CANADA

THE INFLUENCE OF ALUMINUM, LEAD AND IRON ON THE STRUCTURE AND PROPERTIES OF GALVANIZED COATINGS

by

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PREFACE

The work described in this report was initiated in February, 1957, in co-operation with the Canadian Zinc Research and Development Committee. The Committee, which was formed in 1954, consists of members from the zinc producing and consuming industries and from interested research laboratories, including the Mines Branch.

The aims of the Committee are to develop new and improved zinc products, to improve existing techniques for the working and fabrication of zinc products, and to provide a centre for the discussion of mutual problems.

To further these aims, the project described in this report was undertaken at the Mines Branch with the assistance of the supporting companies. The Consolidated Mining and Smelting Company of Canada, Limited, Trail, British Columbia, the Hudson Bay Mining and Smelting Company. Limited, Flin Flon, Manitoba, and the Steel Company of Canada, Limited, Hamilton, Ontario, contributed towards the costs of additional staff required and, also, supplied the special high grade zinc and steel sheet used in the project. The analytical facilities of the Consolidated Mining and Smelting Company were used to confirm some of the analyses completed at the Mines Branch, and this company also carried out the statistical work involved in the project. In order to establish the accelerated corrosion behaviour of the experimental coatings, the services of the Steel Company of Canada were utilized.

Throughout the project the guidance and assistance of the committee members were called on as required, and in all instances these were most willingly given.

John Convey,
Director, Mines Branch,
Chairman, Canadian Zinc
  Research and Development
  Committee.

Mines Branch Research Report R 5

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J. J. Sebisty* and J. O. Edwards**

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ABSTRACT

This report describes the preliminary phase of a statistical study on the influence of aluminium and lead additions in iron-saturated baths on the structure and properties of galvanized coatings prepared by the dry galvanizing technique. Different levels of aluminium and lead, and ranges of bath temperature and immersion time were investigated using two grades of steel sheet.

It was found that the immersion time and aluminium content of the bath had the most significant effect on such factors as coating weight, steel weight loss, iron content and alloy growth in the coating, and ductility and adherence of the coating. The bath temperature was also significant but to a lesser degree.

The lead content of the bath was the most significant variable affecting coating surface appearance.

For immersion times up to 2 minutes, attack of the steel base was largely blanked-off by an addition of 0.2 per cent aluminium. With 0.1 per cent aluminium, vigorous steel attack and continuous iron-zinc alloy growth was apparent even for short immersion times.

Accelerated corrosion tests suggested that aluminium and to a lesser degree lead had a significant effect in promoting "white rusting" of the galvanized coatings.

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CONTENTS

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INTRODUCTION .

In co-operation with the Canadian Zinc Research and Development Committee, which consists of some of the major zinc producers, users and research organizations in Canada, a project was initiated at the Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada, to study the influence of various impurities and addition elements on sheet galvanizing coating structure and properties.

Various reviews (1) (2) (3) have indicated a wide divergence of opinion on the behaviour and effects of aluminium in hot-dip galvanizing. Recent authoritative investigations by Hughes (4) and Haughton (5) have discounted many of the earlier claims and provide much useful information on the role of aluminium. The influence of lead is much less thoroughly understood and little effort has been devoted to its study even though lead is present in greater percentages than any other additive in the bath. In view of the accepted importance of these two elements (particularly in continuous strip galvanizing), an initial study of the effects of aluminium and lead additions, singly and in combination, was undertaken as a basis for future work.

In order to examine the effects of these bath composition changes over as wide a range of conditions as possible, it was

decided to incorporate a number of other galvanizing variables in the test program. These included a series of five bath temperatures, five immersion times, and also two grades of steel sheet surface roughness. To simplify procedure the dry galvanizing technique was used. All baths were saturated with iron since, as shown by Haughton (5), this condition has a major effect on the behaviour of aluminium. To evaluate coating properties and structure, several tests, detailed elsewhere in this paper, were carried out.

A complete coverage of the various factors selected would have entailed a great deal of work and for this reason a statistical approach was adopted in setting up the experimental program. In this method (6), a suitably-chosen preliminary set of experiments is carried out with the results being used to define subsequent trials.

Only the results obtained in the preliminary phase or broad experimental region of the statistical study were available for discussion in this paper.

MATERIALS

Steel

Open-hearth, low-carbon, 24 s.w.g. rimmed steel sheet, bright annealed and temper rolled to two different surface finishes, designated No. 5 and No. 3 (average roughness, 45 and 110 micro in. respectively), was used. All materials were from a single heat, and analysis of sheet samples gave the following results:

Carbon	per cent		0.04
Phosphorus	" "		0.010
Sulphur	" "		.0.026
Manganese	" "		0.12
Silicon	" "	Less than	0.002

Zinc

Special high-grade zinc (99.99 per cent) from two different sources was used in equal quantities in the experimental baths. Quoted spectrographic analyses were as follows:

			Source 1	Source 2
Lead	per cent		0.0016	0.0005
Cadmium	" "		0.001	0.0002
Iron	" "		0.001	0.0002
Copper	" "		0.001	
Aluminium	" "	Less than	0.0005	
Tin	" "	" "	0.0005	

Aluminium

High-purity aluminium (99.99 per cent) was used to make a master alloy of zinc containing approximately 4 per cent aluminium. This was shotted by casting into water.

Iron

Iron was added as a master alloy of zinc containing up to 0.3 per cent iron. This was prepared by dissolving electrolytic iron sheet (99.98 per cent) in zinc at 550°C (1022°F) and pouring to shot in water.

Lead

High-purity lead (99.99 per cent) was added directly to the bath as required.

APPARATUS AND PROCEDURE

Galvanizing Equipment

The galvanizing fixture is illustrated in Fig. 1. This consisted of an electric resistance furnace with a graphite-lined steel pot holding approximately 40 pounds of zinc. Temperatures were maintained to $\pm 2°C$ at all times.

The galvanizing cycle was controlled by an electrical timer which actuated the motor and pulley mechanism of the galvanizing rig.

Galvanizing Conditions

The principal galvanizing test conditions chosen are listed below. The various combinations which were selected to obtain a suitable statistical coverage, and the order in which the melts were prepared, are given in Table 1. A total of nineteen separate baths and thirty different test conditions was involved.

		Levels
Bath temperature	Degrees C	435, 445, 455, 465, 475
	Degrees F	815, 833, 851, 869, 887
Immersion time	Minutes	0.25, 0.5, 1.0, 2.0, 4.0
Aluminium content of bath	Per cent	0, 0.1, 0.2
Lead content of bath	" "	0, 0.5, 1.0
Iron content of bath	" "	Saturated - (about 0.03 per cent at 450°C (842°F) for pure zinc).

Two sizes of specimens were run. In the main, twelve specimens 4 1/2 in. by 6 1/2 in. of each steel finish were galvanized at each test condition, together with three 3 in. by 4 in. specimens of each steel finish to determine steel weight loss due to galvanizing attack.

Specimen Preparation

The sheet materials as supplied were clean and bright with a light coating of oil on the surface. To ensure thorough cleaning the specimens were swabbed and then vapour degreased with trichlorethylene.

Pickling was carried out in a solution of 5 per cent commercial sulphuric acid (66° Baumé) in water with Rodine 92 inhibitor added to the acid to a concentration of 1/2 per cent by volume. The specimens were immersed for 5 minutes in the acid at a temperature of 70°C (158°F) and then scrubbed with a bristle brush in cold running water. The total rinsing period, including scrubbing time, did not exceed one minute. Drying was effected by dipping successively in two acetone baths. An unavoidable interval of 2 to 3 hours between pickling and the following fluxing treatment was normal but this caused only superficial rusting.

The fluxing treatment involved dipping for one minute in an aqueous zinc-ammonium chloride solution with density 10.4° Baumé at 80°C (176°F). The commercial flux preparation used contained zinc chloride and ammonium chloride in the molecular ratio of 1.27:1.35 or approximately 70 to 30 per cent by weight respectively. The specimens were dried in an oven for 2 to 3 minutes at 160°C to 170°C (320°F to 338°F).

In the case of the smaller 3 in. by 4 in. specimens used to determine steel weight loss., it was found that the fluxing treatment resulted in weight losses of 0.0021, 0.0020 grams on the No. 5 and No. 3 finish steel, respectively. These values are averages of six determinations. In comparison with iron loss due to zinc attack, these losses were relatively insignificant except in the case of the 0.2 per cent aluminium baths, where they amounted to 10 to 15 per cent of the total iron loss. The steel weight loss due to fluxing was therefore ignored in subsequent calculations.

