincs without any lead in them were the direct cause of the high dross production. In every plant where dross was excessive and the zinc used did not carry any lead, the dross production was lowered by either putting pig lead into the pot, or purchasing metal with about one per cent of lead in the slab zinc.

Further studies and investigations during the war also proved conclusively that even pure zincs of very high quality, but which did not carry any lead in them, were also excessive dross producers. It was also noted that in plants where a large surface area was coated, and much metal was used for coating purposes, the replacement of zinc carried out by fresh new zinc might compensate for high dross production, but on the other hand, where the production was heavy, and more weight with little surface area, the replacement metal was small because less zinc was used for coating purposes. Dross production in this type of production might become very annoying, and costly. Impurities in the zinc were also found to be an important factor of dross formation, and because of this fact certain types of metal could not be used at all.

The main sources and causes of dross production have been briefly discussed without going into too much detail for any particular cause. The important thing to know is what dross is, and what the principle sources of dross are. These first two phases must be known before the third phase, the possibility of eliminating dross production, can be intelligently discussed. Once it is known what dross is, and where it comes from, then steps to eliminate it follow. There are other factors of great importance that have a bearing on the problem.

## II. Reduction of Dross; Can Dross be Eliminated Entirely?

Great progress has been made in the reduction of dross production, but whether dross can be eliminated entirely seems to hinge on the very foundation principle of hot dip galvanizing. Just what has been accomplished so far will be briefly discussed, and then the question of galvanizing with the complete elimination of dross will be considered. Since dross production was given according to the most important sources and causes of dross formation, the same order can be used to discuss the reduction and elimination of dross.

### From Production

Many attempts have been made to give the articles of production a preliminary flash coating to eliminate the formation of the zinc-iron alloy which settles to the bottom of the pot as dross. The ideas involved here are to prevent any iron going into the molten zinc bath from the surface of the production. The writer conceived that idea many years ago, and developed a copper flash immersion coating which was put on by chemical action in the liquid flux bath. However, the anticipated difficulty developed, namely, that

the copper on the surface of the articles would reach a point eventually that would contaminate the galvanizing bath and make trouble. This is exactly what happened; an ugly red oxide 'smear', due to excessive copper in the bath, appeared after the protective copper flash surface covering had been operating for a short time.

Other research engineers also got the same idea of attempting to stop the iron derived from the surface of the production from getting into the molten zinc bath by coating the work with a flash copper coating. On November 5th, 1929, Irving R. Valentine, of Erie, Pennsylvania, was granted U.S. patent No. 1,734,928 Treatment of malleable castings with a thin copper coating by dipping momentarily in a copper sulphate solution, and then galvanizing. The patent was assigned to The General Electric Company, a corporation of New York. This company evidently found out the same as the writer did, that continually carrying copper into the galvanizing bath finally reaches a prohibitive point where the excessive copper causes finishing troubles, and ruins the coating.

The writer also experimented with other flash coating protection such as immersion tin coating, and even with an electroplated flash zinc coating, but all methods of this kind were eventually discarded as either being failures, or eventually causing trouble, or as impractical. So today there is still no method that is practical that has been developed to stop the dross formed due to the iron dissolved from the surface of the production as it is galvanized.

### **From Corrosion of the Surface of Production**

It was realized early in the study of dross production that excessive corrosion on the surface, after pickling, was a heavy source of dross production. So one of the first things done was to wash after pickling. However, at that time, the old muriatic acid dip flux was standard practice, as well as open steam heating for most of the tanks. The washed, clean surface after dipping in the muriatic acid once again became covered with iron chloride, which formed dross when the work was galvanized. As a direct result of research investigations definitely proving that iron salts from the pickle, iron chloride from the muriatic acid dip flux, and iron from corrosion between pickling and galvanizing, all formed dross, the development of a whole new technique was gradually accepted, namely, that of the liquid flux practice instead of the muriatic acid dip flux. The new method permitted washing after pickling, and then the work was dipped in a liquid solution of zinc-ammonium chloride of a high enough concentration to completely cover the surface with a transparent film that protects the surface from all oxidation from the exposure in the air between pickling and galvanizing. This new liquid flux technique greatly reduced dross production in all fields of galvanizing where it was used. Thus two steps were taken that reduced dross production — washing after pickling, to remove the pickle salts, and the adoption of the new liquid flux technique which eliminated the iron from the muriatic acid dip, and also prevented the formation of corrosion from exposure to the air between pickling and galvanizing operations.

### **From the Pot**

The writer recognized very quickly that the galvanizing pot itself was a source of iron to create dross. A very intensive programme of research investigations proved that molten zinc at galvanizing bath temperatures would attack and

eventually destroy practically all known metals and alloys; some very quickly, others more slowly, but all eventually were destroyed. On December 22nd, 1925 the writer was granted United States Patent No. 1,566,749 for a glass-lined vitreous enamelled galvanizing pot. While the lining could be put on small pots, it was found to be impractical for large pots due to the annealing affects of the heavy steel plates in the pot. It therefore never became practical as either a dross reducing method, or a method of prolonging the pot life, both of which ideas were effective in very small pots. So once again the dross production from the iron from the pot has not as yet been either checked or reduced from the standpoint of placing some kind of a lining on the steel sides that the molten zinc cannot attack. A certain amount of dross is still derived from this source.

### **Overproduction, too high Operating Temperature and Overheating the Bath at Night**

Much progress has been made in regard to excessive dross due to overproduction of the pot. Exact tables of metal capacity, side heating area and production relations have been established, which reduce overproduction to a minimum, and also have established a better balance between heat input through the sides in relation to the metal capacity of the pot. Both of these adjustments have reduced dross production.

Since overproduction was generally the cause of too high a bath temperature, adjusting the production thus also tended to correct dross production from too high an operating temperature.

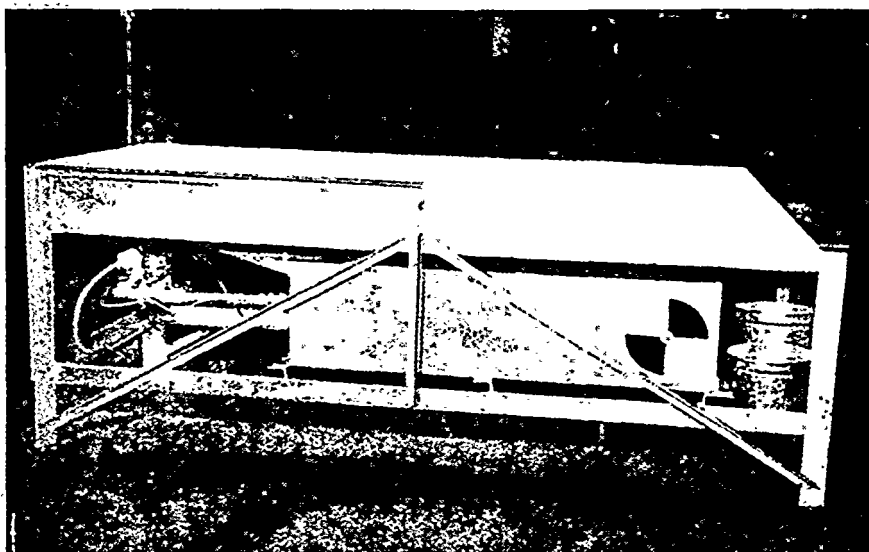
In the meantime both gas and oil fuels began to make heavy inroads on the installations where coke fuel was still used. Today, coke fuel has practically disappeared in favour of gas and oil fuels which permit automatic control of both the bath temperature and the fuel input, as well as correcting the worst source of dross, which was overheating the bath at night. Thus we see that in each source of dross production some reduction has occurred, while work still is in progress to lower the dross from causes more difficult to work with because of practical troubles encountered.

### **From Work lost in the Pot**

Some progress has been made in dross reduction here, but so far the results have not been outstanding. Special baskets and racks have been designed to reduce the work that floats out of the baskets, and nets or special baskets have been used over the dross to catch the lost articles which are lifted out with the basket each night. However, this source of dross is still a very serious one, as progress has not yet been sufficient to reduce the lost articles to the point where they are not a menace to dross production. Recently special racks have been developed, but there has not been sufficient time yet to note what effect there is on dross production.

### **From too long Submersion Time**

Great advancement has been made in reducing dross production due to too long submersion time. Batch pipe galvanizing has been changed to single and double line pipe galvanizing. Another cause of long submersion time was due to 'burning' on the old steel hot plate drier. This caused excessive corrosion, which in turn made it necessary to carry a higher operating bath temperature, and use a longer submersion time to overcome the corrosion and obtain a perfect coating. The use of a hot air drier has not only eliminated corrosion



*Fig. 8. The best method to dry malleable iron pipe fittings before galvanizing, to avoid 'burning' and corrosion on the drier, is to use a hot air drier instead of the old steel hot-plate drier. A hot air drier reduces dross, increases production, and allows a lower galvanizing bath temperature.*

(Courtesy James Hill Mfg. Co., Providence)

on the drier, but also has greatly increased production because of the shorter submersion time, since the corrosion has been eliminated. This new technique of hot air drying therefore has helped to reduce dross production.

#### **From poor Galvanizing Furnace Design, and improper Heat Application**

Enormous strides have been made in the past twenty years in hot dip galvanizing furnace design. The new fuels, gas and oil, which permit of automatic temperature control at all times, and also automatic control of the fuel supply, have greatly reduced dross production until today all sources of dross production give less dross than formerly came from just one source, such as the poor heating conditions of the old coke-fired galvanizing furnace. Today the furnace design begins with the proper pot size in relation to production in pounds per hour, proper balance of heat input between metal capacity of the pot and side heating area and, finally, thicker sides.

Next, the combustion chambers have been enlarged to reduce the heat intensity and also the speed of the combustion products out of the furnace. More time is allowed for the fuel to burn properly, and also for the heat to be taken up by the pot and furnace, rather than be carried swiftly up and out of the stack. The proper location of the flues has also reduced dross production, and a more scientific heat application in the area where the production passes through the bath has also tended to create less dross. In all, the advancement in the design has been marked in many engineering features, all of which have tended to lower dross production, give better operating conditions and increase the life of the equipment.

#### **From the Kind of Zinc used**

During the war when the supply of zinc was very low, every known method had to be used to conserve zinc, and also to reduce dross which wastes zinc

because it is a by-product of galvanizing. Investigations were carried out which very definitely proved that zinc without any lead content was a cause of heavy dross production. In every plant where dross was excessive and the cause was traced to no lead in the zinc, the dross production was immediately corrected by adding pure pig lead to the pot at regular intervals, or by purchasing zinc that carried about an average of 1.00 per cent lead. Thus more knowledge about impurities in galvanizing baths, and in the slab zincs used for galvanizing has reduced dross production.

### III. Conclusion

So the present state of dross production may be summarized in the conclusions illustrated under each source of dross production, namely, that dross production has been greatly reduced, but not eliminated entirely. We still have dross with us in all fields of galvanizing, and the loss from this source is the greatest single factor of hot dip galvanizing. The next question logically follows: 'Can dross be eliminated entirely in hot dip galvanizing?'

It takes a long time to see and understand the simplest things. This statement applies to hot dip galvanizing in the fact that the actual 'wetting' process of the base metal by the molten zinc at galvanizing temperatures means the immediate alloying of the zinc with the iron base metal. Since molten zinc has been proved to attack and dissolve all commercially known metals and alloys, then if we coat the base metal with any other metal or alloy, 'dross' will still form, as with copper the 'dross' is a copper-zinc alloy, along with the iron-zinc alloy. Thus we appear to strike at the very heart of galvanizing when we try to eliminate the formation of the zinc-iron alloy. It is the formation of the zinc-iron alloy that 'wets' the clean pure iron base metal surface, so if there is 'no wetting', no galvanizing can take place.

We have recently seen various statements that the use of high aluminium in the galvanizing bath, with no flux on the bath, reduces dross production. This brings up another very delicate and complicated question, namely: 'Will the aluminium form an aluminium-iron alloy bond that serves the same purpose as the zinc-iron alloy bond of zinc coatings?' It has been definitely proved that a high iron content in the zinc coating greatly deteriorates the bonding qualities of the zinc coating above. It has also been proved that a lead coating alone will not bond to the base metal, but lead containing even very small minute amounts of zinc will give a good lead coating, the zinc being the bonding agent between the iron base metal and lead coating above. It is also a known fact that zinc has a certain bonding power and in the presence of small amounts of aluminium in the bath, the zinc predominates. However, when large amounts of aluminium are in molten zinc, then the aluminium may have strong enough bonding powers to predominate, and in that case the alloy bond would be an aluminium-iron alloy instead of the zinc-iron alloy. So if 'dross' be simply thought of as a by-product, then excessive formation of aluminium-iron alloy might produce a dross of aluminium-iron alloy instead of a dross of zinc-iron alloy. Our present state of knowledge would at this time tend to the theory that, since to galvanize at all, there must be 'wetting' of the base metal by the molten zinc, and since the 'wetting' is the formation of the zinc-iron alloy, and since in the process of formation of the zinc-iron alloy some alloy and iron go to form dross, then the logical conclusion is that at present it is impossible to hot dip galvanize without forming some dross.

## Author's Introduction

MR. H. ARNASON (J. Chr. Jensens Galvaniserings Etablissement) introduced his contribution on new methods of drossing by referring to the ordinary practice of drossing which was, he said, unsatisfactory for two reasons. The zinc content of the dross was too high and the drossing operation took up too much of the working time. In his works they had been working for some time to obtain drosses with higher iron contents and to reduce the time taken up by the actual drossing operation at the side of the bath. Good results had been achieved and drossing was now done by labour not concerned with galvanizing by means of special equipment which removed the dross quickly and dealt with it away from the bath. They had also experimented with pumping dross from galvanizing baths, but had not been able to obtain dross of as high iron content in this way. The operation was, however, rapid and further separation was possible later on.

The work was still in the experimental stage and he hoped to be able to publish further information about it later.

