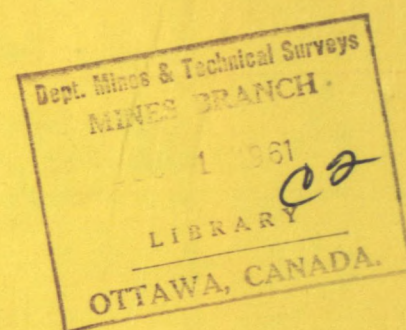




CANADA



THE INFLUENCE OF COMBINED ADDITIONS OF TIN, CADMIUM, ANTIMONY AND COPPER ON THE STRUCTURE AND PROPERTIES OF GALVANIZED COATINGS

DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA

MINES BRANCH
RESEARCH REPORT

R 86

Price 50 cents.

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PHYSICAL METALLURGY DIVISION

AUGUST 1961

Mines Branch Research Report R 86

THE INFLUENCE OF COMBINED ADDITIONS OF TIN,
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by

J. J. Sebisty* and R. H. Palmer**

ABSTRACT

The structure and properties of laboratory-prepared galvanized coatings on steel sheet, as affected by combined additions of tin, cadmium, antimony and copper to iron-saturated zinc baths, have been investigated in a statistically-designed series of tests.

It was found that the most important single factor affecting the thickness, metallographic structure, forming properties, surface appearance and storage-stain corrosion of the coatings was the aluminum content of the bath. The bath temperature and the time of immersion modified the behaviour of aluminum and were thus prominent secondary factors. Statistically, the influence of tin, cadmium, antimony and copper was minor to negligible, except with respect to surface appearance and storage-stain corrosion of the coatings.

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This report was prepared for presentation as a paper at the Sixth International Galvanizing Conference, Interlaken, Switzerland, June 1961.

Direction des mines

Rapport de recherches R 86

INFLUENCE D'ADDITIONS COMBINÉES D'ÉTAIN, DE CADMIUM,
D'ANTIMOINE ET DE CUIVRE SUR LA STRUCTURE ET LES
PROPRIÉTÉS D'ENDUITS GALVANISÉS

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J. J. Sebisty* et R. H. Palmer**

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RÉSUMÉ

La structure et les propriétés d'enduits préparés au laboratoire et appliqués sur des feuilles d'acier ont donné lieu à des investigations dans le cadre d'une série d'essais à caractère statistique, aux fins de déterminer les effets d'additions combinées d'étain, de cadmium, d'antimoine et de cuivre dans les bains de zinc saturés de fer.

On a constaté que la teneur en aluminium du bain est le facteur qui influe le plus sur l'épaisseur, la structure métallographique, le comportement au formage, l'aspect de la surface et la corrosion attribuable aux taches d'entreposage. La température du bain et la durée de l'immersion ont modifié le comportement de l'aluminium, d'où leur importance comme facteurs secondaires. Du point de vue statistique, l'influence de l'étain, du cadmium, de l'antimoine et du cuivre était tantôt faible et tantôt négligeable, sauf en ce qui concerne l'apparence de la surface et la corrosion des enduits du fait des taches d'entreposage.

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Ce rapport a été préparé en vue de la présentation sous forme de communication à la sixième Conférence internationale sur la galvanisation, tenue à Interlaken (Suisse) en juin 1961.

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INTRODUCTION

This investigation is a continuation of research on the hot-dip galvanizing process, started in 1956 at the Physical Metallurgy Division of the Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada, and carried out with the cooperation of the Canadian Zinc Research and Development Committee.

Two major investigations have been completed to date; both were concerned with study of the influence of bath additions on the structure and properties of experimental sheet galvanized coatings. The first of these dealt with aluminum and lead and was reported in two papers^(1,2) presented in 1958 at the Fifth International Galvanizing Conference in Brussels. Complete test data were tabulated in a supplementary report.⁽³⁾ In the second investigation, which forms the subject of this report, similar studies were made on tin, cadmium, antimony and copper. As a matter of interest it can be reported that further work in this field, involving other elements not normally encountered in galvanizing practice, is in progress.

From the literature it is evident that a great deal of attention has been devoted to examining the behaviour of tin, cadmium,

antimony and copper in hot-dip galvanizing. Information on these elements is thus extensive, but from surveys of more recently published literature, ^(4, 5) much of it appears to be controversial. Many investigations have dealt with these elements separately, usually in otherwise pure zinc baths. Much less attention has been devoted to defining cumulative effects involving the presence of two or more together. Where such attempts have been made, the experiments have generally been of limited scope, either with respect to the number of compositions examined, or with respect to the galvanizing time-and-temperature conditions selected. For these reasons, further study in this field was considered warranted. The investigation was carried out in two parts.

In a preliminary programme, experimental coatings were prepared in iron-saturated baths to which tin, cadmium, antimony and copper were added separately, with and without aluminum and lead. The results of this work are summarized briefly in an Appendix to this report and full details may be found elsewhere. ⁽⁶⁾

In the main study, interaction effects resulting from combined additions of aluminum, tin, cadmium, antimony and copper to iron-saturated zinc baths containing lead were examined. With continuous and general galvanizing practice in mind, several concentration levels for each element as well as series of bath temperatures and immersion times were selected. A systematic study

of all possible combinations of factors was clearly not feasible, and this necessitated use of statistical methods to reduce the investigation to manageable proportions. The statistical design for the experimental programme was that based on the principle of determining optimum response. (7)

EXPERIMENTAL PROGRAMME

The independent galvanizing variables and the individual levels of each selected for the experimental programme are listed in Table 1. The concentration of each of the addition elements, as well as the bath temperature and the immersion time, was varied in five steps.

The series of 34 baths and the 86 different test conditions that constituted the basic programme, and the order in which these were run, are given in Table 2. From study it will be noted that the programme was essentially constituted of three different series of tests. Two of these were run with 0.05% and 0.15% Al in the bath and covered tests involving combinations of the four addition elements, bath temperature and immersion time at the mid-low and mid-high levels for each variable. The third series, comprising the bulk of the remaining tests, was made with 0.10% Al in the bath and involved

combinations of the other variables at the intermediate and extreme levels for each.