Dipping Procedure

Immediately after flux drying, the large 4 1/2 in. by 6 1/2 in. specimens were dipped one at a time for the required period in the galvanizing bath. Immersion and withdrawal speeds were 6 fpm and 3 fpm respectively. Before dipping and prior to withdrawal the bath was skimmed to remove dross. Specimens were cooled in air after galvanizing.

Due to the natural variation in coating thickness from top to bottom, dipping of the large specimens in the bath was timed so that a reference position (1 3/4 in. from the top end) was immersed for the specified time. All samples for testing were taken as near as possible to this reference point.

No agitation was used during the immersion period except with baths containing 0.2 per cent aluminium. In these, the specimens were vigorously moved up and down for the first few seconds after complete immersion, in order to effect removal of flux residues which tended to stick to the surface.

In baths containing no aluminium, ammonium chloride was dusted on the bath before and during withdrawal, since oxide formation was so rapid that skimming was not effective in keeping the bath surface clean.

The smaller 3 in. by 4 in. steel weight loss specimens were manually dipped, one or more at a time depending on the immersion time required. For immersion and withdrawal, a speed of approximately 8 fpm was used, and the specimens were quenched in cold water immediately on removal.

Bath Sampling and Analyses

Bath samples were taken at the beginning and end of each run, and also from the middle in the case of a large batch. The sampling technique involved stirring of the bath and pouring to shot.

The bath compositions actually obtained as indicated by chemical analysis are given in Table 2. Approximately half of the bath samples taken were analysed by a second laboratory, and very good agreement with the values listed in the table was obtained even though the analysis techniques differed. As a further check a number of spectrographic analyses for aluminium were made. In the majority of cases these corresponded to the results obtained chemically, and for the remainder, a variation of only ± 5 per cent was encountered. This is of interest, since some statements in the literature suggest that accurate chemical analysis of aluminium in galvanizing baths is not possible.

It is realized that the iron determinations represent the total and not the "effective" iron content of the bath. These analyses were made primarily to ensure that the iron content was uniform in all baths and was as close as possible to the saturated condition. In this connection it should be mentioned that in the baths containing

0.2 per cent aluminium, several additions of both iron and aluminium had to be made during dipping in order to maintain the required levels. With 0.1 per cent aluminium baths, smaller regular additions of aluminium only were necessary.

TESTING PROCEDURE

Of the twelve large specimens of each steel finish galvan-
ized at each test condition, six were sectioned as shown in Fig. 2 to
provide triplicate samples for the following tests:

Coating weight and iron determination - 2 1/4 in. by 2 1/4 in.
Cupping test   3 in. by 3 in.
Lockformer test   4 in. by 4 1/2 in.
Bend test   2 1/4 in. by 1 in.
Metallography   3/8 in. by 1 in.

Surface appearance evaluation of the coatings was carried
out prior to cutting of the above samples.

Of the specimens remaining, one was used for testing "white
rust" susceptibility, two were reserved for atmospheric corrosion
tests, and three were set aside as spares. Quantitative data were
obtained in all tests so that the results could be evaluated statistically.

Coating Weight and Iron Determination

To determine coating weight, the samples were cleaned,
weighed, stripped in 100 ml of 50 per cent hydrochloric acid
solution, and reweighed after rinsing, dipping in acetone and drying
in an oven. Measurement of iron content of the coating was carried
out by diluting the acid solution with 150 ml of water immediately
after removal of the stripped sample and titrating with standard
potassium dichromate.

Cupping Test

Cupping tests with a Tinius Olsen, Erichsen-type machine were used as a measure of the relative coating ductility. To provide suitable data for statistical analysis, the cracking behaviour of the coatings was graded against a set of arbitrary standards.

Lock Seam and Bend Tests

Initial attempts to evaluate coating adherence involved subjecting samples to a flattened "S" bend, using a commercial type Pittsburgh lock seam former. A majority of the coatings behaved poorly in this test, and a reliable grading of the flaking tendency could not be made. A simple bend test through 90 degrees and back through 180 degrees over various radii was therefore used, and the minimum bend radius which did not cause flaking was established.

Metallography

Samples for micro-examination were covered with a baked lacquer coating and mounted in bakelite. Grinding on silicon carbide papers was followed by polishing on micro cloth impregnated with diamond paste, and a final short treatment on silk velvet with Gamal "R" abrasive. Rowland's No. 5 and No. 3 etchants (7), used in that order, gave most satisfactory etching results, except for the high aluminium coatings on which the No. 5 etchant alone was used.

To provide data for statistical analysis, the proportion of alloy in the coatings was calculated on the basis of microscopic measurements of alloy and total coating thicknesses. A representative area on each sample was selected. Due to the general absence of iron-zinc alloy growth in samples prepared in the high aluminium baths, it was impossible to obtain reliable measurements in these cases.

Surface Appearance

Surface appearance was assessed against a set of arbitrary standards, with the coatings being graded on the basis of spangle size, spangle contrast, and surface roughness. The brightness or reflectivity was also measured with a photoelectric cell photometer.

Accelerated Corrosion Tests

The susceptibility of the coatings to "white rusting" was established by exposing the specimens to humidity and water film tests. Initially the specimens were subjected to a two-cycle humidity test. The degree of corrosion was evaluated in several ways. One method involved measurement, with a photoelectric reflection meter, of the ability of the surface to diffuse a vertically directed beam of parallel light. Readings were taken before and after corrosion. The diffusivity values obtained were expressed

in per cent compared to a MgO standard having a diffusivity of 100. Visual examination was also carried out and a corrosion index assigned to the specimens depending on the amount of surface showing both white and black staining. Finally, weight gain and weight loss due to corrosion were established.

Specimens were exposed to the water film test after the humidity test. In this case the degree of corrosion was assessed by visual examination only, with a corrosion index being assigned after 24- and 48-hour exposures.

Steel Weight Loss

Steel weight loss measurements were made on the separate series of small 3 in. by 4 in. specimens. These were weighed after pickling, and again following stripping of the coating according to the procedure outlined in sections 4 and 5 of ASTM Specification A90-53. As already mentioned, the loss due to fluxing was ignored and the difference in weight before galvanizing and after stripping was regarded as the loss due to galvanizing attack. No attempt was made to assess the surface appearance of the stripped specimens.

OBSERVATIONS AND RESULTS

The information provided by the initial statistical study is summarized in Tables 3 and 4. As indicated, apart from the properties relating to surface appearance of the experimental coatings, the galvanizing variables which were found to be of greatest significance were immersion time and aluminium content of the bath. The importance of bath temperature varied and in most cases the lead content and degree of steel surface roughness appeared to have little or no effect. With respect to surface properties such as spangle size, spangle contrast, etc., the lead content of the bath was most significant, with the aluminium content and bath temperature showing varying orders of importance.

On the basis of this evaluation, the test data were appropriately consolidated into a series of graphs showing the relationships between the dependent variables (coating weight, iron content, steel weight loss, etc.) and the most significant independent variables, i.e., aluminium content and immersion time. Bath temperature was ignored as a variable, on the basis of its lower significance generally. For purposes of indicating general relationships this treatment appeared to be valid, since the limited plots obtainable by retaining the temperature variable suggested that the

trend of these graphs was similar and only their disposition was affected to a moderate degree. It will be appreciated, as stated previously, that the whole experiment was designed as a preliminary survey of the field and it is expected that investigations designed to confirm specific points and to establish optimum operating levels will be undertaken later. The various graphs obtained are discussed below, along with metallographic and other observations made during the testing work. Due to the apparent inconsistency of the data relating to surface appearance evaluation, graphical presentation of the effects of the galvanizing factors in these cases was not attempted.

Coating Weight

The effect of immersion time and aluminium content on coating weight is illustrated in Fig. 3. The significant reduction in coating thickness achieved by adding 0.2 per cent aluminium is to be noted. At this higher aluminium level an increase in immersion time, for the range used, had a negligible effect on the coating weight.

At the 0.1 per cent aluminium level the behaviour was entirely different and coating weight was markedly influenced by the immersion time. Since a constant withdrawal rate was used, this relationship can only be explained by a steadily increasing growth of iron-zinc alloy in the coating, and not by variations in thickness of

the outer zinc layer. It is therefore apparent that in an iron-saturated bath, 0.1 per cent aluminium is not sufficient to suppress galvanizing attack of the steel base, even for immersion times as short as 15 seconds at a temperature of 455°C (851°F). This substantiates Haughton's observations (5).