## NOTES ON NEW METHODS OF DROSSING

by H. ARNASON\*

Normal drossing practice leaves much to be desired. This is particularly true in the separation of zinc and hard zinc, as the ordinary commercial hard zinc contains 3.5-4 per cent Fe only, showing that besides the pure crystals of iron-zinc alloy, considerable quantities of pure zinc are removed from the galvanizing bath. Another disadvantage of the usual method is the considerable time required for carrying out drossing operations, which cause undesirable interruptions to production.

As a result of these disadvantages, our firm has investigated the whole question and developed methods (26) which have led to the following results:

- 1 The production of hard zinc with considerably higher iron contents than usual.
- 2 The separation of the mixed zinc and dross away from, and independent of, the galvanizing bath.
- 3 Drossing by pumping.

Investigations concerning points 1 and 2 have resulted in the construction of portable equipment into which the mixture of zinc and hard zinc is fed on removal from the bath; by this means hard zinc with 4.50-5 per cent Fe and zinc with not more than 0.05 per cent Fe are obtained. The equipment is operated in connection with an ordinary spoon for drossing. This procedure results in a dross reduction of about 20 per cent and allows drossing operations to take place during the lunch interval. Our firm has now used this method for many months with completely satisfactory results. An average of 1200 kg. dross with 4.50-5 per cent Fe, corresponding to about 1500 kg. ordinary dross, have been removed during the normal  $\frac{1}{2}$  hour of lunch, and in addition larger quantities could be removed if necessary.

The investigations and experiments concerning point 3 have resulted in the construction of a special dross pump. The dross pumped up is, however, far

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less concentrated than the dross removed by the spoon. To overcome this disadvantage of pumping the dross, special equipment has been constructed for continually separating the superfluous zinc, and in this way hard zinc containing 3.50 per cent Fe has been obtained. Extraction of further zinc takes place away from the pot, and the hard zinc finally obtained contains 4.50-5 per cent Fe. Using the present small pump about 5-600kg. of concentrated dross can be removed in a half hour lunch interval, but the method is still in the experimental stage and it is hoped that the output will be considerably increased later.

## DISCUSSION

## Treatment of Dross

MR. R. STEWART (Smith & McLean Ltd.) inquired whether the slicing of dross to allow the more liquid part to run back into the bath was a worthwhile procedure. A statement he had read recently suggested that it served no really useful purpose, as the liquid part of the dross contained practically as much iron as the solid dross left behind.

MR. ARNASON replied that some tests he had made revealed that the more liquid dross running through the holes in the spoon contained up to 3 per cent of iron.

DR. HAARMANN (Rheinische Röhrenwerke) said that he had been doing some work (27) on methods of increasing the iron content of dross which showed the extent to which working or slicing the dross was of value in increasing its iron content. The extent to which zinc could be recovered depended on the type of dross, which was, of course, not a uniform material but consisted of zinc-iron alloy crystals embedded in a matrix of zinc. Some photomicrographs he had taken showed the extent to which dross could vary. In these, the zinc-iron alloy crystals showed up light against the dark background matrix of zinc. Fig. 1 showed a lot of very small crystals and was a sample of dross obtained from a new bath recently filled with virgin zinc. The crystals had not yet had time to grow, and hence the dross was of a muddy consistency, most of which ran through the holes in the spoon when slicing it. After the bath had been in use for some time, the dross became more granular as shown in Fig. 2. Where conditions were particularly favourable for crystal growth, a coarse structure such as that shown in Fig. 3 could develop.



Fig. 1 ( $\times 25$ )  
Hard zinc containing  
0.66% Pb 3.51% Fe



Fig. 2 ( $\times 25$ )  
Hard zinc containing  
1.17% Pb 3.12% Fe



Fig. 3 ( $\times 25$ )  
Hard zinc containing  
0.52% Pb 3.85% Fe

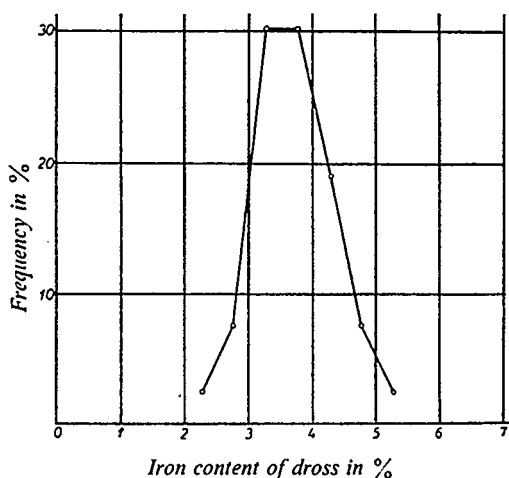


Fig. 4 ( $\times 24$ )  
Single crystals of  $\delta_1$   
phase zinc-iron alloy

The zinc-iron alloy found in dross was of two kinds, distinguished by differences in iron content and crystalline form. In Figs. 1 and 2 the alloy was in the form of monoclinic crystals of the  $\gamma$  phase, containing 6-6.2 per cent iron. Sometimes, however, the zinc-iron alloy in the dross was present wholly or partly as the  $\delta_1$  phase, containing 7-11.5 per cent iron, but usually around 7 per cent. Crystals of the  $\delta_1$  phase were shown in Fig. 4. They belonged to the hexagonal system and were bipyramidal. Although these crystals differed somewhat from those illustrated in Dr. Bablik's handbook in that their height/basal axis ratio was considerably greater, Dr. Haarmann said they were typical of those found in hundreds of samples of dross which had been examined. Fig. 3 showed a section of a  $\delta_1$  phase crystal cut parallel to its basis.



The iron content of normal well-worked dross was usually in the range 3.5-4 per cent, and since the  $\gamma$  phase alloy in Figs. 1 and 2 contained 6-6.2 per cent iron, it followed that between 30 and 40 per cent of zinc must be held in the interstices between the crystals. With  $\gamma$  phase alloy, 4 per cent iron was the maximum likely to be achieved for dross in normal practice, so that 33 per cent zinc still remained entrapped. With dross containing  $\delta_1$  phase alloy, the iron content could rise to 5½ per cent, but there would still be 30 per cent or more of zinc trapped between the  $\delta_1$  phase crystals. The extent to which zinc was trapped in ordinary dross was shown in graph 1, which gave the results of 38 analyses of average samples of dross from different factories. The lowest iron content found was 2.01 per cent and the highest 5.3 per cent. 60 per cent of the samples contained between 3 and 4 per cent of iron.



GRAPH 1

The iron content of dross could be improved by mechanical treatment as the following microphotographs showed. Fig. 5 was normal dross after slicing in the spoon in the ordinary way. The effect of centrifuging it to remove some of the zinc matrix was shown in Fig. 6, whilst Fig. 7 showed the further concentration of zinc-iron alloy crystals which could be obtained by treating the dross in a hydraulic press after centrifuging.



Fig. 5 ( $\times 2$ )  
Not centrifuged



Fig. 6 ( $\times 25$ )  
Centrifuged



Fig. 7 ( $\times 25$ )  
Centrifuged and  
pressed

The effect exercised on dross straight from the bath by working or slicing it on a perforated spoon was shown in Table 1, where four different drosses were examined. The results were set out graphically in Fig. 8, where each complete block represented a sample of dross as removed from the bath. The bottom sections 1 showed the percentage of dross remaining in the spoon after working. The sections marked 2 were the percentage of hard zinc in dross lost through the holes in the spoon and returned to the bath; whilst the small sections 3 at the tops of the columns were the amount of free zinc of low iron content obtained by the process. It would be seen that the amount of dross returned to the bath by working it on the spoon varied in these four cases between 15.3 and 31.5 per cent whilst the amount of good zinc was only from 6.0-15.3 per cent. Dr. Haarmann concluded by saying that whether the treatment of dross on the spoon was justified or not in view of these figures, was for the galvanizer to decide, having due regard for zinc prices and prevailing conditions.

Table 1

SAMPLE			1 FM	2 F	3 L	4 M
I	DROSS IN SPOON BEFORE SLICING	AMOUNT kg	265.6	211.0	140.0	278.0
		%	100	100	100	100
		ANALYSIS Fe%	3.62	4.34	3.84	2.99
		Pb%	0.73	0.55	0.78	0.95
II	CRYSTAL PHASE		$\delta_1$ some $\delta_3$	$\delta_1$		$\delta_1 + \delta_3$
III	RESIDUAL DROSS AFTER SLICING	AMOUNT kg	209	127	78	192
		%	78.7	60.2	55.7	69.0
		ANALYSIS Fe%	4.22	4.45	3.86	3.41
		Pb%	0.91	0.83	0.69	0.84
IV	PASSING THROUGH THE SPOON	AMOUNT kg	56.6	84.0	62.0	86.0
		%	21.3	39.8	44.3	31.0
		ANALYSIS Fe%	3.02	3.52	2.54	2.32
		Pb%	1.19	0.70	0.94	1.24
V	DROSS RETURNED TO BATH	AMOUNT kg	40.5	66.5	40.8	58.5
		% OF ORIGINAL DROSS	15.3	31.5	29.0	21.0
VI	ZINC RECOVERED	AMOUNT kg	16.1	17.5	21.2	27.5
		% OF ORIGINAL DROSS	6.0	8.3	15.3	9.8

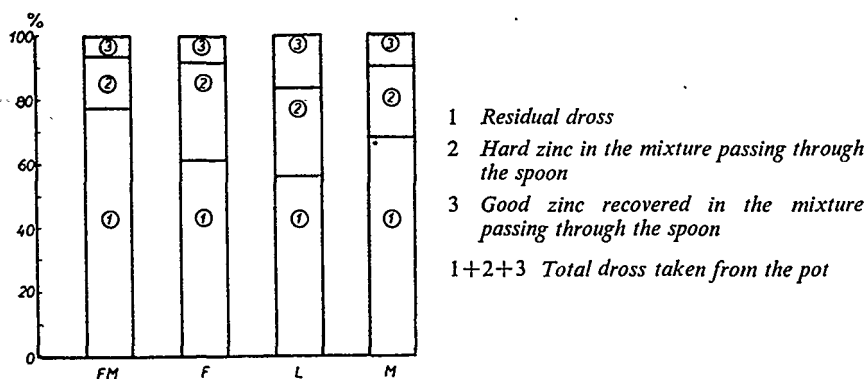


Fig. 8

MR. MONTGOMERY (Fredk. Braby & Co. Ltd.), referring to Mr. Arnason's paper, said that the claims made for the new methods were a very considerable advance on anything he had been able to do, and that to recover from the dross 20 per cent zinc of such low iron content was a very creditable achievement. It was his usual practice to allow zinc-iron alloy crystals to settle out under gravity, and one part of zinc could be removed in this way from three parts of dross. In tests where he had remelted the reclaimed zinc for a second time, he had found that between 30 and 60 per cent of the reclaimed metal went to the bottom of the bath to form dross. Even under the best conditions, such as liquating twice under favourable conditions of time and temperature, he had not been able to obtain an iron content of less than 0.1 per cent in the reclaimed zinc. He thought temperature control was very important in reclaiming zinc from dross, as the iron content of the reclaimed metal rose rapidly as the temperature was increased.

MR. ARNASON said that much depended on the care with which the separation was done. He agreed that temperature control was important, and confirmed that in his experience 20 per cent of the dross could be recovered as zinc of this low iron content by his new procedure.

MR. D. N. FAGG (British Non-Ferrous Metals Research Association) referred to another approach to the problem of dross treatment made by his Association using filtration through a bed of silimanite powder. Starting with a dross containing about 3.75 per cent iron, it had been possible to reduce the iron content by 95 per cent, although so far it had been difficult to obtain a yield greater than 25 or 30 per cent.

MR. A. H. THOMPSON (General Galvanizers Ltd.) said that, although his company had no special way of drossing, they had gone carefully into the question of sweating dross. By sweating he meant putting the dross into a separate pot and raising its temperature so that a fluid zinc could be separated from the more concentrated dross. When he was in America he had learned that galvanizers there never sweated their dross, as they considered that the reclaimed metal was not fluid enough and had a bad effect on the galvanizing bath.

In response to a question from the chair, MR. D. S. BURWOOD (Imperial Smelting Corp. Ltd.) said that his company could not add much to the experience of the galvanizers in reclaiming zinc from dross. They had investigated a simple liquation process for recovering zinc from drossy zinc obtained as a by-product in their refining process, but no metal of satisfactory quality had been recovered by this method. Dross had to be treated as a raw

material and the zinc had to be distilled from it as when producing virgin metal from zinc concentrates. Similarly his company did not recover zinc from ashes in any other way than by treating them as a raw material and processing them in the ordinary smelting plant. Only in this way could a grade of zinc suitable for the general market be obtained.

### Treatment of Ash

M. J. ROUFF (Etablissements Schmid) said he would like to mention his experience in treating zinc ashes using a special salt. The composition of this product was, of course, unknown, it being supplied under a serial number or letter and delivered in sealed drums. Unfortunately the salt was corrosive and the metal drums were soon destroyed. At the same time, the salt, being hygroscopic, attracted moisture and so must not be exposed to the air. Turning to the use of the salt, he said that the ashes made during the day were returned to the bath for a quarter of an hour, and the next day crushed and sieved. First, the sifted ash and the zinc were carefully mixed with the special salt already mentioned and the whole spread on the surface of the bath in a layer of about 3-4 centimetres thick, the temperature of the bath being 450-465°C. After 4 minutes exposure on the bath, the sifted ash had to be worked with a skimming ladle, and the same operation was repeated 4 minutes later, i.e. 8 minutes after first placing the mixture on the bath. The chemical reaction then started and the ashes began to redden. The operator then continued to work the ashes in order to assist the liberation of the zinc until the entire covering layer had become red. This operation took a further 7 minutes. After 15 minutes from the time of putting the mixture of sifted ash and reducing salt on the surface of the bath, the reaction was complete. During the course of the reaction, the ashes smoked and as the reaction proceeded the smoke increased. When the reaction was complete the ashes were removed by means of a skimming ladle. In this way it was claimed that 60 per cent of the ash could be recovered as metallic zinc. In his experience this was not so, and the method had now been abandoned. Mr. Rouff continued by saying that he now preferred another method in which the ash was taken off the bath and sieved the following day. The coarse portion was then mixed with an equal quantity of fresh ash, and the mixture puddled on the surface of the bath. The results obtained with this process were similar to those obtained with the former process.