Attention is drawn to tests 22, 65, 67 and 86 in Table 2. These were added to the programme to assist in studying the effects of tin and cadmium. Tests designated (a) and (b) represented a further addition made to provide information on the behaviour of lead.

All baths were saturated with iron (about 0.03% at 450°C (842°F) for pure zinc) and, except as noted above, the lead content was held at a nominal level of 0.5%.

For each test condition, twelve 4 in. x 6 in. steel sheet test panels were galvanized to provide samples for coating tests. A subsidiary series of smaller panels, 3 in. x 4 in., provided samples for determining steel weight loss due to zinc attack. Three of these were galvanized for each test condition. In the complete programme, a total of 1128 large and 282 small panels were galvanized.

MATERIALS

Test panels were of open-hearth, 24 swg rimmed steel sheet, bright annealed and mill finished by temper rolling to a

surface roughness having a measured average value of 40 micro-inches. The material was representative of normal commercial strip prepared for galvanizing by the Cook-Norteman continuous process. The chemical composition quoted was as follows: 0.07% C, 0.012% P, 0.03% S, 0.34% Mn, and 0.002% Si.

Materials used in the experimental galvanizing baths are listed in Table 3. Zinc, lead, tin and cadmium were added directly, whereas iron, aluminum, antimony and copper were introduced as master alloys which had been shotted by casting into water. Each bath was made up from fresh materials.

APPARATUS AND PROCEDURE

The laboratory galvanizing apparatus and procedure used in this investigation were similar to those used in the previous study on aluminum and lead. The paper on the latter work provides complete details,⁽¹⁾ and additional information in the form of melt and galvanizing logs is reported separately.⁽⁸⁾ To limit repetition, therefore, only general notes are included here.

Pretreatment of test panels involved vapour degreasing with trichlorethylene, and pickling for 5 min in a Rodine-inhibited 5% sulphuric acid solution at 70°C (158°F). Following scrubbing,

water rinsing, and drying in acetone, the panels were stored in a desiccator to reduce superficial rusting which would otherwise have occurred in the interval of 2 to 3 hr before further treatment. To simulate the dry galvanizing technique, the test panels were fluxed in an aqueous solution of commercial zinc-ammonium-chloride having a density of 10.4° Bé at 80°C (176°F). They were dried at 170°C (338°F) and, while still hot, were dipped into the galvanizing bath.

Galvanizing was done in a 40-lb-capacity, graphite-lined steel pot which was electrically heated and controlled to $\pm 2^\circ\text{C}$ by an immersed thermocouple. Control of immersion and withdrawal of the 4 in. x 6 in. specimens was effected by a motor-and-pulley mechanism actuated by an electric timer. These panels were lowered into the bath one at a time at 6 fpm and withdrawn at 3 fpm. The smaller 3 in. x 4 in. panels were manually handled in and out of the bath, in groups of three, at a speed of about 8 fpm and quenched in water immediately after withdrawal. The bath surface was skimmed as required to prevent pick-up of flux and oxide residues. The practice of dusting ammonium chloride on the surface, as was done for particular baths in the previous investigation, was omitted in this work.

All baths were sampled at the beginning and end of every run. An additional sample was taken midway through the

longer runs which covered four different test conditions. Sampling was done by ladling a small quantity from the bath and shotting this by casting into water. Antimony was determined spectrographically, and all other elements by wet analysis.

COATING TESTS

The experimental coatings were examined by tests such as used in the earlier studies; details may be found therein.^(1,6)

The following tests were made:

- (a) Coating weight and iron content of coating (stripping test in 1:1 HCl acid solution).
- (b) Coating ductility (visual grading of behaviour in Erichsen cupping test).
- (c) Coating adherence (visual grading of behaviour in lock seam machine and simple bend test).
- (d) Coating structure (microscopic examination and measurement of iron-zinc alloy thickness).
- (e) Steel weight loss (stripping test on 3 in. x 4 in. panels with standard antimony-inhibited acid solution).
- (f) Surface appearance examination (spangle size, spangle contrast, coating brightness and coating roughness, graded against arbitrary standards).

The susceptibility of the coatings to storage staining was also evaluated by humidity and water film stack tests. The procedure here was also identical with that done in earlier work,

except that each test was done on a fresh panel. This avoided possible errors associated with use of the same panel for both tests as was done previously.

RESULTS AND DISCUSSION

The results of coating property tests, storage-stain corrosion tests and statistical studies were too voluminous for inclusion in the present report. These have been compiled in a supplementary report, ⁽⁸⁾ from which such information as considered necessary to facilitate discussion has been extracted. Typical melt and galvanizing logs, codes for rating of ductility, adherence and surface appearance, and the results of chemical and spectrographic analysis of the experimental baths have also been included in the above report.

Table 4 summarizes the principle findings from statistical studies made on the test data. Assigned values of significance listed indicate the relative influence of the seven galvanizing variables on each of the coating tests made. From this table it can be seen that the tin, cadmium, antimony and copper content of the bath was generally of secondary or minor importance. Thus, the intended treatment of the statistical data to define the combinations of these additions which would give optimum coating

properties was not attempted. In the following discussion, emphasis has therefore been placed on comparison of such specific effects as appeared to be of practical interest. In Table 5 some typical test results are given for the principal quantitative coating measurements made.

Bath Composition

Bath composition changes due to interaction of tin, cadmium, antimony and copper with each other or with the other elements present were not observed. The only variations of any note were associated with aluminum, iron and lead.

No difficulty was encountered in holding aluminum in the bath at or near nominal levels of 0.05% and 0.10%, despite a consistent increase in iron during dipping. This trend was more pronounced in the former case, particularly as the bath temperature was raised. As expected, steel attack and thus the amount of iron in the bath was found to be higher for these conditions.

For the higher aluminum concentrations, extra additions were made in an attempt to maintain the nominal levels during dipping. This was only partly effective and decreases in the aluminum content of up to a maximum of 10% occurred from start to finish of the longer galvanizing runs. The appreciable amount of aluminum normally taken up in coatings formed in such baths

and the formation of iron-aluminum compounds were presumably the main factors responsible for these losses. The iron level in these baths varied but the general trend was represented by a minor increase in iron from start to end of a run.

For unknown reasons the lead content was also subject to minor variations. In some cases the nominal level was not attained at the beginning of a run, despite vigorous stirring of the bath before sampling.