It is evident, however, that for short dipping times aluminium does exert a beneficial effect in limiting the rate or degree of steel attack. This is indicated by the heavier coatings obtained in the absence of aluminium. As dipping time was increased this beneficial effect disappeared, and, as reflected by the coating weight curves for immersion times of the order of two minutes or longer, lower coating weights could be expected in an aluminium-free bath than in one containing 0.1 per cent aluminium.

Iron Content, Steel Weight Loss, Alloy Thickness, and Coating Structures

Since these factors are related, results of the tests are grouped together for discussion purposes, and the graphs showing the influence of aluminium content of the bath and immersion time are given in Figs. 4, 5 and 6.

The principal reason for determining the iron content of the experimental coatings was to establish whether the level of iron present could be related to the ductility or adherence of the coatings. In the present series of tests, although such a comparison was

possible it was of limited value since most of the coatings, except those prepared in the 0.2 per cent aluminium baths, showed inferior ductility and adherence. Apart from this latter group of specimens, continuous iron-zinc alloy growth, varying in thickness with immersion time, was a characteristic feature of the coating structures. Such growth appeared to be the major factor responsible for the inferior ductility and adhesion properties.

An additional reason for running the iron analyses was to compare the amount of iron which appeared in the coatings, against the steel weight loss. Statistically, the two sets of measurements were similar. However, as shown by the disposition of the corresponding graphs in Figs. 4 and 5, particularly in the case of the 0.2 per cent and aluminium-free baths, the steel weight loss values were, on the average, slightly higher. This must also apply with 0.1 per cent aluminium, since all baths containing this amount of aluminium showed a moderate increase in iron content from start to end of a run (Table 2). Experimentally, the only possible source of this increasing iron contamination in the bath was that due to steel attack.

According to Hiscock (8) the zinc-steel reaction is one of the major factors contributing to iron build-up and resultant dross formation in dry galvanizing. However, the tests carried out

served to show that when proper pre-treatment and fluxing practices are observed, iron contamination of the bath from this source can be held to a minimum even when the degree of attack of the steel base is severe.

The graphs in Figs. 4, 5 and 6 show marked similarity to that for coating weight in Fig. 3. This confirms that under the experimental conditions, coating weight was primarily related to the degree of attack of the steel base and the thickness of alloy formation.

The low steel loss and iron content of the coatings shown for the 0.2 per cent aluminium baths indicate that this addition was more or less effective in preventing attack of the steel. Increase in immersion time resulted in little or no change in this behaviour.

Microscopic examination revealed that these high-aluminium coatings were very non-uniform in thickness and varied from a thin superficial layer to heavy deposits of the type described below. Iron-zinc alloy growth was equally haphazard. At the lower bath temperatures used, only occasional patches of alloy, in the form of a thin irregular fringe of crystals at the steel surface, could be observed. These formations were better defined and more extensive at higher bath temperatures, as shown in Fig. 10. However, even in such cases, areas were evident showing no visible alloy.

Frequently very thick deposits were found, and in many areas the structures were typical of electrogalvanized coatings since no observable iron-zinc alloy could be detected. These local thickness

variations were in some cases related to the roughness of the steel surface, as shown in Fig. 11. Generally, however, they appeared to have been caused by variations in zinc pick-up. Although the withdrawal conditions were closely controlled, it was observed that with many of the entire series of samples examined, the eta or outer zinc layer tended to be thicker on one side or portion of one side.

Because of the random scattering of alloy in the high aluminium coatings, measurements or estimates of iron-zinc alloy, and hence graphs of this factor, could not be made. For statistical purposes an arbitrary thickness of 0.001 millimetre was assigned.

The characteristic influence of 0.1 per cent aluminium in retarding or promoting steel attack, depending on the immersion time, can be seen in Figs. 4, 5 and 6. For short dipping times, the iron content, steel weight loss and alloy thickness values were all significantly higher with no aluminium present. With increasing immersion time, each of the above factors increased at a more rapid rate in baths containing 0.1 per cent aluminium. The general slope of the curves clearly indicates the more rapid attack associated with this amount of aluminium.

Specimens prepared in baths containing 0.1 per cent aluminium showed essentially two basic microstructures.

With 1-minute immersion at 455°C (851°F), relatively heavy and uniform iron-zinc alloy growth occurred, with the zeta phase forming the major part of the structure (Fig. 12). This phase usually consisted of a featureless mass and a serrated outer fringe which etched very dark with the picral etchant. The delta and gamma layers were uniformly thin and continuous. At lower bath temperatures and immersion times the alloy structure was, except for some minor differences, similar to that just described. The dark etching material in the zeta phase was very irregular in thickness and formed the major part of this phase. The gamma layer was generally thinner and in some areas was totally absent locally. The delta layer also showed a tendency to discontinuous growth. It was observed that where the latter thinned out or was non-existent, the dark etching part of the zeta layer penetrated to the gamma layer.

A typical section showing the type of structure formed at long immersion times and higher temperatures in baths containing 0.1 per cent aluminium is shown in Fig. 13. The heavy steel attack which occurred was reflected in marked growth of zeta which took on the appearance of a granular mass. The loose packing of this structure is evident. The gamma and delta layers were uniform and continuous but the latter was usually only vaguely defined.

Figure 14 is characteristic of the various structures obtained

in aluminium-free baths for 0.5 and 1 minute at 445°C (833°F) and

455°C (851°F). Somewhat similar coatings were also obtained at

2 minutes immersion at 445°C (833°F). Within these groups, the thick-

ness of the individual iron-zinc layers varied according to the dipp-

ing conditions, with the zeta phase always showing most pronounced

growth. The dense packing of this phase, and the duplex nature of

the delta phase indicative of the concentration gradients in this layer.

were other characteristic features. The delta consisted of a dark

etching layer next to the gamma phase and an outer serrated fringe

of outlined small blocks. These blocks merged into a thick continuous

band with increase in dipping time and bath temperature. This can

be seen in Fig. 15. A change in the zeta phase to a well-defined

crystalline structure is also evident.

Alloy Ratio

As previously noted, it was impossible to estimate the amount

of iron-zinc alloy in the high-aluminium coatings. In the case of the

aluminium-free coatings the calculated alloy ratios showed consider-

able variation. For these reasons a representative graph showing

the influence of immersion time on the proportion of alloy in the

coatings could only be obtained for the specimens dipped in baths

containing 0.1 per cent aluminium where the measurements were

reasonably reliable. This graph is shown in Fig. 7. Although bath

temperature was indicated by statistical analysis to have a significant effect on the alloy ratio determinations, this factor was again ignored for conformity, and separate temperature plots with the data consolidated in Fig. 7 showed that this treatment was justified.

It is clearly shown that for short immersion times the proportion of alloy in the series represented was approximately 45 to 60 per cent. The ratio increased very rapidly with increasing immersion time, to a maximum of approximately 80 per cent for 4 minutes immersion. Thus, for the range of experimental conditions used the aluminium addition in this case was not effective in suppressing steel attack.

The primary factor responsible for the change in alloy ratio was an increase in iron-zinc alloy growth, rather than any significant reduction in the thickness of the outer zinc layer, which is apparently independent of the galvanizing variables under study. This is indicated by comparison of the coating weight and alloy thickness graphs for the corresponding series of specimens in Figs. 3 and 6.

Ductility and Adherence

Although the tests used to establish the relative ductility and adherence of the experimental coatings were essentially rough sorting tests only, three distinct classes of behaviour with changes in immersion time and aluminium content were revealed. These can be ascertained by referring to the graphs in Figs. 8 and 9.

The high-aluminium coatings showed both excellent ductility and adherence, as indicated by the cupping test and simple bend test respectively. No apparent change in properties was noted with increasing immersion time, over the range used. The behaviour in the lockformer test was equally good, with no evidence of cracking or flaking.

The second narrow classification included the coatings which had good ductility but only fair to poor adherence. The specimens which could be grouped in this category were those with relatively thin alloy growth and coating weight which had been galvanized for 0.25 and 0.5 minute in baths containing 0.1 per cent aluminium. The single series dipped for 1 minute at 435°C (815°F) behaved similarly. The satisfactory ductility of these specimens was indicated by the fact that a network of very fine cracks only was formed in the cupping test. These could only be detected by examination under a binocular microscope. The appearance of a typical cup, at very low magnification, which is representative of a ductility rating of two, is shown in Fig. 17. In the simple bend test, which was used as a measure of adherence, these specimens could only be classed as fair to poor since, in the lock seam test, distinct flaking, which was localized along the outer surface of the exposed 180-degree bend, was experienced.