### Closure

MR. F. C. BRABY (Fredk. Braby & Co. Ltd.) then rose and thanked Mr. Arnason for his paper. It was, he said, one further example of the work which was being done by the J. Chr. Jensens Galvaniserings Etablissement to improve the galvanizing industry. He looked forward to hearing more about the pumping of dross and the formation of dross of higher iron content. Finally, he wished to express the meeting's appreciation of Mr. Busch-Jensen's very able chairmanship and his kindness in presiding at the two morning sessions.

## THE CORROSION RESISTANCE OF GALVANIZED COATINGS

The paper considered by the Conference under this heading was specifically concerned with the performance of galvanized steel window frames. These are installed in all types of buildings from houses to factories and are subject to such varied conditions of service that window installations constitute a performance test for galvanized coatings of the widest possible scope. The discussions on this subject were not, however, confined to window frames but covered other fields of service including contact with domestic water supplies. The paper also dealt with the continuous galvanizing process used for treating steel windows and some information about this subject is, therefore, included here as well.

The corrosion resistance of galvanized coatings was considered at the fourth and last Technical Session of the Conference with Mr. A. H. Thompson, the Vice-Chairman of the Hot Dip Galvanizers Association, in the chair.

### Introduction

In the absence of Mr. Pellowe, MR. R. L. STUBBS (Zinc Development Association) introduced the paper. The galvanizing of metal windows, he said, was taken rather for granted in England where several new and modern plants had been installed for this purpose since the war. Steel windows represented the largest new use for galvanizing in the U.K.

In the 1930s the position had been very different and the steel window manufacturers were seriously concerned with corrosion troubles. After considering various methods of rust prevention, hot dip galvanizing had been adopted by a number of window manufacturers as affording the best protection, and this process was now used for rust-proofing the majority of steel windows produced. As a result, steel windows were now a reliable article and were being ever more widely used.

Turning to the paper, he felt sure that it would be read with particular interest by those visitors from other countries where the advantages of galvanized windows had not yet been realized. The paper opened with a discussion of the process, and in the absence of Mr. Pellowe he felt sure that Mr. Wilson, another steel window manufacturer from the U.K., would be pleased to give further information about the process. Mr. Stubbs then referred to the tables showing the corrosion resistance of galvanized coatings under different conditions and quoting the results of tests carried out in the U.K. and U.S.A. He said he was struck by the large number of tests which had been done in England. The paper concluded with a survey showing how widely steel windows were used, and how well they stood up to corrosion under many varied conditions of service.

# THE CORROSION RESISTANCE OF GALVANIZED COATINGS WITH SPECIAL REFERENCE TO GALVANIZED WINDOW FRAMES

by E. F. PELLOWE,\* B.Sc., A.R.I.C., A.I.M.

## Introduction

Some recent statistics published by the Zinc Development Association (28) indicate that in Great Britain the hot dip galvanizing industry consumes more zinc today than any other industry, and that the biggest single factor in this increase since 1939 is that practically all steel windows are now rust-proofed by this method.

Before the 1914-1918 war the steel window frame was a hand-made, comparatively expensive product. With the introduction of standardized production methods and the ready availability of accurately rolled steel sections, and because of the shortage of timber of good quality, the steel window industry in England has steadily expanded and today something like 5,000,000 steel frames are produced every year. These window frames are used in domestic and public buildings in rural, urban, marine and industrial areas. They are also used extensively in factories and industrial buildings of all kinds.

The original finish on these windows, as supplied from the factory to the building site, was two baked coats of priming paint. By the early 'thirties it became apparent that such a finish was hardly adequate, and that if the industry was to maintain its pre-eminence and continue to expand a more robust finish was needed. On its journey from factory to site the steel window often encounters rough handling which will chafe or chip the paint film, and once it has reached the building site it may well lie on the ground for many months awaiting completion of the walls and surrounding brickwork before installation.

To cope with the dual conditions of rough handling and neglect it was decided to rust-proof all steel frames, using the hot dip galvanized coating because of its robustness and long corrosion life.

The hot dip galvanizing process must not be confused with cold galvanizing or electro-galvanizing. The first process depends upon dipping the steel frame into a bath of molten zinc. The last process is better termed 'zinc plating' and the frame is placed in an aqueous solution of a zinc salt and the zinc plated on to the work by an electric current.

Considerable research work was carried out on the hot dip galvanizing process to modify it for dealing with the new product and the present day process is outlined below.

A great deal of attention has been given to the corrosion resistance of hot dip galvanizing in various atmospheric conditions over the last ten years and our experiences in this respect are also outlined below.

## I. Process

A typical plant for galvanizing windows may deal with upwards of 300 tons of windows per week. The frames pass through the plant on specially designed carriers on a monorail, and where it is necessary for the loads to pass

\* Crittall Manufacturing Co. Ltd.

from a high level to a low level monorail they do so by means of a drop hoist. As a general principle inner frames are galvanized separately from their outers. Each frame carries, however, its own hinge leaves, handle brackets, etc., so that subsequent assembly merely means the insertion of hinge pins.

The essence of the whole process is scientific control of temperature; immersion times, acid strength, etc.

- 1 All mill scale is removed by pickling in 10-12 per cent sulphuric acid. This is heated by specially designed lead coils and thermostatic control keeps the temperature at 140°F. The iron content is kept in the range of 6-7 per cent by a Kestner crystallizer. This gives a pickling speed of 15-20 minutes for the hot rolled mild steel of which the sections are made. An inhibitor is used in the acid to restrain over-pickling and to minimize roughening of the steel.
- 2 The acid and iron salts are then removed by washing twice, once in hot and once in cold running water. This running water is kept clean by passing through neutralizing, aerating and filtering operations, and returns to the washing tanks with a purity of one part per million iron and a pH of 8.
- 3 The frames are then immersed in a 30 per cent solution of zinc ammonium chloride ( $\text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl}$ ) at 120°F. This contains a wetting agent and an insistence upon the cleanliness of this tank cannot be over-stressed. The acid carry-over should be kept to a minimum by thorough washing and the pH of the flux should not drop below 4.5. Failure to do this will (a) increase zinc wastage and (b) lower the ductility of the coating.
- 4 The fluxed frames are then dried in a specially designed oven. The essential feature of this oven is that it uses large quantities of clean warm air. Clean air is drawn in from outside the factory and warmed by the products of combustion from the galvanizing pot, utilizing a heat exchanger. The heating rate is such that the temperature of the window frames does not exceed 180°F. This is based on the work of Daniels (3) which deserves to be better known. Over-fierce drying of prefluxed coatings of this kind is a prolific cause of dross.
- 5 The windows are then hot dipped in a pot 8 ft.  $\times$  5 ft.  $\times$  9 ft. deep, which is gas heated using modern forced recirculation methods. The small surface area as compared with the large heating area means that the B.Th.U. input per square foot is low and the pot life correspondingly high. The low flue gas temperature together with forced recirculation means remarkably uniform zinc temperature. A rigid control of temperature in the range 455-460°C. and a mechanized slow withdrawal speed are factors in controlling the evenness of coating and its freedom from blobs and tears. Additions of small amounts of aluminium prove invaluable in de-oxidizing the pot and, by decreasing viscosity, give a better flow off and improved coating uniformity. The best alloy to use is one containing 98 per cent zinc and 2 per cent aluminium and both zinc and aluminium should be of good purity, the latter being silicon-free. The grade of zinc used in the galvanizing pot is American Prime Western or its English equivalent, and additions of tin, antimony or cadmium rich materials are not permitted. So far as distortion is concerned, we get extremely little, and the amount of rectification required after galvanizing is no more than that required in

ordinary window manufacture. This is partly attributed to the modern flash welding methods used, but without doubt a great deal is due to:

- (a) immersion speed
- (b) immersion time
- (c) withdrawal speed

All these are controlled.

- 6 After galvanizing and cooling, the frames are usually etched, and in this they differ from most other galvanized hardware.

Freshly prepared zinc coatings, e.g. zinc plating and hot dip galvanizing are difficult for paint (29) to adhere to, and whilst it is true that natural weathering will not take long to roughen the zinc surface two factors have to be considered:

- (a) the natural weathering, depending on the time of the year and the locality, may take any time from two weeks to three months to roughen the surface adequately.
- (b) the house occupier may wish to install and paint his windows right away.

A third factor cannot be ignored, viz: that sometimes it is necessary to carry out this etching on site using a mordant. Such a method is expensive and unpleasant, and if the mordant is based on copper sulphate then it will detract from the corrosion resistance of the zinc coating.

Usual factory etchants are based on phosphoric acid/phosphate mixtures.

## II. Corrosion Resistance

### Corrosion Due to Mechanical Damage

Some ten years' experience have indicated that the galvanized coating is more than adequate in standing up to rough handling in transit to site and on the site, particularly so far as ductility and adhesion are concerned.

Exposure tests have been in hand for the last four years to determine what happens if the coating does get damaged. In 1946 galvanized bars with a zinc deposit of 2 oz. per square foot were exposed on a factory roof in Essex. They had been maltreated by filing off the zinc coating from areas of various sizes (see photograph).

Bar No. 1 with bare areas  $\frac{1}{8}$  in.  $\times$   $\frac{1}{16}$  in. shows practically no rusting at these areas.

Bar No. 2 has bare areas  $\frac{1}{8}$  in.  $\times$  1 in.,  $\frac{1}{4}$  in.  $\times$  1 in.,  $\frac{1}{2}$  in.  $\times$  1 in. and 1 in.  $\times$  1 in. Slight superficial rusting occurs in the groove  $\frac{1}{8}$  in.  $\times$  1 in. and the zinc edge on either side of it is still intact. The rusting is somewhat deeper on the  $\frac{1}{4}$  in.  $\times$  1 in. groove and the zinc edge is beginning to recede. As the grooves get wider the degree of pitting of the bare steel and the amount of retreating of the zinc edge increases.

Bar No. 3 contains large bare steel areas and small galvanized areas.

This simple exposure test illustrates the sacrificial or anodic protection conferred by zinc coatings and indicates that small damaged areas continue to be protected by the zinc coating. As has been stated elsewhere the life of a zinc coating is essentially proportional to the weight of zinc per unit area and the long protection given to damaged areas as indicated above is due to the heavy zinc coating employed.





*Examples of the sacrificial protection of zinc on steel after  
4 years exposure*

## Corrosion of Unpainted Galvanizing

The corrosion resistance of unpainted galvanizing has been assessed in several publications of A.S.T.M. and the Iron and Steel Institute.

Table 1 (The Iron & Steel Institute. Hudson: Atmospheric Corrosion on Unpainted Irons and Steels. Paper No. 10/1943 of the Corrosion Committee) which has been widely quoted gives estimated lives of galvanized coatings in various areas by measuring the loss in weight over a given period. Since these results were obtained on solid zinc and not on an actual galvanized coating they can only be taken as indicating a tendency, but none the less they have an indirect value.

Table 2 gives the atmospheric details at the various stations.

Table 3, based on work by the American Society for Testing Materials, is of interest for it gives data on the exposure of actual window frames. Those exposed at the State College, Pennsylvania, for 17 years show no trace of rust. At Sandy Hook, New Jersey, a trace of rust occurs after 17 years; at Key West, Florida, no rust occurs after 18 years.

Perhaps the most detailed work on corrosion in recent years is that being carried out by the Iron & Steel Institute and reported in the paper by Hudson & Banfield (Paper No. 21/1946 of the Corrosion Committee). One of the chief difficulties encountered by the authors is in the assessment of failure in hot dip galvanized coatings (vide page 242). As a galvanized coating is gradually weathered it becomes grey and darker grey and finally almost black. It stays in this condition for some time and then gradually stains a pale yellow. At this stage the zinc-iron alloy layers or phases have been reached. When this alloy has been corroded over a large enough area and the basis steel is reached, then the usual red rust is seen. The true break-down position is thus difficult to assess and it is felt that more accurate assessment is only possible where weight losses are measured and the final breakdown interpolated.

From exposure tests being carried out by the writer on samples prepared by the above process and using aluminium in the pot, it looks as if:

- (a) the anodic protection given by the alloy layer is at least as effective as the zinc layer.
- (b) the corrosion losses of the alloy layer are somewhat less than that of the zinc layer.

This possibility is referred to by Hudson & Banfield (*ibid.*, p. 242).

Two further conclusions from this fundamental paper are commented on below.

Metal	Density g./cc.	Coating Required		
		Weight		Equivalent Thickness mils.
		W g/specimen	W oz./sq. ft.	
ALUMINIUM	2.70	51	0.8	3.6
CADMIUM	8.64	272	4.5	6.0
ZINC	7.16	110	1.7	2.9

From this it will be seen that the thickness loss of aluminium is somewhat greater than zinc.