No dross formation as such was encountered with any baths, but skimming losses were relatively high. Such losses were to some extent unavoidable, since care was taken to provide a clean bath surface just prior to withdrawal of the coated panels. Excessive skimming may therefore have been responsible for some of the bath composition variations described.

Coating Weight

Statistically, the most important factors affecting the thickness of the experimental coatings were: the aluminum content of the bath, immersion time, and bath temperature, in that order. The first two of these were shown to be interdependent, thus providing confirmatory evidence of this relationship which has been noted by other investigators. The remaining factors studied, namely the tin, cadmium, antimony and copper content of the bath,

had a minor to negligible influence.

Minimum coating weight was obtained with 0.2% Al in the bath. This was of the order of 0.40 oz/sq ft.*

In the 0.15% Al series of baths, the majority of coatings varied from 0.50 to 0.80 oz/sq ft for the relevant galvanizing conditions. These comprised the mid-low and mid-high levels of immersion time, bath temperature, and concentration of the addition elements. This spread in coating weight was related primarily to the immersion time; the influence of bath temperature and concentration of tin and the other elements was relatively minor. Some typical results are given in Table 5. Significant effects due to the additions were only apparent at the extreme time-temperature combination for this series, ie 80 sec and 465°C (869°F). For these conditions, some baths yielded very thick coatings, reaching a maximum of 1.45 oz/sq ft with the combination of 0.60% Sn and 0.60% Cd. Tin by itself, or with copper, or with cadmium and copper, all at 0.60%, were less effective, although not in that order. This suggests that relatively high levels of these elements can be tolerated in high-aluminum baths except at extended immersion times and high bath temperatures.

* Total coating for both sides of sheet applies to this and all other values quoted.

From these and earlier observations in the preliminary programme summarized in the Appendix, copper and cadmium appeared to be most detrimental.

Coatings prepared in the 0.10% Al baths at the intermediate levels of time, temperature, and concentration of tin and other addition elements, averaged around 1.40 oz/sq ft. This value remained constant when tin, cadmium and copper were separately lowered to 0.075%, and even at the other extreme of 1.2% for each element the coating weight was not significantly altered. In the subsidiary tests added to the programme, the influence of tin and cadmium was again negligible and the only observation of note was a well-defined reduction in coating weight in all cases when lead was absent. From Table 5 it can be seen that 0.5% Pb gave values around 1.40 oz/sq ft, compared to about 1.20 oz/sq ft for lead-free baths. Raising the lead content to 1.0% failed to provide any additional change.

Table 2 shows that the 0.05% Al series of baths duplicated the experimental conditions in the 0.15% Al series except with respect to antimony concentration. At this low aluminum level, coating weight varied between average limits of 1.15 and 2.25 oz/sq ft and was dependent principally on the immersion time. Bath temperature effects were much less pronounced and were also variable. At the longer immersion time of

80 sec, an increase in temperature from 445°C (833°F) to 465°C (869°F) usually resulted in slightly thicker coatings, but at 20 sec immersion this change had no influence or acted in reverse. For example, in baths containing 0.60% Sn, 0.60% Cd, separately and in combination, and in the single bath containing minimum levels of all four additions, this increase in temperature reduced coating weight from 1.3 to about 1.2 oz/sq ft. This reversal in the latter case is illustrated by tests 72 and 75 in Table 5. In contrast, when 0.60% Cu was present alone, or was combined with either 0.60% Sn or 0.60% Cd, coating weight remained constant at around 1.2 oz/sq ft at both temperatures. These apparent inconsistencies are discussed further in a later section dealing with the metallographic structure of the coatings.

Iron Content and Steel Weight Loss

In these tests, the aluminum content of the bath, immersion time and bath temperature were found to be the most significant variables. Interaction between the first two of these factors, and a similar effect of somewhat lesser importance between time and temperature, was observed in analysis of the test data. Influence of the bath additions under study was again minor. Statistically, the relationships in these two tests were considered to be in good agreement, but inspection of the actual test results revealed some anomalies.

Iron content was about 1.3 g/m^2 in the 0.2% Al coatings as compared with a range from 2.0 to 4.0 g/m^2 for the majority of the 0.15% Al coatings. Variations in this range reflected the immersion time and bath temperature effects noted for the coating weight tests. The occasional thick coatings associated with the high additions of tin, cadmium and copper, contained correspondingly high iron, approaching a maximum of 12 g/m^2 . For unknown reasons the steel weight loss measurements for the high-aluminum coatings were somewhat inconsistent and, more pertinent, were considerably higher than the iron values; in some instances they were two to three times as great. Different stripping acid solutions were used in the tests as noted earlier, but it is not considered that this could account for the observed variations in the results. These variations must, therefore, be put down to experimental error, or to inherent differences in the galvanizing behaviour of the separate samples prepared for the tests. Time did not permit further investigation with electrolytic stripping methods.

The iron content and steel weight loss results were in much better agreement for the 0.10% Al coatings and generally ranged between 20 and 22 g/m^2 . In this series no observable effect could be traced to the presence of tin and the other bath additions, even at the maximum concentration for each. This applied also to lead in the extra tests. Minimum iron content and steel weight loss in this complete series was about 13 g/m^2

obtained with a 10 sec immersion at 455°C (851°F).

The amount of iron in the 0.05% Al coatings varied approximately between 15 g/m² and 35 g/m². As with coating weight, variation within these limits was chiefly dependent on the immersion time. Bath temperature was, however, only slightly less important as indicated by a proportionately greater increase in the iron content in going from 20 sec to 80 sec immersion time at the higher temperature of 465°C (869°F). On the average this was 18 g/m², as compared with 11 g/m² for the same change in immersion time at 445°C (833°F). With all of the coatings in this series, tin and the other addition elements failed to exhibit any well-defined influence on the iron level. A further observation was the reappearance of the discrepancies between the steel weight loss and the iron content values. In general the latter were higher, thereby reversing the trend found with the high-aluminum coatings. However, the differences were much less serious and averaged around 25%. Again, no explanation can be offered for this anomaly.