As indicated by the response to the ductility and adherence tests, all of the remaining coatings, whether prepared with or without 0.1 per cent aluminium in the bath, could only be rated as inferior. In the cupping test moderate to severe cracking was observed with this group, which constituted a major share of all specimens galvanized in the program. Typical performance is illustrated in Fig. 18, which represents a ductility rating of four. The heavily-coated specimens which had been dipped for 4 minutes were especially bad, since the coating over the cup was almost completely peeled away. With respect to adherence, the quantitative values obtained in the simple bend test were considered to be indicative of very poor adhesion, since with the associated lock seam test, general and severe flaking and peeling were observed.

Attempts were made to combine the various graphs depicted so as to determine the influence of such factors as coating weight, alloy thickness, etc., on ductility and adherence. However, the available data that were of interest within the range of acceptable coating performance were not sufficiently extensive to permit valid relationships to be established.

Surface Appearance

As indicated in Table 3, the variable which was statistically shown to have the greatest effect on the rated surface appearance factors was the lead content of the bath. The aluminium content and

bath temperature were significant only with respect to the brightness and roughness of the coatings. Steel surface finish was also important, with No. 3 and No. 5 finishes showing significant differences with respect to spangle size and contrast, and coating roughness.

The high-aluminium coatings were generally unsatisfactory in appearance, due to the presence of a variety of defects. Of these the most prominent were randomly scattered ridges or raised streaks of varying lengths which ran across the specimens. Attempts to establish the factors responsible for their occurrence were not successful. Non-uniformity in zinc pick-up as noted in the metallographic work was reflected in local surface unevenness on these coatings. Raised pimples also contributed to roughness of the coatings. These were related to local iron-zinc alloy growths. In the absence of lead with the high-aluminium baths, prominent bare spots developed in the coatings. However, with additions of 0.5 or 1.0 per cent lead, good coverage was obtained and only small pin-holes, not easily detected with the naked eye, were to be found.

Surface appearance of specimens prepared in baths containing 0.1 per cent aluminium varied markedly. With no lead present, a fine sandpaper-like texture,with good reflectivity was obtained. Longer immersion times and higher bath temperatures within the ranges studied increased the degree of roughness, and the coatings took on a dull sheen. No spangles were evident. When 0.5 per cent

lead was added, bright coatings showing good development of spangles with moderate contrast were produced. Spangling was occasionally suppressed locally or over large areas by the occurrence of fine pimples in the coatings. These were related to the presence of iron carbides on the surface of the steel base and consequent excessive growth in the alloy layer. Further increase in lead content to 1.0 per cent, combined with a short immersion time of 0.5 minute at 445°C (833°F), resulted in coatings with an unusual surface appearance. Large spangles had apparently formed but these were only indicated by a network of sharply delineated boundaries. These coatings were very smooth and highly reflective. With an increase in immersion time and/or bath temperature, a moderately rough texture reappeared combined with the development of vaguely defined spangles of irregular size.

By far the roughest coatings were obtained in the baths to which no lead or aluminium had been added. When additions of 0.5 and 1.0 per cent lead were made, the general roughness was considerably reduced and large spangles with little or no contrast were formed. Additions of lead resulted in a considerable reduction in brightness.

Corrosion Tests

The influence of bath composition on "white rust" susceptibility of the experimental coatings was of particular interest. Initial analysis of the test results failed to show any strong relationship

but, as shown in Table 4, statistical analysis revealed that, within the range of galvanizing conditions studied, bath composition was of significant importance.

It is probable that the diffusivity measurements obtained were affected to some extent by the relatively rough surface texture of many of the specimens tested. Despite this, it was shown that the corrosion behaviour in the humidity test was clearly related to the aluminium and lead contents of the baths in which the specimens were prepared. These were the only significant galvanizing variables. The visual, corrosion-index ratings failed to show any significant effect on corrosion in the humidity test.

With respect to weight gain or loss in the humidity test, the steel surface roughness appeared to be an important factor, since with the smoother No. 5 finish steel, all of the galvanizing factors studied, i.e., immersion time, aluminium and lead content, and bath temperature, were shown to be significant. In the case of the No. 3 steel only the aluminium content of the bath was indicated to be significant. This apparent difference in behaviour of the two steels is possibly related to the rougher surface texture of the coatings on the No. 5 finish material.

A similar but vaguely-defined relationship was also evident with the water film tests. Statistically, the corrosion indices assigned after twenty-four and forty-eight hour exposures suggested that corrosion of the No. 3 steel coatings was unaffected by the

galvanizing conditions used. On the other hand, the aluminium content of the bath and the immersion time were shown to be significant with the No. 5 finish steel, particularly after the forty-eight hour exposure. A possible weakness of the water film tests lies in the fact that these were carried out on the same specimens used in the humidity tests and from which the corrosion products resulting from the latter had been removed. The corrosion behaviour may thus have been influenced by the altered surface provided.

From the preliminary statistical evaluation of the corrosion data obtained, it can therefore be concluded that the aluminium content of the bath was significant in promoting "white rust" formation on the experimental coatings. The amount of lead present in the bath also appeared to be significant but the evidence in support of this was less conclusive.

Influence of Steel Surface Roughness

Although statistical analysis indicated that the surface roughness of the two steels used had no significant effect on the coating properties except in the case of corrosion behaviour and surface appearance, a localized difference in behaviour was revealed by micro-examination. This was related to the rougher profile of the No. 3 finish steel which was generally of a wavy character. As illustrated in Fig. 16, the high spots on the surface

were very reactive and resulted in heavy local outbursts of iron-zinc alloy. This was in marked contrast to the thinner, more uniform growth associated with the hollows or low spots. This characteristic behaviour was only found with specimens dipped in the aluminium-free baths. With 0.1 per cent aluminium added, the alloy layers were more or less of uniform thickness and generally followed the contours of the steel surface. Under conditions of severe attack a more or less level steel surface was produced.

Effect of Other Factors

In the course of this investigation, it was observed that the presence of massive carbides on the surface of the steel sheet had a pronounced effect on the structure of the galvanized coating under certain conditions. Also the phenomena of different activity in two similar steels, and pore formation on the galvanized surface, were examined. This work has been reported separately (9).

SUMMARY

As a first step in a more extensive study, the influence of aluminium and lead on the structure and properties of laboratory-prepared galvanized coatings was investigated over a range of bath temperatures and immersion times. Baths were saturated with iron, and steel sheet with two different degrees of surface roughness was used.

On the basis of a statistical evaluation of the data obtained in this preliminary series of tests, some general relationships were revealed with respect to the relative influence of the experimental variables. These and other observations are summarized below:

(1)   For the experimental conditions studied, immersion time and aluminium content of the bath had the most significant effect on such factors as coating weight, iron content in the coating, steel weight loss, iron-zinc alloy thickness, proportion of alloy in the coating, and ductility and adherence of the coating. The bath temperature was also significant but, in general, to a lesser degree than the immersion time and aluminium content of the bath. Variation in steel surface roughness and the lead content of the bath had no significant effect on the factors listed above.

(2)   With respect to surface appearance characteristics such as roughness, brightness and spangling behaviour, the only galvanizing variable which exerted a consistent significant effect was the lead content of the bath. The bath temperature, steel surface roughness, and aluminium content showed varying orders of importance.

(3)   The addition of 0.2 per cent aluminium to iron-saturated baths was effective in largely blanking-off attack of the steel base for immersion times up to 2 minutes.

On the other hand, 0.1 per cent aluminium promoted vigorous steel attack and continuous alloy growth even at short immersion times. For short immersion times only, the degree of attack was less severe than when aluminium was absent, but with increasing dipping time this beneficial effect disappeared and 0.1 per cent aluminium in the bath promoted a more rapid rate of attack than occurred with no aluminium present.

(4)   Although the results were somewhat erratic, differences in corrosion behaviour as determined by accelerated corrosion tests suggested that aluminium had a significant effect in promoting "white rusting", and this applied to a lesser degree to the lead content of the bath.

For the practical galvanizer, the following additional points

may be inferred from this preliminary investigation:

(a)   Lead additions to the baths appear to have no effect on such properties of the galvanized coat as adhesion and ductility, but do affect its appearance.

(b)   In sheet galvanizing, where the coating thickness can to some extent be controlled by manipulation of the exit rolls and withdrawal speed, the results suggest that short immersion times and a high aluminium content will produce better quality sheet. There are indications, however, that aluminium increases the tendency to white rust formation.