The superiority of zinc coatings on iron compared with cadmium coatings in industrial atmospheres is in agreement with the results of other

THE CORROSION RESISTANCE OF GALVANIZED COATINGS

TABLE I  
Rates of Atmospheric Corrosion of Zinc. Probable Lives of Galvanized Coatings

HOME			
Station	Corrosion Rate of Zinc Oz. per sq. ft. per year	Ratio of Rates for Ingot Iron and Zinc	Calculated Life of Galvanized Coating (0.75 oz. per sq. ft.) Years
Calshot	0.080	20.1	9
Dove Holes Tunnel	1.92	1.0	0.4
Llanwrtyd Wells	0.073	19.0	10
Motherwell	0.103	21.0	7
Sheffield	0.405	7.5	2
Woolwich	0.089	26.4	8
Derby	0.183	17.8	4
Frodingham	0.244	20.7	3
Sheffield University	0.136	19.4	6
OVERSEAS			
Abisko	0.013	9.8	58
Apapa	0.025	23.9	30
Aro	0.037	8.5	20
Basra	0.026	14.3	29
Congella	0.095	20.4	8
Khartoum	0.012	3.6	63
Singapore	0.021	16.8	36
Berlin-Dahlem	0.065	19.3	12
Sandy Hook, N.J.	0.062	30.6	12
State College, Pa.	0.021	30.9	36
Pittsburgh, Pa.	0.181	15.1	4

**TABLE II**  
*Particulars of the Corrosion Stations*

HOME						
Station	Type of Atmosphere	Mean Annual Temp. °F.	Rainfall In.	Relative Humidity %		
Galshot	Marine	51	26	84		
Dove Holes Tunnel	Railway tunnel	—	—	—		
Llanwrtyd Wells	Rural	47	55	79		
Motherwell	Industrial	48	32	82		
Sheffield	Industrial	48	30	84		
Woolwich	Industrial	50	23	81		
OVERSEAS						
Station	Type of Atmosphere	Position		Temp. °F.	Rainfall In.	Relative Humidity %
		Lat.°	Long.°			
Abisko, Sweden	Sub-polar	68N.	19E.	30	11	74
Apapa, Nigeria	Marine-tropical	7N.	4E.	80	72	79
Aro, Nigeria	Inland-tropical	7N.	3E.	77	45	84
Basra	Dry-sub-tropical	31N.	48E.	75	7	64
Congella, South Africa	Marine	30S.	31E.	71	43	76
Khartoum	Dry tropical	16N.	33E.	85	6	31
Singapore	Marine-tropical	2N.	104E.	81	95	80

THE CORROSION RESISTANCE OF GALVANIZED COATINGS

TABLE III

Exposure of Galvanized Window Frame Sections at Sites in U.S.A.

Exposure	10 yrs.	12 yrs.	14 yrs.	16 yrs.	18 yrs.	19 yrs.
Window Frame Sections No. 209. Coating 3.10 oz./sq. ft.						
Key West, Fla.	0	0	0	.0	0	0
Altoona, Pa.	<10R	10R	All Specimens Removed			
State College, Pa.	0	0	Specimens Removed			
Sandy Hook, N.J.	Specimens Removed after Rack Collapsed					
Window Frame Sections No. 792. Coating 2.60.oz./sq. ft.						
Key West, Fla.	0	0	0	0	0	0
Altoona, Pa.	15R/30Y	40R/60Y	All Specimens Removed			
State College, Pa.	0	—	0	0	0	0
Sandy Hook, N.J.	0	TrY	10Y	TrR/5Y	2R/10Y	2R/20Y
Window Frame Sections No. 161. Coating 2.97 oz./sq. ft.						
Key West, Fla.	—	—	0	0		
Altoona, Pa.	Specimens Removed after Rack Damaged					
State College, Pa.	0	0	Specimens Removed			
Sandy Hook, N.J.	Specimens Removed after Rack Collapsed					

Key: 0—no rust; figures are approximate percentages; Y—yellow or orange-yellow rust; Tr—trace.

investigators. For instance, Passano states that in atmospheric-exposure tests in New York City, cadmium coatings were found to weather 2.6 times more rapidly than zinc coatings; in other atmospheric tests on electro-deposited coatings then in progress at the Bureau of Standards, a cadmium coating of 0.36 oz./sq. ft. of surface had given about the same service as a zinc coating of 0.12 oz./sq. ft. of surface.

The life of unpainted galvanized coatings of the order of 1.8-2.2 oz./sq. ft., using Table I as a basis, is given below:

Location	Type of Atmosphere	Probable life in years
Khartoum	Dry tropical	150
Basra	Dry inland	80
Singapore	Marine tropical	70
Llanwrtyd Wells	Rural	25
Calshot	Marine	25
Woolwich	Urban and Industrial	20
Motherwell	Urban and Industrial	15
Sheffield	Industrial	5

Similar figures (allowing for somewhat different climatic conditions) have been obtained by the author in exposure tests over the last three years in:

Barbados, West Indies	Basra
Port Elizabeth, South Africa	Cairo
Johannesburg, South Africa	Bombay
Baghdad	

The method of loss in weight was used in this case to assess the amount of corrosion.

From the point of view of windows being dispatched to site and left there for long periods unpainted, there is obviously no need for worry. Indeed for large areas of the world there is no need to paint galvanized frames at all, and in many parts of England there is no need to paint them for a generation.

### Corrosion of Painted Galvanizing

It is a fact that most people paint their galvanized window frames, presumably from aesthetic considerations, and because of this the writer has given this aspect a great deal of attention. Hudson & Banfield have touched upon composite protective schemes (metallic coatings plus paint) (*ibid.*, p. 248).

So far as ordinary domestic windows are concerned, the householder or decorator appears to use the same paints and colour schemes as he used before on the ungalvanized windows. These paints are purchased from the local ironmongers shop and may be based on practically any oil and contain any usual pigment. Since the window is phosphate etched before it is dispatched no troubles occur with paint adhesion. One difference, however, has been observed, viz: that the paint lasts longer and the frequency of painting is much less. The reason for this is that on the ungalvanized window the necessity for painting became obvious when rust started showing through. In other words the rust determined the frequency of repainting and not the paint film breakdown. With galvanized steel, repainting need not be done until the paint film disintegrates; even then it need not be done as the zinc coating will last unprotected for many years.

As with any painting project, however, the better the paint the longer it lasts. The biggest cost in painting a building is the labour involved and if good quality selected paints are used the frequency of repainting can be reduced very considerably. (30)

### Galvanized Window Frames in Industrial Service

*Sugar Beet Factories.* A full scale test has been carried out in a sugar beet factory for the last six years. The atmosphere is very hot and humid and in parts of the factory water is continually running down the walls. The atmosphere is further contaminated with sugar dust and protein acids. A window has been exposed to such conditions since 1944. Various paints have been applied to the galvanized bars and some bars have been left bare.

Once every two years the window is removed, cleaned up and examined. The following facts emerge:

- (a) where a chromated red oxide primer followed by an aluminium pigmented synthetic second coat is used, the paint film is still reasonably intact, even after 6 years.
- (b) one coat of chromated alkyd followed by an uninhibited second coat is also satisfactory.

- (c) two chlorinated rubber coatings are just beginning to disintegrate.
- (d) two coats of cheap oil-based paints have long since disintegrated, although they were based on metallic zinc/zinc oxide pigment.

Where no paint was used, the bare galvanizing has reached the dark grey stage and still has several years of useful life.

*Gas Works.* Several bars and windows with various paints, and some with no paints, were exposed on the roof of a large London Gas Works for 20 months.

At the end of this time the samples were removed and exposed for 12 months in a duct carrying away steam, coke fumes and sulphur oxides from coke quenching sprays. Conditions were permanently wet from condensation except during very hot weather.

Upon removal and examination it was apparent that the various paint films were beginning to disintegrate in places but the zinc film was still intact, as was proved by cleaning up the frame. A microsection of the coating indicated that about 2/3 of the protective zinc layer remained. This window received treatment that no window would be required to stand up to in practice.

Arising from these two exposures, it was apparent that:

- (a) in heavy industrial conditions the impermeability of the paint film to moisture is the biggest single factor for good. Thus modern synthetic vehicles were better than oil and both bituminous and chlorinated rubber materials gave good accounts of themselves.
- (b) the undercoating should be inhibitive, i.e. contain chromates, and that these should preferably be 'mixed', i.e. contain soluble and insoluble portions. The leafing properties of aluminium in the second coat are to be considered as improving water resistance.
- (c) a painted zinc coating is more resistant to corrosion than the sum of a paint coating and a zinc coating acting alone.
- (d) the thicker the zinc coating the better.

Further samples exposed at a gas works on the sea coast in the South of England and in Old Trafford, Manchester, at the beginning of 1948 confirm this.

Based on the above principles, galvanized products have been incorporated in the following industrial applications with success:

*Concrete drying sheds* (1947). The conditions are high humidity and alkaline dust. Paint used — chromated red oxide and aluminium second coat.

*Pickle Factory* (1947). In such a factory the actual corrosion agent is presumably acetic acid, but, as with so many of these industrial atmospheres, it is in such a dilution as not to be particularly serious.

*Chromium Plating Shops.* Here the active agent is chromic plus sulphuric acid, but the degree of extraction as required by the Factory Acts is such that the air inside the plating shop is little worse than the outside air. Time and time again it is found that where the air is fit for a man to work, a galvanized window will be satisfactory.

*Cow Barns, Public Lavatories and Refrigerating Plants.* In such installations, presumably the active agent is ammonia, which is not particularly corrosive to zinc. One case is reported of liquid ammonia exploding all over bare galvanized windows without any serious effect.

*Gas Works.* Here the active agent is usually reported as sulphur dioxide. From an examination of many samples it is apparent that at least two other factors are involved, viz.:

- (a) the scouring action of wind-blown coke dust, and
- (b) the soot or carbon deposits which tend to form particularly in protected places under eaves, etc.

*Furniture and Wood Factories.* Here the active agent is generally considered to be the wood acids leached from oak dust, etc. An isolated examination of one sample of wet oak dust gave a pH of 6 which could also be explained by the carbon dioxide content. It is felt that this is not particularly corrosive.

*Tanneries, Paper Mills and Breweries.* An examination of the atmospheres in these industries is at present being carried out.

In that portion of the tannery where the hairs are removed from the hides, a lime slurry is used and whilst the atmosphere is humid it is slightly alkaline and will not be particularly corrosive.

In that area where actual tanning is carried out, using sulphite solutions, galvanized coatings plus a coat of paint as indicated above should be successful for many years.

*Textile and Tobacco Factories.* An examination of atmospheres in these particular industries suggests that humidity is the main factor involved and that conditions are no worse than in Sugar Beet Factories.

*Pit Head Baths.* Conditions here are similar to those reported under the previous heading.

*Laboratories, etc.* In recent years, a great deal of building of research blocks has been carried out both on industrial premises and in our centres of learning, and the writer is frequently asked whether galvanizing is satisfactory in view of the acids and other chemicals frequently used in such places.

In practice, the contamination of such atmospheres is rarely heavy enough to cause corrosion nor does the atmosphere remain contaminated for long.

The new Research Block recently built by the Company for whom the writer works has galvanized windows which are not, and will not be, painted.

### Corrosion on Sites

The writer has given considerable attention to the general behaviour of galvanized frames on site, both whilst the building is being completed and after. As a result it is apparent that:

- (a) zinc coatings are much more resistant to alkalis than they are given credit for, and have the advantage of aluminium in this respect. Unpainted galvanized frames frequently get covered with mortar, concrete, etc., whilst building is going on, and this may not be cleaned off until some weeks later when glazing and painting are carried out.
- (b) Dissimilar metal contact is not to be feared. Although galvanized windows frequently carry brass or gunmetal attachments, little trouble has been encountered with dissimilar metal action. No doubt this is due (i) to the relatively small surface area of the copper-bearing part as compared with the large zinc area, and (ii) the practice of painting and thereby insulating the junction.



When galvanized frames awaiting building in have been left stacked on edge on site for several months, the writer has noted one or two instances where rapid corrosion occurs on the bottom edges, i.e. in contact with the ground. This coincided with the existence of old ashes. An examination of these showed no unduly acidic nature and it is suspected that the cause of such corrosion is bacterial in origin.

### III. Summary

The metal window industry has widely adopted hot dip galvanizing as a finish for their product. Some ten years of experience indicates that the potentialities of such a finish are not completely explored, and that with a hot dip galvanized coating the steel window can enter fields that were hitherto closed to it. In terms of cost per year of rust-proof life, it is probably the cheapest finish there is both to buy and to maintain.

## DISCUSSION

## Galvanizing Process

MR. E. M. WILSON (Henry Hope & Sons Ltd.) opened the discussion by saying that he had been very interested to read Mr. Pellowe's description of his window galvanizing process, and that he would like to add some remarks about his own works where hydrochloric acid was used instead of sulphuric acid for pickling. His reasons for choosing this acid were ease of disposal (in his particular case without neutralizing) and the flexibility which the use of cold pickling allowed when fluctuating quantities and various types of work had to be processed. A further consideration was that his works were very near a supplier of hydrochloric acid, so that carriage charges were correspondingly low. Sulphuric acid had advantages when the process was a continuous one and the loss of heat due to intermittent use did not arise. In his works the steel was degreased before pickling and there were none of the scum troubles which were liable to occur when using hot sulphuric acid either with or without a wetting agent both as degreaser and pickler.

When using a continuous process, such as metal window galvanizing, in which the articles were hung on racks, a special difficulty was sometimes encountered. This was that a black patch sometimes occurred in the corner from which a metal window was suspended, and it was difficult to discover which part of the process of pickling, degreasing, washing, fluxing or dipping was really to blame, since any or several of these treatments could be partly or wholly responsible.

MR. PELLOWE (in a written reply) said that in pickling smaller tonnages or where tonnage fluctuated, hydrochloric acid was satisfactory and probably cheaper. He could not see that the disposal question was any easier, but agreed that it was useful to be located near a hydrochloric acid manufacturer. With large constant tonnage there was little doubt, however, that sulphuric acid was the best proposition, since it gave a constant pickling speed; moreover since the ferrous sulphate content could be kept constant by using a crystallizer, the disposal problem need not arise. Obviously grease from sheet, etc., should be removed beforehand, but if this was incompletely done, sulphuric acid did possess de-emulsifying properties, and if a little scum was left on the pickle tank, it could easily be kept in the middle and away from the exit and entry and acted as a fume blanket.

As regards black patches in the suspended corner, Mr. Pellowe suggested three causes: (1) There was an air pocket and zinc could not get in. (2) The flat steel hook was preventing acid from getting in. (3) The prefluxing tank was heavily contaminated with acid and iron, and had lost its 'bite'.