Iron-Zinc Alloy Measurements and Coating Structures

As in the previous tests, the galvanizing variables of maximum significance were: the aluminum content of the bath, immersion time, and bath temperature. Interaction of these, and the relatively minor effects associated with the remaining bath

composition factors, represented additional similarities between the statistical relationships for the coating weight, iron content and iron-zinc alloy measurements.

Because of the nature of iron-zinc alloy formation in the high-aluminum coatings, the measurements can be considered as approximations only. The results generally reflected the trends in the coating weight tests, and the bulk of the coatings contained from 7 to 15% alloy depending on the time-temperature conditions used. This increased up to 40% in the thicker coatings formed in the presence of tin, cadmium and copper for the combinations previously mentioned in the coating weight tests. The microstructures in this series showed the typical features characteristic of high-aluminum coatings. Where aluminum had effectively suppressed steel attack, the iron-zinc layer appeared as a thin, sometimes discontinuous, fringe of crystals next to the steel surface, as in Figure 1 (a) and (c). As this inhibition was lessened by the factors referred to above, local iron-zinc alloy outbursts became more numerous and contributed to a heavier dispersion of free-floating crystals in the outer zinc layer. These local growths, which represented sites of heavy steel attack, increased in size and eventually covered large areas, thereby causing pronounced pick-up of zinc and non-uniformity in thickness of the coatings on the same as well as opposite sides of a sheet. These effects were most pronounced with the combination of 0.60% Sn

and 0.60% Cd at the longer immersion time of 80 sec and higher bath temperature of 465 °C (869 °F). Typical iron-zinc alloy outbursts are shown in Figure 1 (b) and (d).

The 0.10% Al coatings, which were generally of constant weight as noted earlier, showed similar uniformity with respect to iron-zinc alloy thickness and the proportion of alloy. The latter averaged around the high value of 60% which confirms similar observations⁽¹⁾ made on the limited inhibition of steel attack provided by this amount of aluminum in an iron-saturated zinc bath. The characteristic features of the microstructures were the well-defined and uniformly continuous layers of the individual iron-zinc phases. The zeta phase was always appreciably thicker than the delta prime and gamma phases. Reference has been made to an increase in coating weight in the extra series of tests when lead was added to the bath. Microscopic examination showed this increase to be related to the presence of a thicker eta layer, as per Figure 2 (a) and (b), which thus contradicts the accepted improvement in zinc fluidity usually associated with lead. It must therefore be assumed that the variable zinc drag-out was related, rather, to the tin and/or cadmium present and that the influence of these elements was modified when lead was also present. Evidence supporting this possibility is provided by surface appearance effects described later.

In the 0.05% Al coatings, iron-zinc alloy formation represented from 45 to 80% of the total thickness. Immersion-time and bath-temperature effects only were clearly defined and the measurements failed to account for the coating weight anomalies described earlier. A possible explanation was provided by observed differences in the mode of growth of the zeta phase which could have affected the thickness of the eta layer and the coating as a whole.

One of these inconsistencies, it will be recalled, was the reduction in coating weight from 1.3 to 1.2 oz/sq ft, produced by an increase of temperature for 20 sec immersion in the bath containing minimum concentrations of all four additions, as well as in the baths with 0.60% Sn and 0.60% Cd, separately and together. In these coatings the zeta phase showed characteristic columnar growth with large, loosely-packed crystals providing an irregular serrated edge next to the eta layer, as illustrated in Figure 3 (a). Such roughness would be expected to promote heavier drag-out of zinc. However, to account for a reduction rather than an increase in coating weight, it must be assumed that the excessive zinc present tended to drain away more completely, being assisted by its lower viscosity at the higher temperature. As a result, the thickness of the eta layer and the coating as a whole would be decreased. To what extent zinc viscosity was influenced by the alloying additions is not known.

In the corresponding high-copper coatings, the crystalline structure of the zeta phase was replaced by a densely-packed granular mass as in Figure 3 (b). The outer surface of this layer was somewhat smoother than in the coatings above and zinc drag-out must have been proportionately less. Thus, the constant weight of 1.2 oz/sq ft for these coatings when dipped for 20 sec at 445 °C (833 °F) and 465 °C (869 °F) represented more normal behaviour, in that the increase in iron-zinc alloy thickness caused by this temperature change was compensated by a proportionate reduction in the thickness of the outer zinc layer as a result of its lower viscosity.

It is known that this type of granular structure in the zeta phase can be caused by rapid zinc attack at high temperatures and long immersion times. In most of the 0.05% Al coatings, this modification was only evident with a dipping time of 80 sec at 465 °C (869 °F). By comparison, the same structure was well developed at 445 °C (833 °F) in the high-copper coatings. From these observations it appears that, for the applicable galvanizing conditions, the addition of 0.60% Cu altered the time-temperature relationship of the iron-zinc reaction and indirectly affected zinc drag-out.

Coating Ductility

Ductility was evaluated by comparing the performance of the experimental coatings in cupping tests. Arbitrary standards showing various stages of cracking and break-up served as the basis for rating the behaviour in this test.

From Table 4 it can be seen that this property was principally dependent on the aluminum content of the bath and the immersion time. Temperature of the bath and the addition of tin and cadmium exerted a minor influence, whereas the remaining elements, antimony and copper, had no effect. No interaction between any of the variables was evident.

Comparison of actual test results showed that most of the coatings prepared with 0.15% and higher aluminum in the bath withstood the cupping test without cracking and were therefore classified as having excellent ductility. Coatings dipped for the extended time of 80 sec at 465°C (869°F) generally exhibited only moderate cracking; by comparison, the behaviour of the thick, tin- and-cadmium-containing coatings formed under these conditions was much inferior.

The only coatings yielding good ductility in the 0.10% Al series of tests were those dipped for 10 sec at 455°C (851°F) and for 40 sec at the minimum temperature of 435°C (815°F). All others

showed moderate to relatively severe cracking in the cupping test and were rated as having only fair to poor ductility. This suggests that for the conditions used, up to 1.2% each of tin, cadmium and copper, and to 0.2% Sb, did not modify the basically poor performance evident in this series. The effect of lead from nil to 1.0% in the subsidiary tests incorporated in the test programme was likewise negligible.

Coatings from the third major group of tests made with 0.05% Al in the bath also performed poorly according to the standards set. Severe cracking was evident with even the thinnest coatings in this series.

Coating Adherence.