(c)   The fact that virtually all of the iron dissolved from the experimental specimens was accounted for by the iron in the coatings suggests that under properly controlled conditions it should be possible to maintain a low level of dross formation in dry galvanizing.

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TABLE 1

Experimental Galvanizing Conditions

Bath Number	Test Number	Bath Temp. °C	°F	Immersion Time, min.	Aluminium %	Lead %
1 and 1A	1	465	869	0.5	0.2	0.5
	2	465	869	2.0	0.2	0.5
	3	445	833	0.5	0.2	0.5
	4	445	833	2.0	0.2	0.5
2	5	455	851	1.0	0.1	0.5
3	6	455	851	1.0	-	-
4	7	455	851	1.0	0.1	0.5
5	8	455	851	1.0	-	1.0
6	9	455	851	1.0	0.2	-
7	10	455	851	1.0	0.1	0.5
8 and 8A	11	465	869	0.5	0.1	1.0
	12	465	869	2.0	0.1	1.0
	13	445	833	0.5	0.1	1.0
	14	445	833	2.0	0.1	1.0
9	15	455	851	1.0	0.2	1.0
10	16	455	851	1.0	0.1	0.5
11 and 11A	17	465	869	0.5	0.1	-
	18	445	833	0.5	0.1	-
	19	445	833	2.0	0.1	-
	20	465	869	2.0	0.1	-
12	21	455	851	1.0	0.1	0.5
13 and 13A	22	465	869	2.0	-	0.5
	23	445	833	2.0	-	0.5
	24	445	833	0.5	-	0.5
	25	465	869	0.5	-	0.5
14 and 14A	26	435	815	1.0	0.1	0.5
	27	455	851	1.0	0.1	0.5
	28	475	887	1.0	0.1	0.5
	29	455	851	0.25	0.1	0.5
	30	455	851	4.0	0.1	0.5

TABLE 2

Galvanizing Bath Analyses

Bath Number	Sample Number*	Iron %	Aluminium %	Lead %
1	N	0.03	0.2	0.5
	1	0.030	0.19	0.50
	2	0.033	0.20	0.49
	3	0.027	0.19	0.49
	M	0.030	0.19	0.49
1A	N	0.03	0.2	0.5
	1	0.030	0.20	0.50
	2	0.034	0.19	0.49
	3	0.026	0.19	0.49
	M	0.030	0.19	0.49
2	N	0.03	0.1	0.5
	1	0.028	0.10	0.51
	3	0.030	0.09	0.51
	M	0.029	0.10	0.51
3	N	0.03	-	-
	1	0.031	-	-
	3	0.032	-	-
	M	0.032	-	-
4	N	0.03	0.1	0.5
	1	0.030	0.10	0.50
	3	0.032	0.09	0.49
	M	0.031	0.10	0.50
5	N	0.03	-	1.0
	1	0.027	-	0.77
	3	0.029	-	0.99
	M	0.028	-	0.88
6	N	0.03	0.2	-
	1	0.029	0.20	-
	3	0.032	0.20	-
	M	0.030	0.20	-
7	N	0.03	0.1	0.5
	1	0.029	0.10	0.52
	3	0.032	0.10	0.52
	M	0.030	0.10	0.52

(Cont'd)

*
N - nominal composition. 1 - sample at start of run. 2 - sample after 24 specimens dipped. 3 - sample at end of run. M - mean analyses.
**-sample after 48 specimens dipped.

(Table 2, cont'd) -

Galvanizing Bath Analyses

Bath Number	Sample Number*	Iron %	Aluminium %	Lead %
8	N	0.03	0.10	1.0
	1	0.027	0.10	0.95
	2	0.031	0.11	1.01
	3	0.032	0.10	1.01
	M	0.030	0.10	0.99
8A	N	0.03	0.10	1.0
	1	0.030	0.10	1.00
	2	0.033	0.10	1.03
	3	0.035	0.11	1.03
	M	0.033	0.10	1.02
9	N	0.03	0.2	1.0
	1	0.034	0.20	0.95
	3	0.028	0.19	1.00
	M	0.031	0.20	0.98
10	N	0.03	0.1	0.5
	1	0.030	0.10	0.51
	3	0.032	0.10	0.51
	M	0.031	0.10	0.51
11	N	0.03	0.1	-
	1	0.030	0.09	-
	2	0.032	0.10	-
	3	0.035	0.09	-
	M	0.032	0.09	-
11A	N	0.03	0.1	-
	1	0.030	0.10	-
	2	0.033	0.11	-
	3	0.036	0.11	-
	M	0.033	0.11	-
12	N	0.03	0.1	0.5
	1	0.030	0.10	0.50
	3	0.032	0.10	0.50
	M	0.031	0.10	0.50

(Cont'd)

*

See footnote, bottom of page 35.

(Table 2, cont'd)

Galvanizing Bath Analyses

Bath Number	Sample Number*	Iron %	Aluminium %	Lead %
13	N	0.03	-	0.5
	1	0.031	-	0.52
	2	0.033	-	0.52
	3	0.035	-	0.53
	M	0.033	-	0.52
13A	N	0.03	-	0.5
	1	0.031	-	0.49
	2	0.031	-	0.49
	3	0.032	-	0.48
	M	0.031	-	0.49
14	N	0.03	0.1	0.5
	1	0.030	0.10	0.48
	2	0.032	0.10	0.48
	**	0.033	0.10	0.47
	3	0.035	0.09	0.47
	M	0.032	0.10	0.48
14A	N	0.03	0.1	0.5
	1	0.032	0.11	0.51
	2	0.031	0.11	0.50
	**	0.033	0.11	0.50
	3	0.034	0.11	0.50
	M	0.032	0.11	0.50

*

See footnote, bottom of page 35.

TABLE 3

Statistically-Determined Influence of Galvanizing Variables
on Coating Structure and Properties*

	Immersion Time	Aluminium Content	Bath Temp.	Lead Content	Steel Roughness
Coating Weight	1	1	3	4	4
Iron Content	1	1	2	4	4
Steel Weight Loss	1	1	2	4	4
Alloy Thickness	1	1	3	4	4
Ratio - Alloy: Coating Thickness	1	1	1	4	4
Ductility	1	1	3	4	4
Adherence	1	1	2	4	4
Spangle Size No. 3 Steel	4	3	4	1	)2
No. 5 Steel	4	4	4	1	)2
Spangle Contrast No. 3 Steel	4	2	4	1	)2
No. 5 Steel	4	4	4	1	)2
Brightness	4	1	2	1	4
Roughness No. 3 Steel	1	1	1	4	)2
No. 5 Steel	4	1	1	4	)2

* 1. Most significant
  2. Significant
  3. Minor significance
  4. Not significant

- 38 -

TABLE 4

Statistically-Determined Influence of Galvanizing Variables on "White Rusting"
Properties as Determined by Accelerated Corrosion Tests*

	Immersion Time	Aluminium Content	Bath Temp.	Lead Content	Steel Roughness
% Gain in Diffusivity					
No. 3 steel	4	1	2	1	
No. 5 steel	4	1	4	1	3
Corrosion Index - Humidity Test	4	4	4	4	4
Weight Gain					
No. 3 steel	4	1	4	4	
No. 5 steel	1	1	1	1	2
Weight Loss					
No. 3 steel	2	1	4	4	
No. 5 steel	4	1	4	4	3
Corrosion Index - Water Film Test (48 hr)					
No. 3 steel	4	4	4	4	2
No. 5 steel	2	1	4	4	