MR. M. L. HUGHES (B.I.S.R.A.) asked why Mr. Pellowe thought it necessary for the alloy used for adding aluminium to the bath to be silicon-free.

MR. PELLOWE (in a written reply) said that some years ago he had been experimenting with aluminium additions to galvanizing baths and had run into difficulties with black spots at low aluminium concentrations where, according to published work, no troubles of this sort were to be expected. He had then been adding aluminium in the form of L.33 type alloy of relatively high silicon content. More recent experiments, in which commercially pure aluminium was added, had allowed him to use higher concentrations of aluminium before the black spot difficulty appeared, and were more

in line with the published results of other workers on aluminium additions. He had concluded that it was the high silicon content of the alloy which was to blame.

### Corrosion of Galvanized Coatings

PROFESSOR J. L. MANSA (Maskin Laboratoriet, Copenhagen) was invited to address the meeting, and spoke of his work during the last five years as Chairman of a committee considering the corrosion of galvanized iron pipes used for carrying cold water to Copenhagen's houses. Much trouble had been experienced from failure of these pipes through corrosion, and his committee had examined various possible causes including stray currents, defects in the steel, and the corrosive effects of the water. None of these factors had, however, been found to be responsible. The water had been tested by German and American methods, and shown to be one that deposited calcium salts, i.e. a good water from the corrosion standpoint. The question before the committee was how the iron could be attacked whilst in contact with the zinc coating. A divided cell had been set up with zinc and cold running water on one side of the membrane, and iron on the other side in which the water was not flowing. At first, the zinc was anodic and the iron cathodic so that the ordinary electrochemical protection of the iron by sacrificing the zinc was operative, but after fourteen days the polarity of the iron and zinc was reversed. Turning to the pipes, micrographical.

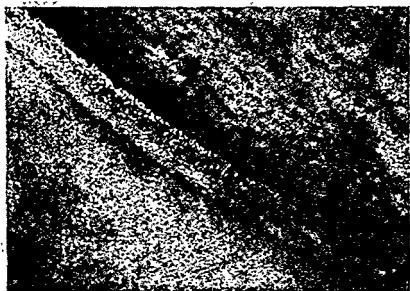


Fig. 1 Coating on interior of pipe galvanized by firm I. Quality considered good. ( $\times 50$ )

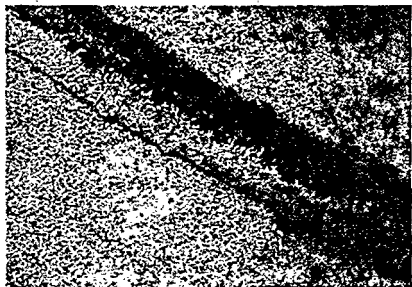


Fig. 2 Coating on interior of pipe galvanized by firm III. Questionable quality. ( $\times 50$ )

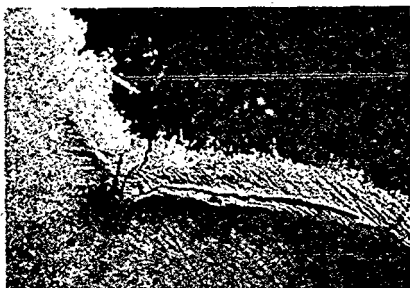


Fig. 3 Coating on interior of pipe galvanized by firm V. Questionable quality. ( $\times 100$ )



Fig. 4 Coating on interior of pipe galvanized by firm I. Questionable quality. ( $\times 50$ )

examination had revealed porosity in some of these, as shown in the accompanying micrographs prepared by Dr. Niels Engel. Professor Mansa now believed that the pores were acting like the experimental divided cell. Examination of the pipes in this way now enabled him to pick out those pipes which were likely to fail in service. By way of confirmation, he had done some tests in which water had been allowed to run slowly down lengthwise sections of pipes which he suspected of having defective coatings, and these had revealed microscopic rusting.

M.R. M. L. HUGHES, invited by the Chairman to reply, congratulated Professor Mansa on his approach to the problem. He thought the committee had done well in being able to pick out those pipes which would cause trouble. A polarity reversal in cold water would have led to failures by pitting, and Professor Mansa confirmed that the failures were of this sort. He asked Professor Mansa to let him have details of his metallographic technique, as it was not easy to obtain good micrographs of zinc coatings. He suggested tentatively that the cracks might be due to contraction in the zinc coating during cooling, the zinc having the higher expansion coefficient. The coating was unusually thick, the galvanizers having generously supplied a coating of perhaps 20 oz. to the sq. ft. in the case of the coating shown in Fig. 4.

In response to a question from the Chair, DR. R. HAARMANN (Rheinische Röhrenwerke) said that he had no experience on this particular problem. He was most interested and impressed by Professor Mansa's results, and intended to put some work in hand to see whether failures of this type were connected with any particular method of galvanizing.

M.R. HUGHES suggested that the reversal in the polarity might be due to corrosion products on the zinc preventing it from giving protection. He drew a parallel from the behaviour of filmed aluminium in contact with steel. Aluminium in the unfilmed condition was even more anodic than zinc, but the electrochemical protection afforded to steel by aluminium, once it became covered with an oxide film, was of a low order, and the cut edges of hot-dipped aluminium coated steel sheets were not protected by the aluminium. (Incidentally, aluminium was a very successful coating in resisting heat, though it did not always give such good corrosion protection.) If it were corrosion products on the zinc which caused the reversal, the potential change should have occurred only on the zinc side of the cell. PROFESSOR MANSÁ confirmed that this was so, and that there was no change in the steel potential during the tests.

M.R. C. H. FREWER (Boulton & Paul Ltd.) thought his experience with some very large tanks used during the war for fire-proofing timber might throw some light on the problem. A solution of mon-ammonium phosphate was used. After operating for some time, galvanized pipes passing through the tank disappeared completely. It was eventually found that a small copper sleeve insert about  $2\frac{1}{2}$  in. long and  $1\frac{1}{2}$  in. dia. introduced traces of copper into the water, which had caused the trouble. He wondered whether minute traces of copper introduced from Copenhagen's copper roofs could be responsible.

M.R. F. C. BRABY (Fredk. Braby & Co. Ltd.) wondered whether any changes had been made in recent years, such as in the type of galvanizing or the water supply, which might have caused the trouble; and asked how long ago it started.

PROFESSOR MANSA replied that the first indications were in the middle 'thirties. Although new wells had been brought into use then, he was sure that the water was not to blame. The water was treated by aeration and filtration. It had a pH of 7.7, a permanent hardness of 19 German degrees and a temporary hardness of 16 degrees.

MR. R. S. BROWN (Rylands Bros. Ltd.) then raised the question of the effect of aluminium and other additions on the corrosion life of galvanized coatings. Although considerable attention had been given at previous sessions to the effect of various alloying additions on the physical nature of the coating, little had been said about the effect of these additions on its corrosion resistance. In his opinion this was of paramount importance, particularly for atmospheric exposure.

MR. R. STEWART (Smith & McLean Ltd.) said he would like to know whether aluminium in the coating had any effect on the formation of white rust.

MR. D. N. FAGG (B.N.F.M.R.A.) said that the zinc alloying metals covered by their paper had been shown to have little effect on the life of coatings exposed to industrial atmospheres, and that his Association had found that galvanizing in a bath containing about 0.15 per cent aluminium tended to give a coating more resistant to pitting by hot waters. Mr. Hughes had, however, produced some evidence that, when aluminium and lead were present together in the coating, it was less resistant to corrosion. On the question of white rusting Mr. Fagg said that aluminium did tend to delay the onset of this type of corrosion, as his Association's recent work on white rust formation showed. (31)

MR. HUGHES said that his results on the attack of hot water and steam, on coatings containing both lead and aluminium, were in line with the earlier observations of Schreiber that hot dip galvanized samples from aluminium-alloyed industrial galvanizing baths (which would have contained lead) showed an unusually high loss of weight in boiling water.

M. R. DE BIE (Tréfileries Léon Bekaert) then asked about the corrosion resistance of the alloy layer in galvanized coatings, and inquired whether the fact that the alloy layer dissolved more easily in acids meant that it had a lower corrosion resistance.

MR. HUGHES replied that, although it had previously been thought that the alloy layer in hot dip galvanized coatings had no protective value, it was now known that this layer contributed substantially to the protection afforded by the coating. When using the B.N.F. jet test for measuring local coating thicknesses, the alloy layer actually dissolved more slowly in the testing solutions, although different effects could be obtained with different corroding solutions. MR. FAGG referred to Britton's work (4) on the measurement of coating thickness by electrolytic dissolution, in which the voltage changes across the cell during dissolution of the coating allowed the thickness of the zinc and alloy layers to be determined. Atmospheric corrosion tests done by his Association on annealed coatings containing about 20 per cent iron had shown these to have considerably longer lives than normal hot dipped coatings.

MR. STEWART said that he was sorry that Mr. Pellowe was not present, but he would like to know if anyone could give some enlightenment on the photograph in his paper on p. 125, and inquired what the test was intended to show.

MR. HUGHES said that tests of this sort had been done by many workers, the first of whom was perhaps C. E. Richards of the Post Office Laboratory (32). The test showed that zinc had the property of preventing rust from spreading beneath the coating and that it gave protection over small areas where the steel was exposed through damage. J. C. Hudson had followed up Richards's earlier work on damaged wires by tests on 'damaged' zinc coated steel panels, and these had also demonstrated the effect of zinc in giving sacrificial protection to uncoated parts of the steel.

MR. HUGHES then referred to some examples of corrosion of galvanized steel with which he had had to deal. He thought it was important that the customer should be educated not to regard galvanizing as a panacea for all corrosion troubles. Galvanizing could not, for example, be expected to resist sulphurous atmospheres and conditions of high humidity. He recalled a case of severe corrosion from the fumes of a coke fire and another where heavy corrosion occurred in a cowshed which was inadequately ventilated. He suggested that more general use should be made of chromate treatment for minimizing the white rusting of galvanized surfaces. A specific question which had come his way was the resistance of galvanizing to attack by silage made from grass and molasses, and he would be glad to have further information on this point.

MR. R. W. BAILEY (Zinc Development Association) said he had made some inquiries about the nature of silage. There was no doubt that acids were liberated during the process of fermentation and he thought it unlikely that galvanized sheets would prove very serviceable as materials for the construction of silage vats. He saw no reason why galvanized containers should not be used for transferring the material from storage to the feeding troughs, as the presence of sugars tended to inhibit the action of the acids, and the troughs were often galvanized in any case. Some cases had occurred where pigs had suffered temporarily from excessive amounts of zinc picked up from feeding troughs in which acid foodstuffs had been allowed to stand for long periods, but in general it could be said that galvanized coatings had no harmful effects on livestock.

MR. J. J. STORDY (Stordy Engineering Ltd.) said he was interested in the subject of pig troughs as he thought that the galvanized mild-steel trough suffered from defects in design. It was not heavy enough with the result that the pigs easily tipped it over. He thought the troughs should be redesigned to obviate this difficulty.

MR. A. H. THOMPSON replied that manufacturers usually competed in trying to reduce the weight of the troughs. He doubted whether any addition to their weight to save them from being overturned would be appreciated sufficiently for the buyers to be willing to pay more for them.

## THE FUTURE OF GENERAL GALVANIZING

The final session of the Conference was devoted to the consideration of a paper on the future outlook of the industry and to the discussion of special questions of interest to Members which could not otherwise be accommodated in the comparatively small compass of the four morning sessions. The questions dealt with in this chapter are not, therefore, confined solely to the subject matter of the paper but also cover the disposal of waste pickling liquors, welfare in the galvanizing shop and the painting of galvanized steel surfaces. Mr. A. H. Thompson, Vice-Chairman of the Association and Chairman of its Technical Committee, presided at this last session of the Conference.

### Author's Introduction

Introducing his paper, on the Outlook for General Galvanizing, M R . R . L . STUBBS (Zinc Development Association) suggested that it differed from the others presented to the Conference in several respects. It was the last to be written, the last to be printed, the last to be distributed, the last to be considered by the Conference, and so, in one sense at least, the last word. Again it differed from the other papers in that it was not highly technical, and finally it was probably the only paper which, owing to its late arrival, had not been read by Members of the Conference.

Mr. Stubbs said that his paper opened with an optimistic survey of statistics. Some new figures had now been given him by one of the representatives from Holland, showing that comparative figures for that country were: consumption of zinc 10,000 tons per year and consumption of steel 1,600,000 tons per year, giving 14 lb. of zinc per ton of steel, Holland thus tied with the U.K. for second place in the consumption of zinc for galvanizing on a steel consumption basis. Australia, with its high sheet steel production, took first place, the U.S. coming a close fourth. He then turned to the section of his paper dealing with the main competitors of galvanized coatings, mentioning aluminium coatings as of first importance among these, aluminium being a cheaper metal than zinc, and of good corrosion resistance. He hoped that the discussion would be a very general one, as he was conscious of the many gaps in the programme which had been put before the Conference. He suggested that some discussion on pickling would be useful, and that working techniques and conditions were particularly worthy of consideration. Attention to methods of handling and dipping could, he thought, produce as spectacular results as researches into fluxing and additions to galvanizing baths. Finally, he reviewed briefly the various ways in which galvanizing was used in different countries, suggesting that they could each learn much from one another. In Switzerland the railways used a lot of galvanizing on the permanent way, while in the U.K. some tests were projected to show how the galvanizing of railway-wagons could reduce maintenance costs. Galvanizing could withstand abrasion in a way paint never could. He thought the galvanizing of automobile exhaust systems in America an

important development, as unless these were protected they corroded rapidly. He was sorry that the complete galvanizing of the Land-Rover chassis had been discontinued owing to increasing overall costs. Building technique in Britain and elsewhere was changing and instead of steelwork being encased in cement which prevented rust, the steel framework was simply clad inside and outside with suitable building materials. Many buildings had been erected in which this otherwise unprotected steelwork had been hot dip galvanized. Mr. Stubbs concluded by asking particularly for the views of people of other countries, since an exchange of information on these and similar technical points would be of the utmost value to those attending the Conference.