For the adherence tests, 1 in. strips were clamped in a jig and manually bent through 90° and back through a reverse bend of 180°. Mandrel radii ranged from 0.05 in. to 0.40 in. in eight steps. The bend radius yielding no significant flaking of the coating was recorded. Edge effects were ignored. The information from this test was supplemented by examining the forming behaviour of additional samples which were subjected to a flattened "S" bend in a lock seam machine.

Statistical evaluation of the bend test data revealed that the aluminum content of the bath was the most significant galvanizing

factor. Immersion time and bath temperature were only slightly less important, presumably because of their effect on coating weight which would have a direct bearing on adherence as measured in the bend test. The presence of tin, cadmium and antimony was found to be of minor significance only, and no effect could be traced to copper in the bath.

The test results revealed maximum coating adherence to be associated with the very thin coatings obtained with 0.2% Al in the bath. These could be folded flat on a zero radius with no evidence of flaking.

The 0.15% Al series of coatings was somewhat less satisfactory, but still had moderately good adherence. These showed an increasing tendency to flake as immersion time and bath temperature were raised, so that the minimum bend radius varied from 0.07 in. for 20 sec immersion at 445°C (833°F) to 0.14 in. for 80 sec at 465°C (869°F). Raising the concentration of tin, cadmium and antimony from 0.15% to 0.60%, separately and in various combinations, also contributed to reduced adherence. Although these effects were inconsistent, the general trend of the results indicated that the higher alloy additions were definitely harmful for extended time-temperature conditions.

The coatings prepared with 0.10% Al in the bath could be given a fair-to-poor adherence rating only in the bend test. Apart from the extremely thick coatings formed at 160 sec, the minimum bend radius for this group was consistent around an average value of 0.25 in. This behaviour was not affected by variations in concentration of tin, cadmium, antimony, copper, as well as lead, within the ranges studied.

The adherence of the 0.05% Al coatings was also inferior. The only effect observed here was a further pronounced deterioration in bend performance with increases in immersion time and bath temperature.

Inspection of the samples subjected to lock seam forming confirmed the results of the bend tests. In general, only the high-aluminum coatings, which had been rated as acceptable in the latter, withstood the stresses imposed in formation of the "S" seam without any significant flaking or peeling.

Surface Appearance

The various surface properties evaluated were spangle size, spangle contrast, coating brightness and coating roughness. The statistically major influence of aluminum on all of these properties is indicated in Table 4. Other factors of similar importance

in some respects were the tin content, bath temperature and immersion time. These tended to modify the effect of aluminum and some of the relationships were found to be extremely complicated, particularly in the case of spangle size. This can be inferred from the fact that all except two of the seven galvanizing variables exhibited a dominant role in spangle development. The secondary influence of cadmium, antimony and copper on the other surface properties evaluated is also to be noted from Table 4.

All of the high-aluminum coatings were characterized by a moderately bright appearance which lacked conventional visual appeal because spangles were generally small, vaguely-defined, and showed little or no contrast. Only when all four addition elements were present together, at the highest concentration level for each, was any moderate improvement noted. Surface appearance was also marred by the presence of projecting pimples in the coatings dipped for the longer immersion time of 80 sec in the more highly alloyed baths. Partial neutralization of the inhibiting effect of aluminum was thus indicated, since the pimples clearly represented sites of local heavy steel attack and formation of outbursts of iron-zinc alloy. Because of the gravity drainage conditions used, these growths were not effectively blanketed by the thin outer zinc layer common to such high-aluminum coatings. In this series of tests, good zinc coverage was

obtained without any evidence of bare spots.

Excellent surface smoothness combined with well-defined, high-contrast spangle formation in all except lead-free coatings were the outstanding features of the 0.10% Al series of tests. Variations in immersion time and bath temperature from the intermediate levels of 40 sec and 455°C (851°F) were reflected in characteristic alterations in spangle size, but the appearance was otherwise not affected. So far as bath composition was concerned, only tin and antimony produced any major effects. Reducing the tin content to 0.075%, and holding cadmium, copper and antimony constant at their intermediate levels, resulted in poorer spangle contrast so that the coatings had a flat dull sheen. At the opposite extreme of 1.20% Sn, the spangles were markedly larger than the average and had a more pronounced frosty appearance; the characteristic fern-like structure was also clearly evident. Similar behaviour was apparent with 0.20% Sb, except that the latter feature was somewhat more exaggerated.

One of the more obvious surface effects apparent in the subsidiary tests on tin, cadmium and lead was the total absence of spangles in the lead-free baths, even with as much as 0.15% Sn or up to 0.60% Cd present. The typical metallic appearance is illustrated by Figure 4. Additions of tin up to 0.60% were

also relatively ineffective and produced only very small spangles (Figure 5). These same additions with 0.5% Pb in the bath, however, reproduced the more or less typical features described above, except that spangle contrast and size were much less pronounced with cadmium. Increase in concentration of the latter actually tended to reduce the spangle size. Of particular interest also was the marked improvement in coating brightness where the lead content was raised to 1% in baths containing 0.15% of tin or cadmium (Figure 6). An accompanying feature was minor depression of the spangle boundaries. Surface smoothness was restored with 0.60% of either tin or cadmium, but at the expense of lower reflectivity. The reduction in spangle size with increasing cadmium was also again evident.

In the 0.05% Al tests, the smoothness of the 0.10% Al coatings was essentially duplicated, but coating brightness and spangle contrast in some cases were less pronounced. Maximum contrast and brightness were obtained with the bath compositions combining 0.60% Sn and 0.60% Cd, separately and together, with 0.04% Sb. Spangle size varied widely from about 0.0625 in. in diameter up to a maximum in excess of 0.75 in. Some typical surfaces are reproduced in Figure 7. The concentration of tin in the bath was a dominant factor affecting spangle development, whereas bath temperature and immersion time were of secondary

importance, except for the combination of 465°C (869°F) and 80 sec, respectively, which exaggerated the effect of tin considerably. For these conditions, the presence of 0.04% Sb also contributed to spangle growth and to the formation of the fern-like structure mentioned earlier. Increase in cadmium content again tended to reduce the spangle size, but copper had no effect in this connection.