* 1. Most Significant
2. Significant
3. Minor significance
4. Not significant
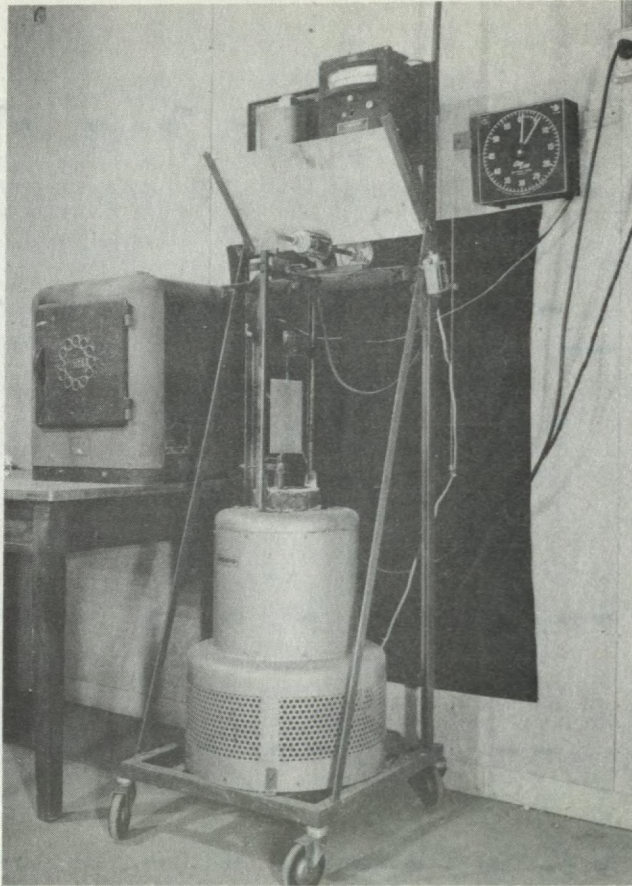
Fig. 1. - View of galvanizing fixture.
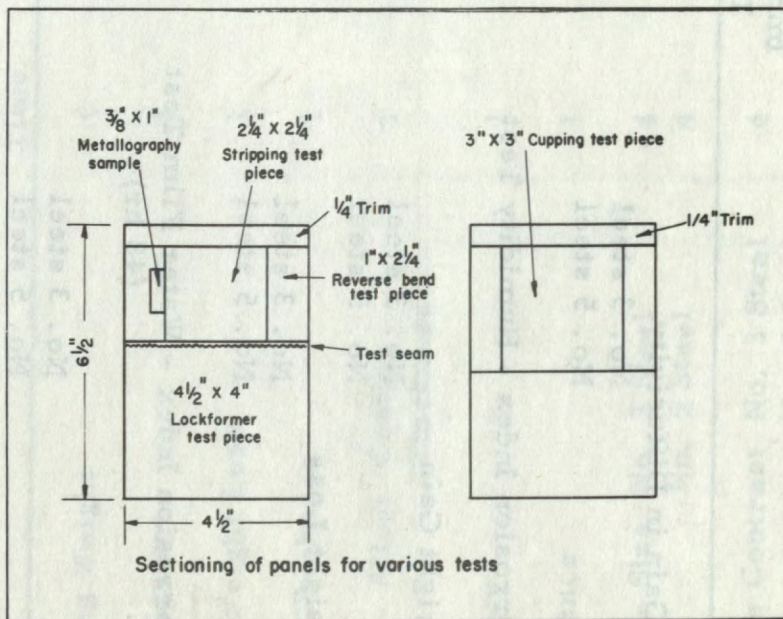
Fig. 2.
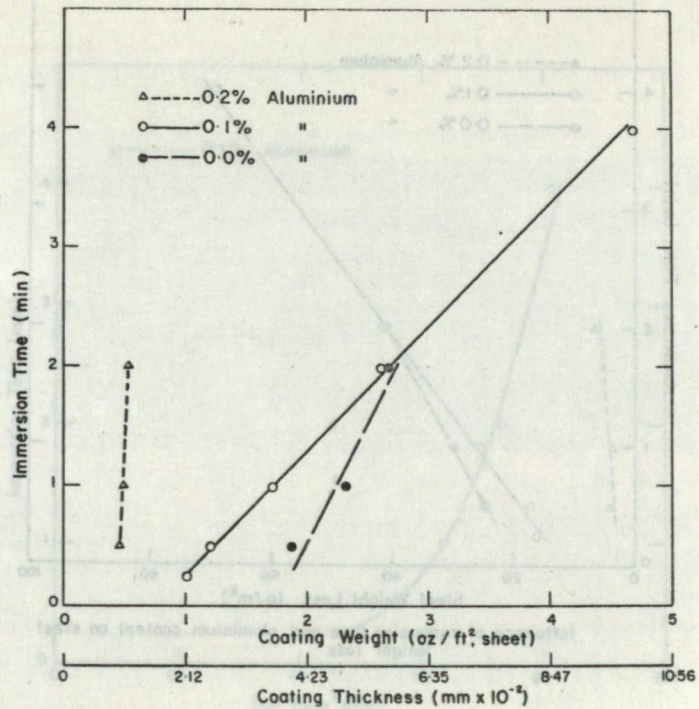
Influence of immersion time and aluminium content on coating weight.

Fig. 3
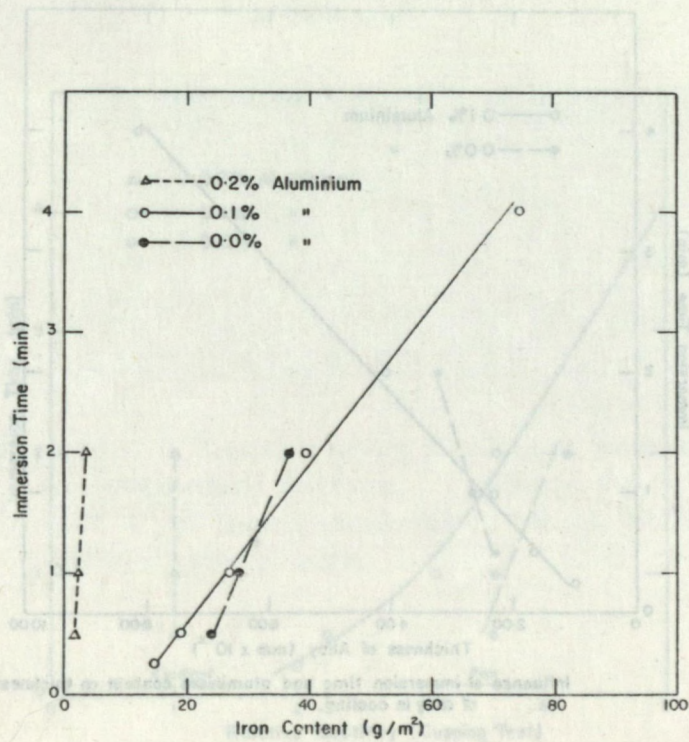
Influence of immersion time and aluminium content on iron content of coating.

Fig. 4

Influence of immersion time and aluminium content on steel weight loss.

Fig. 5.