## THE OUTLOOK FOR GENERAL GALVANIZING

by R. LEWIS STUBBS\*, A.R.I.B.A.

### Introduction

Since galvanizing was first introduced its use has increased all over the world and today it is accepted as the most economical long term protection for steel. Galvanizing, however, is still not employed to anything like the same extent in all industrial countries. Thus in the U.S.A., the largest steel consuming country in the world, 11 lb. of zinc are used in galvanizing for every ton of steel consumed, whereas in France — the country in which the process was invented — only 4 lb. of zinc are used for each ton of steel.

Consumption in other countries for which data are available falls between the figures for Australia (32 lb. of zinc per ton of steel) and those for France and Western Germany. The following table gives some other figures for comparison:

GALVANIZING STATISTICS — 1949

	<i>Consumption of Zinc for Galvanizing†</i>	<i>Total Zinc Consumed</i>	<i>Percentage of Total Zinc used for Galvanizing</i>	<i>Consumption of Steel in terms of crude ingot metal†</i>	<i>Pounds of Zinc used for Galvanizing per ton of Steel consumed</i>	<i>Pounds of Zinc used for Galvanizing per head of population</i>
U.K.	89,000	286,000	31	14,400,000	14	3½
U.S.A.	311,000	628,000	50	64,100,000	11.	5
France (including Saar)	15,000	105,000	14	8,300,000	4	¾
Italy	9,000	27,000	33	2,100,000	10	½
Western Germany	16,000	97,000	17	8,400,000	4	½
Australia	23,000	44,000	52	1,600,000	32	6½
Canada	18,000	41,000	44	4,000,000	10	3

*Figures in long tons of 2240 lb. except where otherwise stated.*

† If expressed in terms of finished steel, all the figures would be somewhat smaller.

\* Director, Zinc Development Association



The figures given in this table, which are to some extent estimates, cover all types of galvanizing, but on the whole the proportion used in each country for general galvanizing, with which this paper is concerned, can be assumed to be about the same—roughly a third. Australia is an exception, the sheet galvanizing industry being highly developed to supply the farming communities throughout Australasia.

The table—a useful summary of the present status of galvanizing—is perhaps of value mainly to the galvanizers in each country, since it enables them to assess the possibilities of expansion; it is no guide to the future prospects of galvanizing all over the world. Whereas it may rightly be inferred that there is much room for advance in France and Germany where more propaganda is perhaps needed, on the other hand the countries where there are many galvanizing works and where the value of the process is already appreciated are in a stronger position for an early extension of its application. Again, countries with a long coastline and an established shipping industry can safely be regarded as big potential users of galvanizing and the same applies to countries with highly developed farming industries needing up-to-date buildings and equipment, fencing and so on. Most galvanizers would agree with these assumptions—there are good prospects for expanding the use of galvanizing everywhere, provided the necessary capital is available for industrial and agricultural improvement, and provided also that galvanizing continues to be the most economical method of rust-proofing. Statistics showing the upward surge of galvanizing over the last twenty years are reassuring, but there is always the danger of new protective processes being developed. Before considering the steps which the industry should take for its own advancement it is well to examine such possibilities.

## I. Possible Rivals to Galvanizing

**Other metallic zinc coatings.** Other types of zinc coating are often erroneously regarded as the only real and serious competitors of galvanizing, since if applied in equal weights per square foot they afford a similar measure of protection. In practice, however, the cost of applying coatings equal to those commonly found on galvanized goods is considerably greater, except in the plating of wire and strip for which special plant is available. In many cases, too, the processes are not suitable for treating the miscellaneous shapes met with in general galvanizing. On the other hand each process has its own particular merits and is unrivalled for certain types of work.

*Zinc spraying*, for example, enables a heavy zinc coating to be applied to extensive surfaces such as ships' hulls and to other fabricated items which are unsuitable for hot dipping either by reason of their size or the effect of the heat. Spraying is also invaluable for coating existing structures such as bridges and for repairing damaged galvanized or other metallic coatings which cannot be dismantled for dipping. Where a subsequent paint finish is important, spraying is sometimes preferred to hot dipping on account of the good key provided for the paint without any special pretreatment.

*Zinc plating (or electro-galvanizing)*, apart from its application on strip and wire, is mainly used for small articles, e.g. radio and telephone components, for which a fine finish is required. Since the thickness can be closely controlled, the process is suitable for mating parts with small dimensional tolerances. The coating can be brightened by means of chemical dips, and the brightness preserved by clear lacquers. The biggest application of

zinc plating is to wire, where the plating sometimes forms part of the electrolytic reduction of the zinc ore, the metal never appearing in ingot form. The same process is used for coating strip in the U.S.A. under the name of Bethanizing, the strip having good properties for deep drawing.

*Sherardizing* is a process limited to articles which can be accommodated in a sherardizing drum, and is generally used for nails, screws, nuts and bolts, brackets and other small fabricated items. Although the coating is thin, sherardizing has the advantage over other coating processes of retaining the original sharpness of the outline of the parts being treated and producing a coat of very high abrasion resistance.

*Zinc metal-pigmented paints* provide an easy if somewhat expensive way of applying a metallic zinc coating without the use of special equipment. They are used for ships' drinking water tanks, ships' hulls, parts of the frames of road vehicles and for maintenance work in the field. New formulations are constantly being developed based on different vehicles and improvements are to be expected.

*Another method* of zinc coating which may perhaps be considered as a rival to hot dip galvanizing for the treatment of small parts has been invented in America. The work is agitated with granulated zinc in a revolving drum heated to a temperature about the same as that used in sherardizing. The process enables large tonnages of small articles to be zinc coated quickly and easily.

These other zinc coating processes are, with this one possible exception, therefore not competitors to galvanizing, but rather methods of applying zinc coatings where hot dip galvanizing is unsuitable. Although they have made excellent progress recently, it can be authoritatively stated that the zinc consumed in these processes amounts to only a few per cent of that used for galvanizing. Furthermore, hot dip galvanizing as done by the general galvanizer retains the advantage of being the only process which ensures a heavy zinc coating. The sheet and wire galvanizing industries have at one time or another injured themselves by the production of goods with too thin a wiped coating which has not fulfilled the customers' expectations.

### Aluminium Coatings

The three facts which every galvanizer must know about aluminium are first that it is cheaper by volume than zinc (and at the time of writing by weight also); secondly, that when used as a coating it is as effective as zinc under many, but not all, conditions; and thirdly that the melting point is  $660^{\circ}\text{C}$ . as against  $419^{\circ}\text{C}$ . for zinc. Clearly it is the most dangerous potential competitor known at present. As generally applied now by spraying, aluminium is not likely to be an important rival to galvanizing, but should methods of hot dipping be developed, it might become so. Here it should be noted that steel strip is already being coated by hot dipping in molten aluminium in the U.S.A., although it is not yet being put forward as a challenge to galvanizing. The process is costly and difficult, since all oxide must be removed from the steel before dipping, and care be taken to avoid forming the brittle alloy  $\text{FeAl}_3$ . Another drawback to hot dipping in aluminium is the shortness of the bath life and the unpleasantness of working near a large quantity of metal at the high temperature — almost a dull red heat. The aluminium coatings sometimes superimposed on tin or zinc are obviously not competitive.

Aluminium spraying suffers from the same limitations as zinc spraying, which has already been discussed, and may be more properly considered as a rival to zinc spraying rather than to galvanizing.

### **Tin**

The only other metal applied by hot dipping on a commercial scale is tin. There can however be no comparison between tin and zinc coatings both on account of the price of tin and because it gives a non-sacrificial coating which generally allows the underlying metal to rust as soon as the continuity of the coating is broken. Tin is also applied to strip steel by electro-plating.

### **Paints**

The most effective protective paints, apart from those pigmented with zinc powder, which are in fact merely another and somewhat expensive way of applying a rather thin zinc coating, are those employing the comparatively expensive rust inhibiting pigments such as red lead and zinc chromate. Although these paints are not so tenacious as a galvanized coat and cost about the same to prepare and to apply, they will always find uses, often complementary to galvanizing. In spite of recent developments in paint vehicles, e.g. synthetic resins, silicones, silicates, etc., which have appeared during the last few years, it seems unlikely that paints can ever possess the abrasion resistance and general wearing qualities of galvanized coats. Ordinary decorative paints are also protective for a time, but unless constantly renewed cannot provide long term protection under the severe conditions of exposure against which galvanizing is so valuable. A more elaborate painting procedure is now being used on motor car bodies, and may well find wider applications in the future. The process requires the steel to be pickled and phosphate treated before spraying with a synthetic stoving enamel. Developments in radiant heating may make it economical to extend the technique to heavy gauge steelwork.

### **Plastic Coatings**

Great advances have been made in this field in the last few years, and while plastic coatings are not yet used to provide permanent protection to steel, some of the recent developments should be watched closely, e.g. the use of plastic envelopes to preserve large pieces of war equipment, and close fitting sheaths to protect steel tools during transport and storage. Inside the envelopes an inhibitor such as sodium benzoate may be used to counteract the effects of trapped moisture. The paper used for wrapping razor blades is impregnated with a solution of this type. Before such coatings are likely to rival galvanizing, much progress will have to be made in improving their adhesion and hardness.

### **Chromium Diffusion**

A cement containing chromium powder is coated on to the steel and on heating the chromium is caused to be diffused into the steel surface. The process, which has been developed in France, is said to give a heavy (effective thickness 0.10 mm.) bright coating of good corrosion resistance.

### **Non-Rusting Structural Materials**

So far only coating has been considered as a method for rust-proofing. There is however, always the possibility of replacing the steel itself by

a non-rusting metal, either a stainless steel or a non-ferrous alloy. Among recent developments in the latter field, ductile titanium is arousing considerable interest in America. Its strength is between that of steel and aluminium and its corrosion resistance is said to be excellent. Aluminium alloys are already finding structural applications for roofs, bridges, motor bus bodies, etc., and large aluminium alloy castings are being used on ships to replace parts previously made of galvanized iron or steel. There is no doubt that, as long as aluminium, zinc and steel remain at their present prices, aluminium goods will tend to be used in place of galvanized steel articles. It is, however, difficult to believe that the present price relationships of the three metals will last, and aluminium is likely before long to lose much of its present advantage.

### Summary

Summing up the position, it is evident that while there appears to be no immediate threat to the supremacy of galvanizing as a rust-preventing process, galvanizers have no grounds for complacency. Much energy is being devoted to research into other processes and at any time the work may suddenly bear fruit.

The galvanizing industry, to remain healthy and prosperous, must be ready to meet any unexpected competition and the very fact of this Conference being held is welcome evidence of the imaginative outlook of the industry today. Until recently the continued expansion of the industry and the isolation in which individual firms have operated have given little encouragement to improving technique, and there has been little change in the galvanizing process during the 100 years of its existence.

Since the prospect of competition is probably greater now than at any time in the past, this change of heart is a very healthy sign and it will be useful to consider what the industry should do to prepare for the future and to insure itself against surprise developments elsewhere. The situation may conveniently be surveyed under two headings—the process and its applications.

## II. Future Developments

### Improvement in the Process

As the Conference papers have shown, work to improve the efficiency of the galvanizing process is going on actively all over the world. Hall, Fagg and Hughes have described the laboratory work done by the B.N.F.M.R.A. and B.I.S.R.A. covering dipping technique, bath composition, alloying and dross formation, as well as corrosion resistance, a subject also dealt with by Pellowe. Bailey's second paper describes the beginning of co-operative work by members of the Hot Dip Galvanizers Association who are examining the behaviour of baths under working conditions. The close co-operation now being established between the laboratories and works should bring real benefits to the industry before long. The work described in these papers covers only a few aspects of the process, and much remains to be done elsewhere. A start has been made by the H.D.G.A. with the Research Associations on the study of pickling procedure, and practical information should soon be available on the efficiency of different inhibitors. More data are needed on the disposal of waste pickle liquors and on methods of recovering iron salts in a useful form.

The B.N.F.M.R.A., in conjunction with the H.D.G.A., has already begun to examine a wide range of fluxes, with particular reference to the use of higher aluminium contents in the galvanizing bath. Work in this field will obviously continue to be done as long as galvanizing is practised, since more fluid baths and more even coatings could lead to cheaper and better galvanizing. It seems rather strange that so little work has been done before now on improving this critical stage of the process.

Bablik and Liban have discussed the merits of flux and dry galvanizing, and both methods have their adherents, each having its advantages for particular kinds of work. Dry galvanizing perhaps enables work to be more speedily done, and this is an aspect of the process which is referred to later.

With the recent high price of zinc, much attention has been focused on the possibility of reducing the formation of zinc ash and dross, and the survey described in Bailey's paper has confirmed, as some experts have long believed, that on the average only about 60 per cent of the zinc put into the bath emerges in the form of a coating. In the best works 84 per cent of the zinc is already being used effectively, while at the other extreme there are works in which only 41 per cent of the zinc is applied to the steel. In the past there have been many misleading statements made on the subject of bath efficiency, and unless the method of measurement is clearly explained, all figures should be treated with reserve. Imhoff has done well to show that dross can probably never be eliminated altogether, as it arises from so many causes, but it can undoubtedly be reduced.

Another aspect of the problem is the recovery of the zinc from the residues, a subject on which the B.N.F.M.R.A., as well as individual galvanizing firms, have carried out research. Many firms have now built their own equipment for zinc recovery from ash, which does not command as good a price as dross in the open market. Arnason has dealt with the new approach which galvanizers are making to the problem of dross formation. While there is a limit to the economy that can be effected in reducing residual formation, the figures in Bailey's paper show that most works could improve their zinc economy appreciably.

Faulty bath heating increases dross formation, and Bailey, in his first paper, has described some of the best methods of bath heating and stressed the advantages of even heating and close temperature control.