Corrosion Tests

The humidity and water film tests used to evaluate the storage-stain susceptibility of the coatings were both stack tests which, however, differed in the method of wetting the surface and in the conditions of exposure. In the former, the sample was chilled and then wetted by condensation of moist air on the surface; it was then sandwiched between glass plates which had been similarly treated and placed in a humidity cabinet at 35°C (95°F), 95% relative humidity, for 16 hr. A drying treatment followed and the whole cycle was then repeated. In the water film test, the sample was sandwiched between glass plates under water and stored in warm air for 48 hr. By way of explanation, the term "diffusivity" in Table 4 refers to the light-scattering properties of the sample surface. This measurement was made with a photoelectric cell reflectometer. The corrosion-index designation

applies to tests involving visual estimates of the amount of the surface showing white and black staining after exposure. More complete details of both corrosion tests are reported separately. (3)

Interactions between the galvanizing variables were again prominent in the statistical relationships derived from the corrosion data. All factors were involved in varying degrees, but the most important by far was the aluminum content of the bath. Bath temperature and immersion time modified the behaviour of aluminum to a limited extent in the humidity test, presumably by virtue of changes in surface roughness which could affect the corrosion characteristics of the coating. Such interdependence was not found in the water film test, which suggests that small variations in surface roughness have a minor effect on corrosion under conditions of complete water immersion.

The substantial secondary effects due to cadmium, copper and antimony in both tests are to be noted. Strong interdependence between these was found, particularly between cadmium and copper, and a similar relationship between antimony and aluminum was also apparent. The relatively prominent role of antimony was unexpected and cannot be explained on the basis of its effect on surface finish alone, in view of the behaviour of tin. The latter exhibited a much more powerful influence on surface finish but was a negligible factor in corrosion in the humidity test.

In the water film test, tin and antimony produced similarly important effects. From the observations made in these tests it is clear that the storage-stain susceptibility of the coatings was affected to a major degree by aluminum. Although less detrimental, tin and the other addition elements exhibited sufficiently prominent effects to suggest that the concentration of these should be limited in coatings where resistance to this type of corrosion is desired.

To evaluate atmospheric corrosion behaviour of the experimental coatings, representative panels from the entire series of tests in the programme have been set out at a fully-instrumented site in a semi-industrial atmosphere. Information from these tests will be published at some future date.

SUMMARY AND CONCLUSIONS

The structure and properties of laboratory-prepared galvanized coatings on steel sheet, as affected by combined additions of aluminum, tin, cadmium, antimony and copper to iron-saturated zinc baths, have been investigated in a statistically-designed series of tests. Ranges of immersion time, bath temperature and concentration of the above elements were covered. From consideration of the experimental test results, various conclusions were reached, of which the following appear to be of most practical interest and importance.

The most important single factor affecting the thickness, structure, forming properties, surface appearance and storage-stain susceptibility of the experimental coatings was the aluminum content of the bath. Bath temperature and immersion time modified the behaviour of aluminum, and this interdependence was reflected in the prominent secondary role of these time-temperature factors in most of the coating tests made. Statistically, the influence of tin, cadmium, antimony and copper was minor to negligible, except with respect to surface appearance and storage-stain corrosion of the coatings.

With 0.15% or higher aluminum in the bath, it appears that up to 0.60% each of tin, cadmium and copper, and 0.04% Sb, separately and in combination, have relatively little effect on coating properties so long as the immersion time is short and the bath temperature is at or near the optimum of 450°C (842°F). If these time-temperature conditions are appreciably exceeded, partial neutralization of the inhibiting effect of aluminum, and development of non-uniform coatings with relatively poor ductility and adherence, can be expected, particularly in the presence of copper and cadmium. Although lower concentration limits would be desirable in production of thin-gauge continuous strip to avoid the danger of excess build-up in the bath, it appears that complete elimination of these elements is not vital to production of satisfactory coatings on steel sheet.

For lower aluminum concentrations which are not sufficient to prevent appreciable iron-zinc alloy formation, it is concluded that :

- (a) No improvement in the basically poor forming properties of such coatings can be expected, even with excessive additions of tin, cadmium, antimony and copper to the bath. Where these are present in significant amounts, an aluminum addition of the order of 0.05%

appears to serve no useful purpose other than as a brightener, since the normal reduction in coating weight to be expected with this amount of aluminum gradually disappears with increase in immersion time and bath temperature.

(b) The only practical advantage to be expected from deliberate alloying of the bath with tin, cadmium and antimony is an improvement in surface appearance, particularly with respect to production of a lustrous spangled finish. This type of finish offers no technical superiority but cannot be discounted in view of widely-quoted customer demand for spangled coatings. In this connection, the tests demonstrated that spangle size and contrast, as well as coating brightness, can be varied widely by individual or combined additions of these elements, depending on the time-temperature conditions used and the amount of aluminum and lead in the bath.

(c) Tin or cadmium at high concentrations in excess of 1% appears to be ineffective in promoting appreciable spangle growth with lead-free baths. However, a much superior response can be obtained

with significantly smaller amounts when 0.5% Pb is also present. It is likely that a lower lead level would provide comparable behaviour. Under these conditions, formation of a thicker outer zinc layer is apparently favoured thus altering the spangle growth characteristics of the coating.

(d) A high lead content is beneficial in promoting brighter coatings but an accompanying disadvantage is a reduction in surface smoothness due to depression of spangle boundaries. The latter could be overcome by lowering the lead level but, in production operation, this would limit other benefits relating to dross formation and removal which are generally associated with excess lead in the bath. Addition of tin and/or cadmium in amounts of the order of 0.60% appears to offer an alternative solution.

(e) Copper promotes more rapid zinc attack of the steel surface and is also detrimental to coating surface appearance. Since it offers no practical advantages to offset these harmful effects, the use of zinc with a high copper content, or adding copper for alloying purposes, should be avoided.

Storage-stain susceptibility tests demonstrated that such corrosion is dependent to a major degree on the presence of aluminum in the coating. Tin, cadmium, antimony and copper are somewhat less detrimental but exhibit sufficiently prominent effects to suggest that the concentration of these should be limited in coatings where resistance to this type of corrosion is desired.

ACKNOWLEDGMENTS

The authors wish to thank the Director, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada, and the Canadian Zinc Research and Development Committee, for permission to publish the results of this investigation.