Influence of immersion time and aluminium content on thickness of alloy in coating.
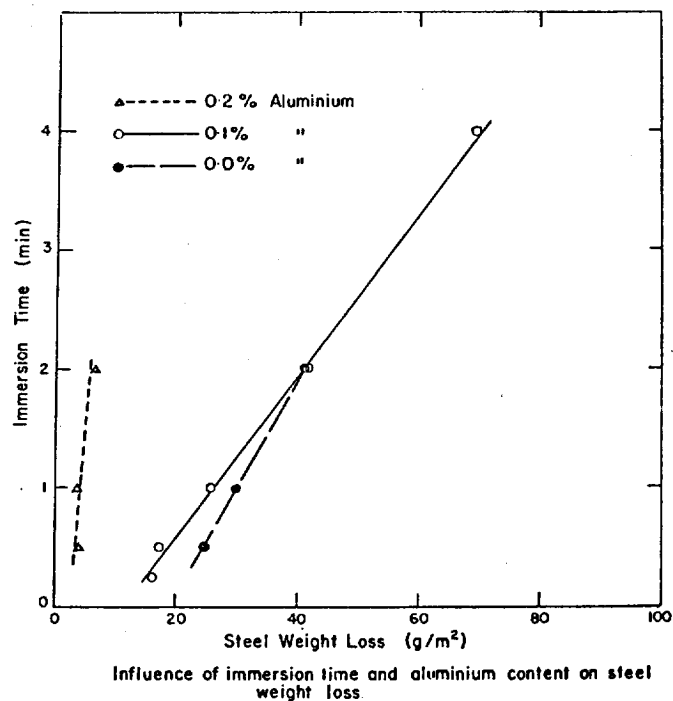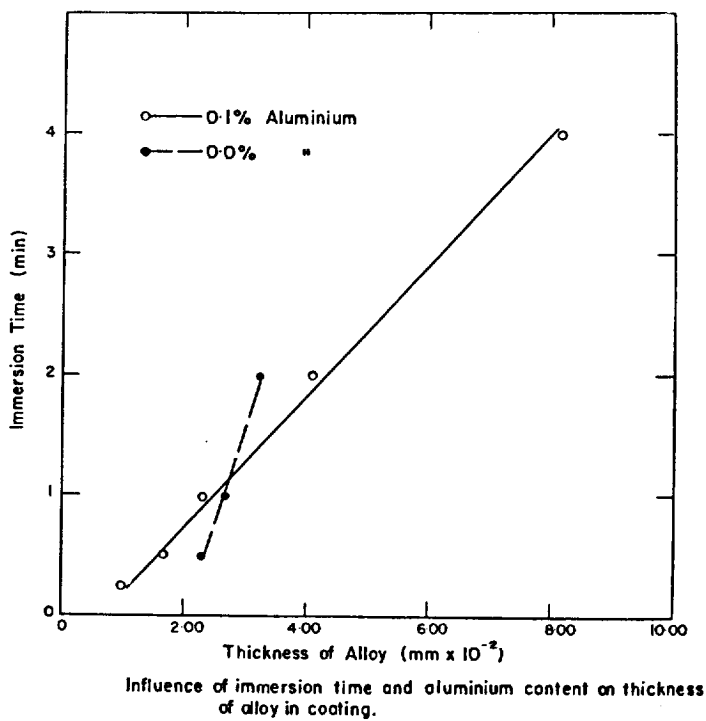
Fig. 6.
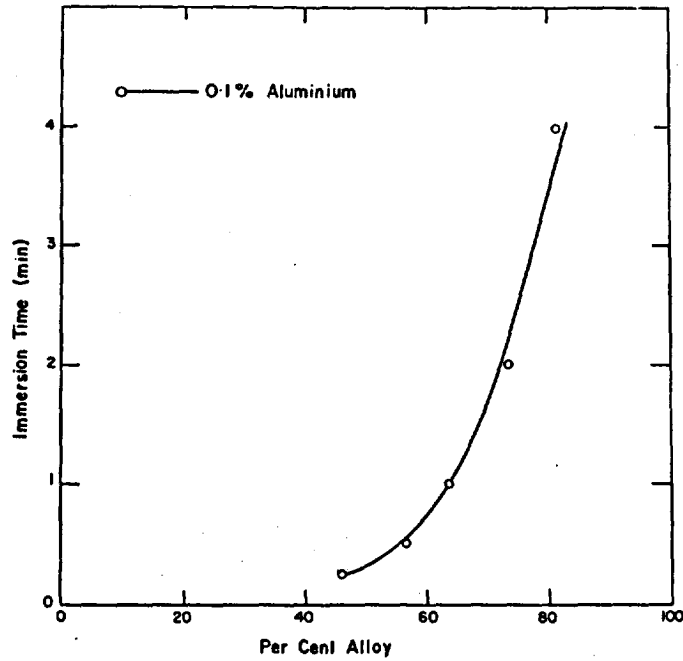
Influence of immersion time on per cent alloy in coating.

Fig. 7.
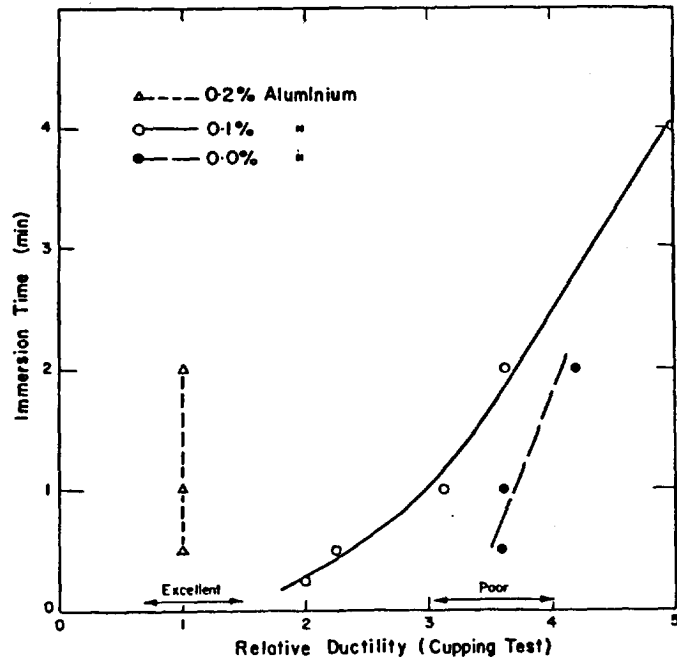
Influence of immersion time and aluminium content on
coating ductility.

Fig. 8.
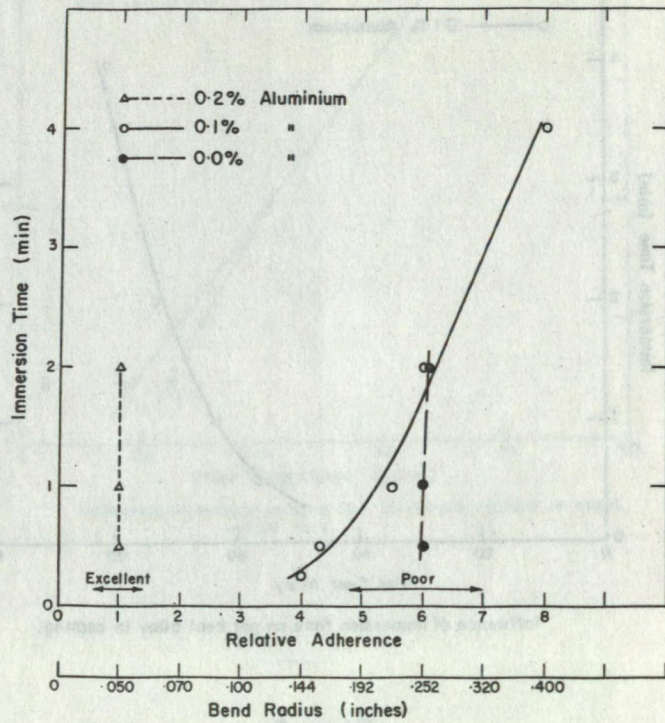
Influence of immersion time and aluminium content on coating adherence.