It will be seen that while much still needs to be done in improving the efficiency of the galvanizing process, a good start has been made. If the results are applied with the same energy as has been put into the research, and if the research is continued, the industry may well soon reach the maximum technical efficiency admitted by the process.

An aspect of galvanizing not mentioned in the Conference papers, and yet one of the utmost importance, is working technique — a term used here to cover handling and dipping procedure and works organization. Although this side of galvanizing has not so far been scientifically investigated, it is not unreasonable to assume that the formation of residues, for example, depends to some extent on the manner in which the work is manipulated during dipping. The survey described in Bailey's second paper suggests that the most efficient baths are those with a high throughput of work and a controlled rate of immersion and withdrawal. It is known that in fully mechanized plants, such as those used for galvanizing metal windows, where these factors are not affected by individual workers, the general efficiency is very high. During their visits to plants outside Britain, experts from the Association

have often found the technical efficiency of the plants inferior to that of many of their own, but that this deficiency was counterbalanced in varying degrees by the skill with which the work was handled. This seems to be a good field for mutual improvement by the exchange of visits and information. In particular, the forthcoming visit by a specialist team from the H.D.G.A. to America is expected to throw new light on this subject.

Most galvanizers are already conscious of the need for well-planned and well-ventilated buildings. New works recently erected and those still under construction in the U.K. have been designed with much attention to these points, as well as to other matters affecting the workers' welfare, such as the provision of well-equipped changing rooms, canteens, etc. It is hoped that this will make the industry attractive to the best class of worker.

### **The Applications of Galvanizing.**

Although the use of galvanizing has been expanding steadily, the position since the end of the war has not been at all clear owing to the pent-up demand for galvanized goods and the slow improvement in the supply of steel. However, if the expansion which has taken place is to be maintained in the face of competition with other materials and processes, it seems likely that it will be necessary to find new applications for galvanizing. A brief survey shows that the prospects are by no means bad.

**Agriculture.** The current trend in the mechanization of agriculture provides many opportunities for the general galvanizer, since most agricultural equipment has to suffer hard wear and long exposure to all kinds of weather. Up to now surprisingly few makers of agricultural equipment seem to have realized the effectiveness of galvanizing for protection under these conditions. A straw in the wind was the initial galvanizing of the complete chassis of the Land Rover (a British all-purpose vehicle resembling the Jeep), which has been dropped for the time being in order to reduce the cost of the vehicle. Most of its other steel parts, however, are still galvanized, because the makers recognize the unsurpassed value of galvanizing for permanent protection. Buckets, troughs, milking equipment and many other smaller farm items have of course been galvanized for years. The farmer well knows the value of galvanizing and would welcome its extension for the protection of his machinery.

**Rail Transport.** Railways find corrosion a serious problem, and it is one to which galvanizing has not been applied to any extent. Few countries seem to have made any study of the maintenance costs for the huge quantities of painted steel accessories used along the track. The Swiss, however, changed over from painted to galvanized supports for their overhead power lines some ten years ago, and claim that despite the higher initial cost maintenance has been substantially reduced. Galvanizing is being used similarly on the electrified railways in Austria, and other railway authorities would do well to consider following this lead when electrifying their lines.

Another development of interest to railway engineers is the galvanizing of a complete general purpose wagon, a practical experiment being contemplated in the U.K. at the present time. If successful, this experiment may lead to the galvanizing of exposed steelwork on all kinds of rolling stock where corrosion is serious.

*Road Transport.* In recent years increasing attention has been paid to the protection of the chassis of motor vehicles, though only on the Land-Rover has the chassis been completely galvanized. Most motor bus and lorry chassis are now painted with metal-pigmented paints, some containing zinc dust, but these will clearly not prove so effective as galvanizing would; it may be hoped that the makers will decide to go the whole way before very long. In the last year news has come from the U.S.A. of the galvanizing of motor car exhaust systems, a protective measure long overdue. If it is as successful as the reports suggest, the practice should soon become universal.

*Bridge Construction.* The use of the Bailey bridge during the war has led to an extension of the unit construction principle in bridge building. Many of these units are being galvanized for use in the tropics, as were the original Bailey bridges, and there is no doubt that the galvanized bridges will stand for a long time with little maintenance. Bridge handrails are also being galvanized in increasing numbers, and a useful Californian law requires all road bridges in the State to be fitted with galvanized steel railings which can be readily replaced if damaged in accidents.

*Building Frameworks.* The trend in modern building is to provide first of all a skeleton structure of light steel sections, which are then clad externally and internally. Much of the steel is thus hidden and has to be permanently protected from rusting since it is not encased in concrete, as in older steel-framed buildings. In England the new schools erected by the Hertfordshire County Council are good examples, and much of their hidden steel work has been galvanized. Galvanized light steel trusses are also being introduced into houses and small buildings. This will obviously be an increasing field for the galvanizer in view of the need to develop simpler building techniques to reduce site work.

*Rainwater Goods.* Galvanized steel rainwater goods, although widely used in the U.S.A., have not found much favour in Europe, except perhaps in Switzerland and Sweden. These gutters and pipes have in fact excellent corrosion resisting properties, and are superior to the ordinary cast iron goods which require frequent painting. The extra cost of the galvanized article is a very small part indeed of the total cost of a building, and most householders would support it as a worthwhile expenditure.

*Window Frames.* Before the war the corrosion of steel window frames was becoming a severe problem, and Pellowe has described in his paper how galvanizing has completely overcome it. It is perhaps strange that the same solution has not been applied in other countries, although it is being contemplated in the U.S.A. There must be many other products for which corrosion is an equally serious problem which could be solved just as successfully by galvanizing.

*Painting after Galvanizing.* In his account of the galvanizing of metal windows, Pellowe has referred to the need for treating galvanized coatings so that they are ready for immediate painting. This is an aspect of galvanizing which every general galvanizer should consider. Paint applied over phosphated galvanized coatings has a remarkably long life, and steel so treated can be regarded as everlasting if the paint is renewed every ten or fifteen years.

The phosphated zinc provides an excellent basis for all kinds of decorative finishes which would not by themselves afford adequate rust prevention.

*Other Applications.* A useful study could certainly be made of all the steel-using industries to see what gaps still remain. In the U.K., engineers are well aware of the effectiveness with which galvanizing is used for hollow-ware, tanks and drums, ships' fittings, power transmission towers, telegraph pole fittings, etc. In other countries, other applications must be equally well known to the local engineers, and an exchange of information about such uses could benefit galvanizers all over the world. This International Conference is perhaps a good occasion for the start of such an exchange. Denmark itself is a country from which much can be learned about the galvanizing of marine goods, since the sea coast plays so important a part in the national economy.

### III. Conclusion

The vigorous approach to galvanizing problems shown in the Conference papers is a good augury for the future. General galvanizing is largely a local trade, and the very fact that there is little or no competition between Britain and Europe, or between the continental countries themselves, has been a contributing factor to the very satisfactory international attendance at this Conference. If the future prospects outlined in this paper are to be fully realized by galvanizers everywhere, a close collaboration on all galvanizing matters is essential, and must exist not only between the general galvanizing firms in the U.K., which at present constitute the membership of the Hot Dip Galvanizers Association, but between firms all over the world and doing all types of galvanizing.

### Acknowledgments

The estimates of the consumption of steel were kindly prepared by the Statistical Department of the Iron and Steel Federation, to whom thanks are due. The author also wishes to thank his colleagues at the Zinc Development Association for their assistance and suggestions, and in particular Mr. A. R. L. Chivers with whose collaboration the paper was prepared.



## DISCUSSION

### New Uses for Galvanizing

MR. J. J. STORDY (Stordy Engineering Ltd.) said he thought there were many new uses for hot dip galvanizing which had not yet been exploited and that he would like to call attention to one not mentioned in the paper. He knew that large stocks of Bailey bridges were held by the Government and that to prevent them rusting they were being degreased, phosphated, dried and painted. He thought that the money could perhaps be better spent in galvanizing them and asked whether this possibility had been explored. He realized that distortion might introduce difficulties, as the bridges were made to close tolerances for assembly, but he thought that if they were jigged and drilled after galvanizing this disadvantage could be overcome and a more permanent protection given to the parts than by the present procedure of painting.

MR. C. P. H. WEDGE (B. E. Wedge Ltd.) said he was interested to hear Mr. Stordy's views about the Bailey bridge parts, as he had some time ago arranged to galvanize a sample for a Government Department. Unfortunately, he had since then heard nothing further about the work.

### Painting Galvanized Steel

MR. STUBBS introduced the subject of painting by saying that he had been very interested to read the reports in Pellowe's paper of the long lives of up to fifteen years enjoyed by paint films applied to phosphated galvanized steel. He thought that many new fields would be opened up if metal users realized how good phosphated galvanized coatings were as a basis for paint.

MR. STORDY said he had been interested to read the suggestion in Mr. Stubbs's paper that more use should be made of phosphating and painting galvanized materials before dispatch from the factory, and wondered whether this could not be applied to galvanized roofing sheets. The manufacturer should, he suggested, consider the customer more by colouring the galvanized sheets to increase their sales appeal. By phosphating and painting, the sheets could be made more beautiful as well as given a longer life.

MR. M. L. HUGHES (B.I.S.R.A.) replied that he thought the customer for galvanized sheets was already being considered when the sheet galvanizer added tin to his baths to increase spangle. He doubted whether the treatment of galvanized roofing sheets in this way would be a practical proposition, as the market for these sheets was a very competitive one. The provision of a phosphated and painted finish might well make them too expensive. He knew that one firm had already entered the market for coloured sheets and was supplying vitreous enamelled ones.

MR. E. M. WILSON (Henry Hope & Sons Ltd.) said he doubted whether phosphating was often necessary unless the galvanized surface had to be painted immediately, as his experience with galvanized metal windows had shown that weathering on the site was usually quite sufficient to ensure good adhesion. He remembered some trouble which had been experienced with B.I.S.F. house parts where condensation occurring between phosphating and dip painting had interfered with the durability of the paint film.

MR. R. W. BAILEY (Zinc Development Association) said that in his view insufficient attention had been given to the virtues of phosphated and painted galvanized surfaces. It was not of course always possible to allow the galvanized surface to weather before painting, but even when this could

be done there was evidence to suggest that the phosphated and painted surface offered the best protective system. Zinc was an expensive metal and it was a pity to allow it gradually to waste away unprotected. If phosphated and painted, as Pellowe had pointed out, permanent protection could be obtained. The paint had a longer life and only needed renewing at infrequent intervals. He was sure that phosphated, painted, corrugated galvanized sheets could be produced very much more cheaply than vitreous-enamelled sheets, and that these sheets would overcome the failure so often experienced in the lap-over between roofing sheets, a failure caused by trapped moisture.

MR. F. C. BRABY (Fredk. Braby & Co. Ltd.) said he agreed that roofing sheets would fail at the lap-overs if not painted, but that most users of galvanized sheets for roofing already painted the laps.

MR. A. E. HAY (Richard Thomas & Baldwins Ltd.) referred to a trouble he had experienced with a galvanized hot water tank which had failed badly after it had been painted inside with a proprietary paint. He was studying this failure and had put another tank into service painted in this way. He doubted whether bitumastic paints could really give protection in hot water, and considered that under certain conditions some types of paint might destroy the underlying galvanized coating.

MR. BRABY said that a survey he had made several years ago revealed that no manufacturer of paint would guarantee complete water resistance at higher temperatures, and that in any case rough handling could always damage a paint film.

MR. BAILEY expressed his interest in Mr. Hay's tests, as he understood a paint of the type referred to was recommended for the treatment of ships' hulls. He recalled, however, how the rudder of a well-known liner had been finished in this way and had subsequently had to be stripped and the heavy corrosion craters filled with zinc by spraying. The whole surface of the rudder had finally been zinc sprayed before the ship was put back into service, since when no further trouble had been reported.

### Acid Disposal

MR. G. J. PHILLIPS (Liver Galvanizing (Manchester) Co. Ltd.) asked for some information about the disposal of waste acid and the most economical methods of treating it.

MR. BRABY said that the disposal of acids was usually done by passing the acid through large neutralizing tanks in which lime was held. In his Liverpool works it was neutralized with carbide sludge.

MR. R. S. BROWN (Rylands Brothers Ltd.) said his firm was a large, and perhaps the largest, user of hydrochloric acid for pickling wire rods. He was particularly fortunate in having a ferric oxide recovery unit nearby, and the whole of his spent acid was utilized for this purpose. The practice of neutralizing spent acid with lime and feeding it to the sewer was far from satisfactory, and regulations would certainly be tightened up in the future to prevent this method of disposal. On this account many big users of acid were changing over to the sulphuric process where the iron sulphate could be recovered from the spent pickle and the liquor recirculated.

MR. E. W. MULCAHY (John Thompson (Dudley) Ltd.) agreed that the satisfactory neutralization of either hydrochloric acid or sulphuric acid presented difficulties. If lime was to be effective, it must be used as a slurry, and run into a mixing tank with the acid and thoroughly mixed. Sludge disposal could, however, be as big a difficulty as acid disposal,

particularly if acetylene waste lime were used. Satisfactory treatment with a minimum of sludge called for the use of the best quality lime. As an example of the difficulties he mentioned a plant disposing of 1500 gal. per hour of 12 per cent sulphuric acid using 90 to 100 tons of lime a week. The plant deposited 6000 lb. of sludge per hour, and the quantity would have been considerably greater if the best quality lime had not been used to give a treatable sludge. The most satisfactory alternative was, of course, the use of sulphuric acid pickling and a regenerative recovery process for the iron sulphate. He suggested that any plant using 10 tons or more of commercial  $\text{H}_2\text{SO}_4$  a week would benefit by the use of such a process.