The valuable assistance of the following cooperating firms is gratefully acknowledged: The Consolidated Mining and Smelting Company of Canada, Limited; Hudson Bay Mining and Smelting Company, Limited; and The Steel Company of Canada, Limited.

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TABLE 1
Galvanizing Variables

<u>Variable</u>			<u>Levels</u>			
Aluminum content	- %	-	0.05	0.10	0.15	0.20
Tin content	- %	0.075	0.15	0.30	0.60	1.20
Cadmium content	- %	0.075	0.15	0.30	0.60	1.20
Copper content	- %	0.075	0.15	0.30	0.60	1.20
Antimony content	- %	-	0.0016	0.008	0.040	0.20
Bath temperature	- °C	435	445	455	465	475
	- °F	815	833	851	869	887
Immersion time	- sec	10	20	40	80	160

TABLE 2
Experimental Programme*

Bath No.	Test No.	Al %	Sn %	Cd %	Cu %	Sb %	Bath Temp		Immersion Time, sec
							°C	°F	
1	1	0.05	0.15	0.15	0.60	0.0016	465	869	80
	2						465	869	20
	3						445	833	80
	4						445	833	20
2	5	0.20	0.30	0.30	0.30	0.008	455	851	40
3	6	0.05	0.15	0.60	0.15	0.0016	465	869	80
	7						465	869	20
	8						445	833	80
	9						445	833	20
4	10	0.05	0.15	0.60	0.60	0.040	445	833	80
	11						445	833	20
	12						465	869	20
	13						465	869	80

(Continued -

TABLE 2 (Continued)
Experimental Programme*

Bath No.	Test No.	Al %	Sn %	Cd %	Cu %	Sb %	Bath Temp		Immersion Time, sec
							°C	°F	
5	14	0.05	0.60	0.15	0.15	0.0016	445	833	80
	15						445	833	20
	16						465	869	20
	17						465	869	80
6	18	-	0.30	0.30	0.30	0.008	455	851	40
7	19	0.10	0.30	0.30	0.30	0.008	455	851	40
	20						435	815	40
8	21	0.10	0.30	0.30	1.20	0.008	455	851	40
9	22	0.10	-	0.15	0.30	0.008	455	851	40
	22(a)	as for test 22, but with no lead.							
	22(b)	as for test 22, but with 1.0% Pb.							
10	23	0.15	0.60	0.60	0.60	0.040	465	869	20
	24						465	869	80
	25						445	833	80
	26						445	833	20
11	27	0.10	0.30	0.30	0.30	0.008	475	887	40
	28						455	851	40
12	29	0.10	0.30	0.30	0.30	-	455	851	40
13	30	0.05	0.60	0.60	0.15	0.040	445	833	20
	31						445	833	80
	32						465	869	20
	33						465	869	80
14	34	0.10	0.30	0.30	0.30	0.20	455	851	40
15	35	0.15	0.15	0.15	0.60	0.040	465	869	80
	36						465	869	20
	37						445	833	80
	38						445	833	20
16	39	0.15	0.15	0.15	0.15	0.0016	465	869	80
	40						465	869	20
	41						445	833	20
	42						445	833	80

(Continued -

TABLE 2 (Continued)

Experimental Programme*

Bath No.	Test No.	Al %	Sn %	Cd %	Cu %	Sb %	Bath Temp		Immersion Time, sec
							°C	°F	
17	43	0.10	0.30	0.30	0.30	0.008	455	851	10
	44						455	851	40
18	45	0.15	0.60	0.60	0.15	0.0016	445	833	80
	46						445	833	20
	47						465	869	20
	48						465	869	80
19	49	0.15	0.60	0.15	0.60	0.0016	465	869	20
	50						465	869	80
	51						445	833	20
	52						445	833	80
20	53	0.10	0.30	0.30	0.075	0.008	455	851	40
21	54	0.10	0.30	0.30	0.30	0.008	455	851	40
	55						455	851	160
22	56	0.10	0.30	1.20	0.30	0.008	455	851	40
23	57	0.05	0.60	0.15	0.60	0.040	445	833	20
	58						445	833	80
	59						465	869	80
	60						465	869	20
24	61	0.15	0.15	0.60	0.15	0.040	465	869	80
	62						465	869	20
	63						445	833	20
	64						445	833	80
25	65	0.10	0.60	-	0.30	0.008	455	851	40
	65(a) as for test 65, but with no lead.								
	65(b) as for test 65, but with 1.0% Pb.								
26	66	0.10	1.20	0.30	0.30	0.008	455	851	40
27	67	0.10	-	0.60	0.30	0.008	455	851	40
	67(a) as for test 67, but with no lead.								
	67(b) as for test 67, but with 1.0% Pb.								

(Concluded -

TABLE 2 (Concluded)
Experimental Programme*

Bath No.	Test No.	Al %	Sn %	Cd %	Cu %	Sb %	Bath Temp		Immersion Time, sec
							°C	°F	
28	68	0.05	0.60	0.60	0.60	0.0016	465	869	80
	69						465	869	20
	70						445	833	80
	71						445	833	20
29	72	0.05	0.15	0.15	0.15	0.040	445	833	20
	73						445	833	80
	74						465	869	80
	75						465	869	20
30	76	0.10	0.30	0.075	0.30	0.008	455	851	40
31	77	0.15	0.60	0.15	0.15	0.040	465	869	80
	78						465	869	20
	79						445	833	20
	80						445	833	80
32	81	0.15	0.15	0.60	0.60	0.0016	445	833	80
	82						445	833	20
	83						465	869	80
	84						465	869	20
33	85	0.10	0.075	0.30	0.30	0.008	455	851	40
34	86	0.10	0.15	-	0.30	0.008	455	851	40
	86(a)								
	86(b)								

*Except as otherwise noted, all baths contained 0.5% Pb.