Fig. 9.
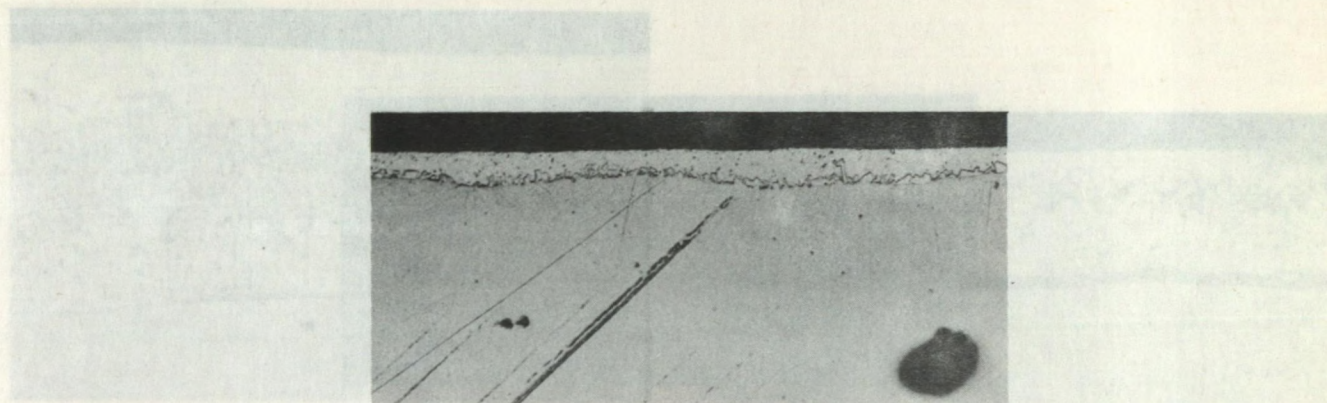
Fig. 10. - Typical iron-zinc alloy growth at high bath temperature. 0.5 minute dip at 465°C (869°F) in bath containing 0.2% Al, 0.5% Pb, 0.03% Fe. X500; nitramyl etch.
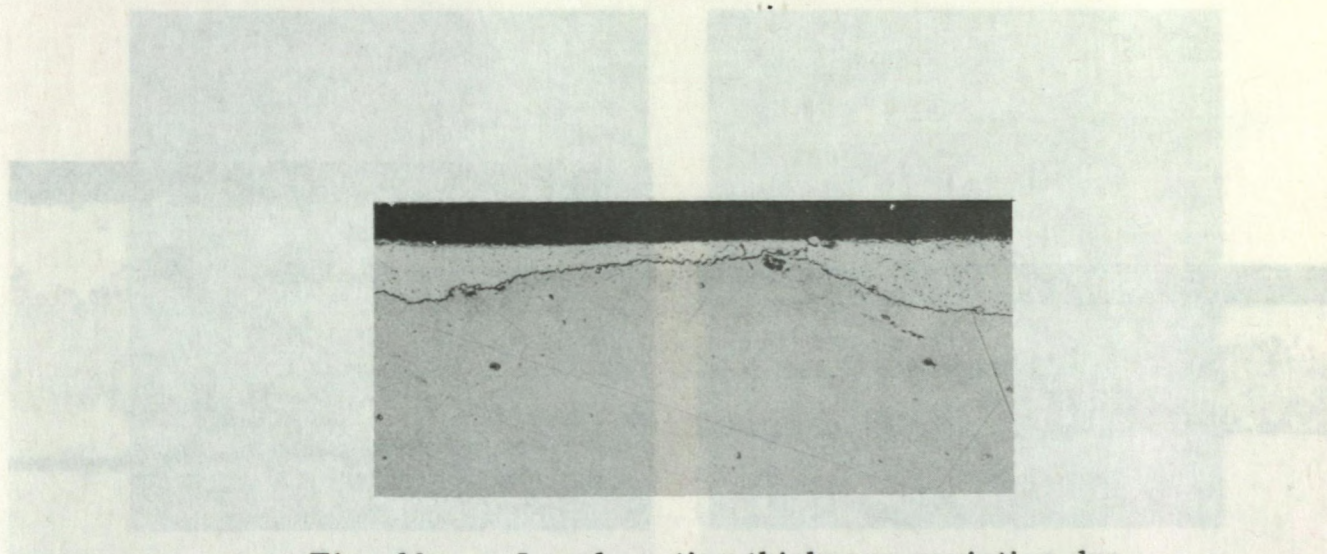
Fig. 11. - Local coating thickness variation due to rough steel surface. 1 minute dip at 455°C (851°F) in bath containing 0.2% Al, 0.03% Fe. X500; nitramyl etch.
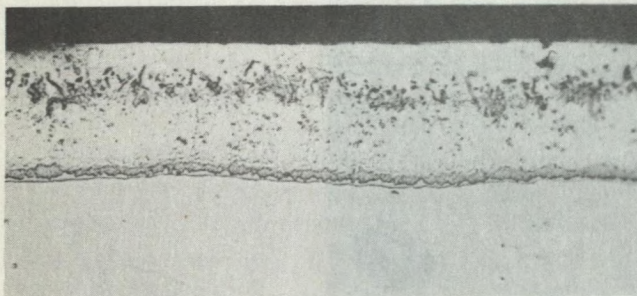
Fig. 12. - Typical structure with
1 minute immersion at 455°C
(851°F) in bath containing 0.1% Al,
0.5% Pb and 0.03% Fe.
X500; nitramyl and picral etch.
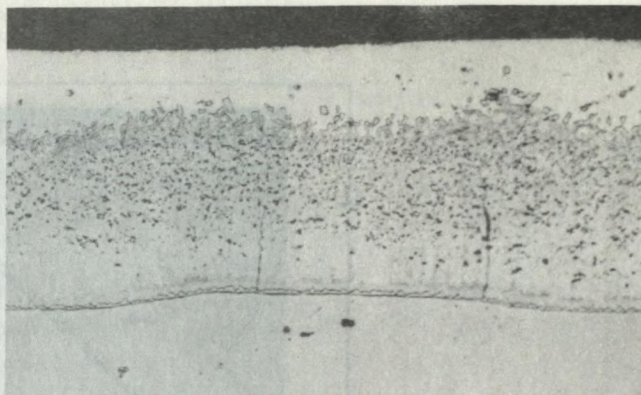
Fig. 13. - Typical structure with
2 minute immersion at 465°C
(869°F) in bath containing 0.1% Al,
1.0% Pb and 0.03% Fe.
X500; nitramyl and picral etch.
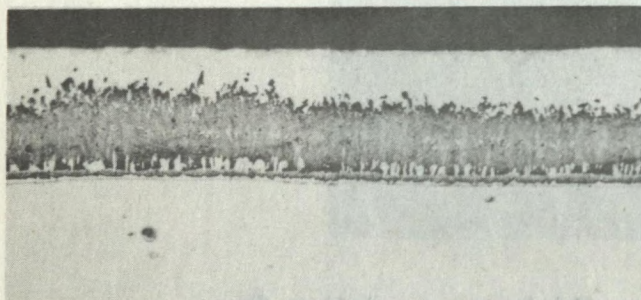
Fig. 14. - Typical structure with
0.5 minute immersion at 445°C
(833°F) in aluminium-free bath
containing 0.5% Pb and 0.03% Fe.
X500; nitramyl and picral etch.
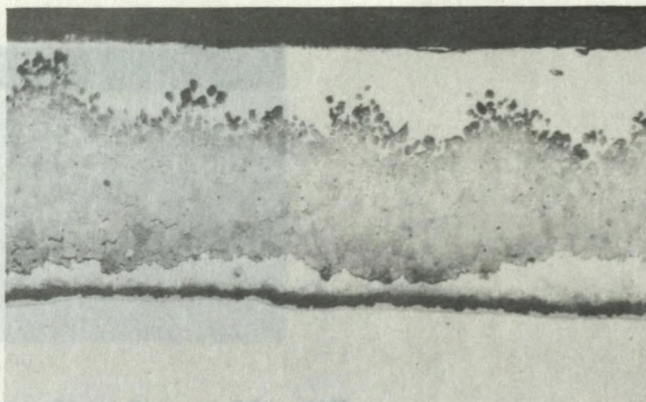
Fig. 15. - Typical structure with
2 minute immersion at 465°C
(869°F) in aluminium-free bath
containing 0.5% Pb and 0.03% Fe.
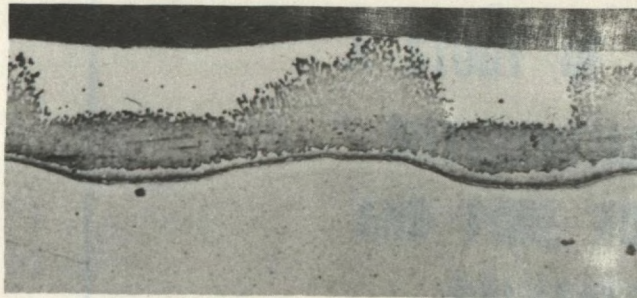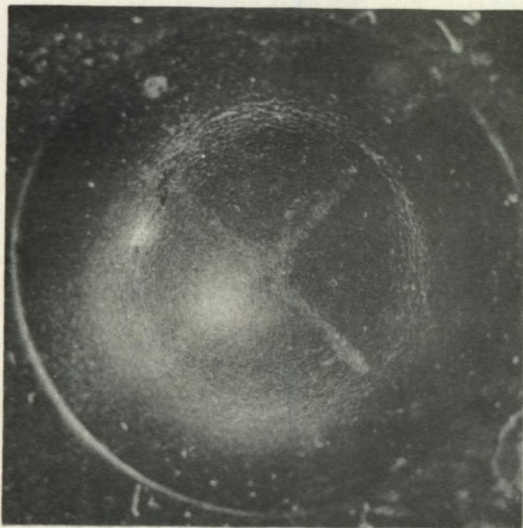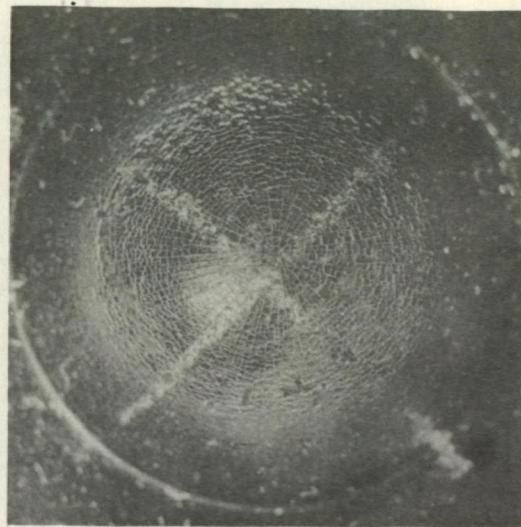X500; nitramyl and picral etch.

Fig. 16. - Typical non-uniform alloy growth
on No. 3 finish steel in aluminium-free bath.
X200, nitramyl and picral etch.

X 2 1/2

Fig. 17. - Appearance of cupping
test sample with ductility rating
of 2.

X2 1/2

Fig. 18. - Appearance of cupping
test sample with ductility rating
of 4.

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JJS:JOE:(PES)PG.