MR. HUGHES said his Association had been working at the Sketty Hall Laboratory on the recovery of acid and iron from spent sulphuric acid pickling liquors. Concentrating the solution by evaporation and subsequent cooling allowed ferrous sulphate to be crystallized from a mother liquor of increased acid content which could be returned to the pickling vats. Roasting the ferrous sulphate gave on the one hand iron oxide which could be returned to the blast furnaces, and on the other hand sulphur-dioxide/sulphur-trioxide vapours which could be dissolved in water and oxidized, using a specially developed technique, to give sulphuric acid of 20 to 30 per cent strength suitable for pickling.

### Competitive Processes

MR. HUGHES congratulated Mr. Stubbs on his paper which held such a fair balance between competitive processes for protecting steel from rust, and which looked to the future. He thought it warned the galvanizers to be prepared. He would like to comment on some of the points made in the paper, and turned first to the statement that the thickness of electrodeposited coatings could be closely controlled. Although this was true for the total amount of coating applied, it was difficult, if not impossible, for the plater to control the distribution of thickness over the surface of the work, except when very simple shapes were being processed. Recesses were nearly always comparatively thinly coated. He thought that the two main fields for plating were in the deposition of very thin coatings, as in tin-plate manufacture, and the deposition of very thick coatings, for example on wire. Both these fields were outside the coating range of ordinary hot dipping processes. Turning to the threat of competition from aluminium coatings, he said that the rate of alloying when hot dipping in aluminium was very great indeed. It had been found, however, that the addition of 6 per cent of silicon to the aluminium prevented the thick alloy layer from being built up and gave a thinner coating with good bending properties. Hot dipped aluminium coatings had also been found very good for protecting exhaust systems of motor cars, and to be superior to zinc in their corrosion resistance to sulphurous atmospheres. Turning to chromium diffusion, he did not think this would ever be competitive with galvanizing. It was very expensive, being done by a batch process at a temperature of  $1100^\circ\text{C}$ . It was a coating of very high corrosion resistance; e.g. if a sample of steel tube chromized on the outside was immersed in a strong nitric acid, everything would be dissolved except the chromized coating.

DR. R. HAARMANN (Rheinische Röhrenwerke) said that in Germany aluminium was in good supply and that further outlets were being sought for the metal. An interesting development trend was the use of aluminium sheets as a roofing material, although much trouble from pitting had been ex-

perienced. He had heard that the addition of small amounts of molybdenum to the aluminium seemed to prevent this kind of attack, and special sheets of this type were now being tested.

MR. STUBBS said that aluminium had also been used on a small scale for roofing in England. It was a modern and fashionable metal. MR. HUGHES thought that the competition from aluminium was very real. It was used for roofing in South Wales, sometimes with a rectangular corrugation. Trouble had, however, been experienced with corrosion, particularly from the undersides of the roofs. Here condensation had caused a form of white rusting which, being non-adherent, fell away from the sheet and contaminated the materials being processed in the building. Electrochemical effects at the fixing points had also caused difficulties, and insulating washers had been found necessary.

MR. BROWN said that he had been surprised to read in Mr. Stubbs's paper that *electrogalvanizing* was a competitor of 'galvanizing'. His firm sold almost 1,000 tons of wire a week as galvanized wire, all of which was, in fact, electrogalvanized. Should not the paragraph have referred to the rival claims of electrogalvanizing and 'hot galvanizing', to make the matter quite clear? He was also not at all happy about the statement that damage had been caused to the reputation of zinc coatings because wiped wire had been sold in which much of the zinc coating had been removed. He thought it only fair to point out that wiped wire was not sold to specification and was, in fact, only supplied when ordered for special purposes.

MR. MULCAHY said his firm had done some work in connection with a large plant being erected in the U.K. for the zinc plating of steel windows, and asked whether the coating of irregular thicknesses which Mr. Hughes had described would prove satisfactory, or whether specially shaped anodes would have to be used to ensure uniform plating. He would like to know whether chloride solutions would be more satisfactory than cyanide solutions for zinc plating these windows.

MR. HUGHES agreed that if a difficult shape was to be zinc plated, a specially shaped anode or a subsidiary anode would have to be used. He said acid plating solutions could be operated at very much higher current densities than cyanide solutions.

MR. BAILEY said that the important difference between acid solutions and the cyanide solutions was the high current density which could be used with these solutions of higher conductivity in the plating of simple shapes such as wire or strip. The cyanide solutions had the higher throwing power, the chloride solutions being very similar in their general properties to sulphate solutions, but having a somewhat higher conductivity. They were, however, naturally more corrosive and greater care had to be taken in protecting the plant.

### Welfare

MR. STORDY said he had been pleased to read the remarks in Mr. Stubbs's paper about the importance of giving more attention to handling and dipping procedure. He thought that much more could be done here, and doubted whether the problems raised by mechanical handling in galvanizing plants had yet been properly faced.

MR. J. ROUFF (Etablissements Schmid) then described some difficulties he had met in satisfying the factory authorities in France, where the molten zinc baths were at a height of only 25 centimetres above the ground. It had

## DISCUSSION

been proposed that protective railings should be built to prevent the men from falling in. Such railings would, however, have prevented the work from being done. It was then suggested that the men should be harnessed to pulleys on a monorail running alongside the bath. This idea was, of course, ridiculous. He asked what was done in other countries and what proposals were acceptable from a safety standpoint.

Turning to protective equipment for the workers, he explained that he employed coloured workers from Algeria. He had supplied them with asbestos gloves, asbestos leggings and spectacles with good side view and good ventilation, but the gloves were too hot, the leggings hampered their movements, and the spectacles were a nuisance. The authorities did not know how to act in view of these objections from the workers. He asked what protective equipment was used in other countries.

MR. M. BRODBECK-KELLER (Verzinkerei Pratteln) referred to similar difficulties in Switzerland, where their zinc baths were only 30 centimetres above the floor. The Municipal Society for the Prevention of Accidents in Factories had asked for a railing as in France, but this was of course unsuitable. He provided his workers with shoes in wood and leather, and the workers were quite contented with those. They did not, however, like wearing glasses as these fogged over during work. He had declined to meet the objections of the Accident Prevention Society in any further way.

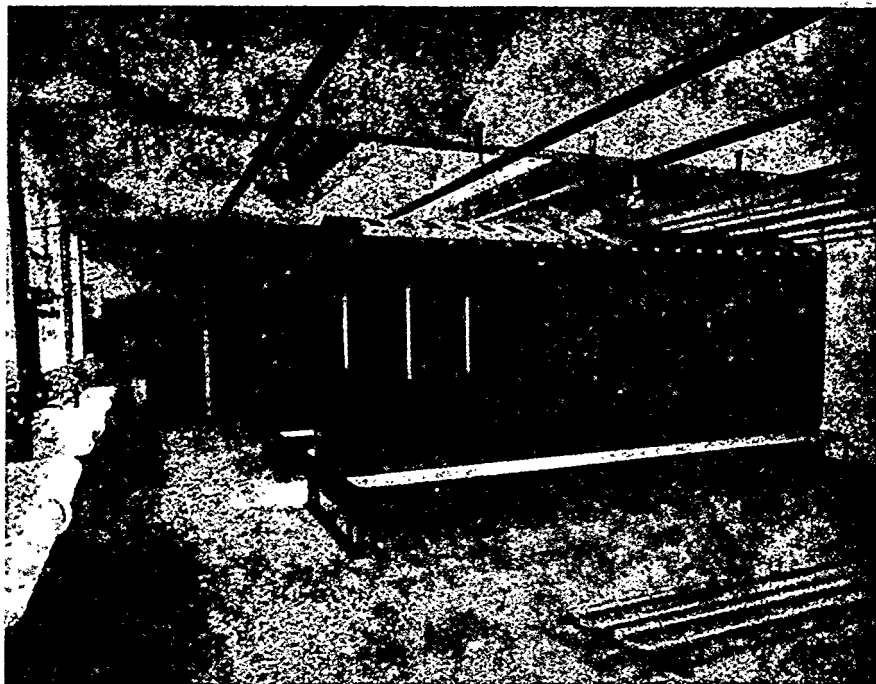
MR. H. T. EATWELL (G. A. Harvey & Co. (London) Ltd.) then showed some pictures of his new galvanizing works, in which the specially designed (16) gas heated baths stood 2 ft. 6 in. above the level of the working floor, which was at loading bay height. All the services to the baths were below the floor, so that the galvanizing shop was clear of everything except



Fig. 1 Gas heated galvanizing bath showing height above floor level in U.K.

the control instruments for the bath and the cranes for handling the work. Fig. 1 (p. 153) shows part of the galvanizing shop. In the foreground is a bath 10 ft. by 4 ft. by 4 ft. 6 in. deep of patented gas-fired construction (15), illustrating the height of the bath above the floor level. Behind this and to the right is another bath with heat insulating covers in position.

Mr. Eatwell continued by referring to two pictures showing the welfare facilities at his plant. Fig. 2 shows the changing rooms during construction. It will be noticed that each locker is double-compartmented, one for day clothes and one for working clothes, and in the foreground is seen a heating



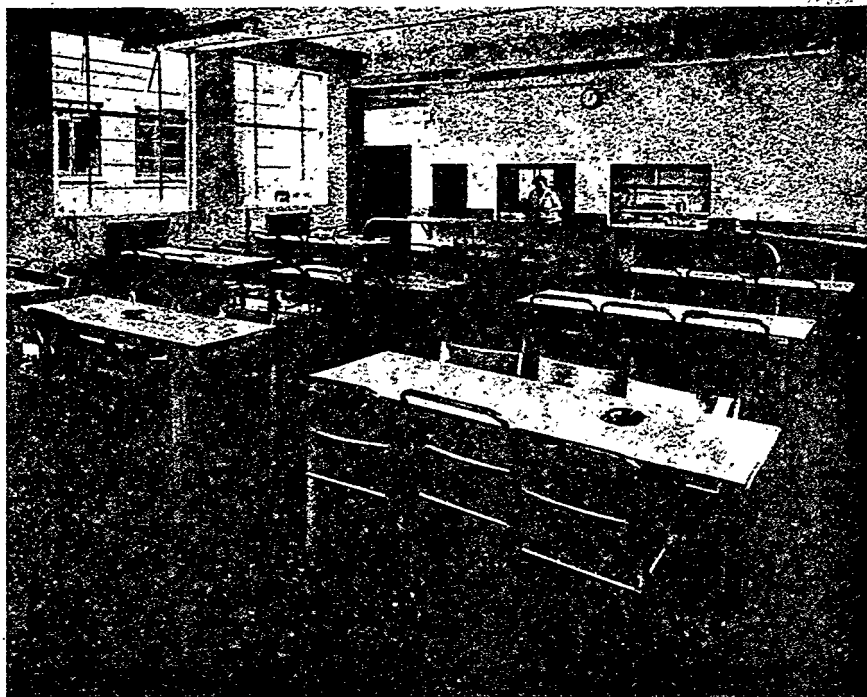
*Fig. 2 Changing rooms during construction showing heated clothes lockers*

coil over which the lockers are erected and these consequently have warm air passing through them all the time through perforated bottoms. There are also shower baths, although these are not shown in the photographs. Separate changing rooms are provided for picklers and galvanizers, the detailed design differing to some extent.

Fig. 3 shows part of the auxiliary canteen provided for the picklers and galvanizers, the main feature here being that the table tops, seats and backs of chairs are of acid-resisting plastic material. Mr. Eatwell said that this was wearing extremely well, and was very easy to keep clean as it only required wiping over with a wet cloth instead of intensive scrubbing as with wood.

MR. BRABY said that he had been chairman of a small committee which had sent out a questionnaire to the Founder Members of the Association in its early days asking for confidential information about practice in their works. Although the Factories Act required that baths containing corrosive liquid should be built or fenced to a height of 3 ft. above the floor or platform used by the workers, it allowed some discretion to the Chief Inspector of Factories,

to whom it had been pointed out that owing to the difficulty of working a bath of such height the men were tempted to stand on the edge. He had agreed that a height of not less than 2 ft. 3 in. would be acceptable. As Mr. Eatwell's pictures showed, a height of 2 ft. 3 in. or 2 ft. 6 in. had been generally adopted in the U.K. In the case of hydrochloric acid at a normal pickling strength of 13 per cent, the Chief Inspector had decided that this was not a corrosive liquid within the meaning of the Act, but he had asked that similar precautions should be taken, and in practice the baths were always raised above the floor level.



*Fig. 3 Canteen with chairs and table tops in acid-resisting plastic*

Turning to protective clothing, he said that the men disliked wearing heavy clothing such as asbestos suits, and in his works it was the practice to supply old clothes, sacking and similar coverings. The men wore gloves and rubber boots when pickling: some of the galvanizers were supplied with a hinged visor of the type used by welders, which they found satisfactory. His men still quite often received minor injuries from splashes, particularly on arms and neck, and he thought it important that all burns from this cause should be promptly treated. MR. H. BUSCH-JENSEN (J. Chr. Jensens Galvaniserings Etablissement) said that a special type of perspex visor was in use in his works, and that it had been found very satisfactory in use. The visor is shown in fig. 4 (p. 156).

MR. EATWELL said that cold hydrochloric acid pickling was used in his works, and he did not think there was any real danger to the men working with this acid. It did, of course, depend how the work was handled, and he had known several cases of men falling into the tank. They were, however,

#### THE FUTURE OF GENERAL GALVANIZING

speedily dealt with by being pulled out, stripped, hosed down with particular attention to the eyes, and then taken to hospital as a precaution. None had suffered any ill-effects other than those of minor shock.



*Fig. 4 Perspex visor used in Denmark*

#### Closure

The Chairman, MR. THOMPSON, then brought the Conference to a close by thanking all those who had contributed so freely from their galvanizing experiences and helped to make the meetings so successful. He felt sure that the Conference had given them all an opportunity of forming friendships and getting to understand one another better, and that everyone who had attended would have benefited from the Association's work. It was important that in times of comparative prosperity, such as now, Members should reorganize their works and take the fullest possible advantage of the information they had obtained so that they would be ready to meet whatever competition from other coating processes lay ahead, knowing that their own industry was really efficient and progressive.



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