TABLE 3

Bath Materials

Metal	Grade	Master Alloy Composition
Zinc	Special high grade - 99.99%	
Lead	99.99%	
Tin	99.99%	
Cadmium	99.97%	
Iron	Electrolytic iron sheet - 99.98%	Zn + 0.3% Fe
Aluminum	99.99%	Zn + 4% Al
Antimony	99.75%	Zn + 2.5% Sb
Copper	Cartridge brass (70 Cu-30 Zn)	Zn + 4% Cu

TABLE 4

Statistical Significance of Galvanizing Variables on Coating Structure and Properties*

	Aluminum	Tin	Cadmium	Copper	Antimony	Bath Temperature	Immersion Time
Coating Weight	1	3	3	3	3	2	1
Iron Content	1	3	3	3	3	2	2
Steel Weight Loss	1	3	3	3	3	2	2
Alloy Thickness	1	3	3	3	3	2	2
Proportion of Alloy	1	3	3	3	3	2	2
Coating Ductility	1	3	3	3	3	3	1
Coating Adherence	1	3	3	3	3	2	1
Spangle Size	1	1	3	3	1	2	1
Spangle Contrast	1	2	2	3	3	3	3
Coating Brightness	1	2	3	3	3	2	2
Coating Roughness	1	3	3	3	3	1	1
<u>Humidity Test</u>							
% Gain in Diffusivity	1	3	2	1	2	2	2
Weight Gain	2	3	3	3	2	3	3
Weight Loss	2	3	3	3	2	3	2
White Corrosion Index	1	3	2	2	2	3	3
<u>Water Film Test</u>							
White Corrosion Index (24 hr)	1	2	2	3	2	3	3
White Corrosion Index (48 hr)	2	2	2	2	2	3	3

*1 - Most Significant. 2 - Significant. 3 - Minor to Negligible Significance.

TABLE 5

Average Coating Test Results*

Bath Composition	Test No.	Bath Temp	Immersion Time, sec	Coating Wt, oz/sq ft-sheet	Iron Content, g/m ²	Steel Weight Loss, g/m ²	Alloy thickness, mm x 10 ⁻³	Proportion of Alloy %
0.15% Al (Sn, Cd, Cu-0.15% each; 0.0016% Sb)	41	445°C (833°F)	20	0.50	1.9	4.0	1.1	10.1
"	42	"	80	0.72	3.3	7.3	2.2	14.7
"	40	465°C (869°F)	20	0.51	2.6	4.1	1.5	13.9
"	39	"	80	0.63	3.8	7.4	2.3	17.3
0.15% Al (Sn, Cd, Cu-0.60% each; 0.04% Sb)	26	445°C (833°F)	20	0.60	1.7	2.0	0.9	7.4
"	25	"	80	0.67	3.1	4.4	1.9	13.5
"	23	465°C (869°F)	20	0.66	3.1	3.3	1.7	11.9
"	24	"	80	1.03	5.7	8.0	2.6	12.4
0.10% Al (Sn, Cd, Cu-0.30% each; 0.008% Sb)	19	455°C (851°F)	40	1.42	21.7	20.1	18.2	60.6
as above but 1.20% Sn	66	"	40	1.35	21.1	20.3	17.7	61.7
as above but 1.20% Cd	56	"	40	1.33	20.0	20.9	17.5	61.1
as above but 1.20% Cu	21	"	40	1.37	27.7	23.6	18.1	62.5
as above but 0.20% Sb	34	"	40	1.51	20.8	22.1	17.9	56.1
0.05% Al (Sn, Cd, Cu-0.15% each; 0.04% Sb)	72	445°C (833°F)	20	1.33	16.4	16.9	12.3	43.8
"	73	"	80	2.12	27.0	35.2	26.5	59.0
"	75	465°C (869°F)	20	1.21	17.8	20.9	13.6	53.2
"	74	"	80	2.24	35.9	40.8	35.1	74.3
0.05% Al (Sn, Cd, Cu-0.60% each; 0.0016% Sb)	71	445°C (833°F)	20	1.14	15.7	12.8	10.4	43.1
"	70	"	80	1.85	26.5	26.4	27.4	70.1
"	69	465°C (869°F)	20	1.18	17.8	14.6	13.9	54.2
"	68	"	80	2.08	33.7	33.4	31.3	71.2
0.10% Al 0.0% Pb (0.60% Sn, 0.0% Cd, 0.30% Cu, 0.008% Sb)	65(a)	455°C (851°F)	40	1.16	20.6	21.1	16.7	68.3
0.5% Pb (")	65	"	40	1.39	21.2	21.4	17.6	59.8
1.0% Pb (")	65(b)	"	40	1.44	21.6	20.5	17.4	57.5

* Each value is the average of three determinations except iron-zinc alloy values which are averages of twenty measurements on single samples.

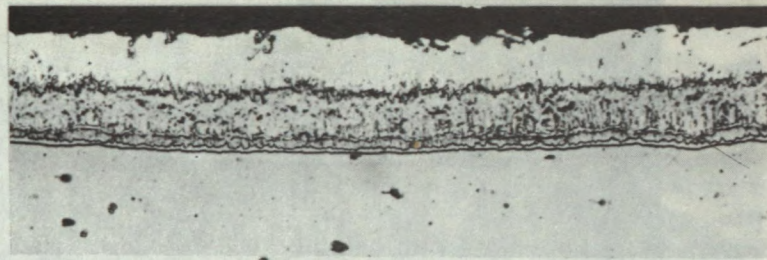
(a) 20 sec immersion at 465°C (869°F)
0.60% Sn, 0.60% Cd, 0.60% Cu, 0.04% Sb,
0.15% Al, 0.5% Pb, 0.03% Fe.

(b) 80 sec immersion. Bath temperature and
composition as for (a).

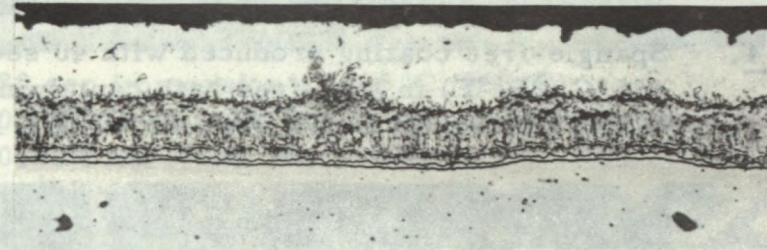
(c) 80 sec immersion at 445°C (833°F).
0.15% Sn, 0.60% Cd, 0.15% Cu, 0.04% Sb,
0.15% Al, 0.5% Pb, 0.03% Fe.

(d) 80 sec immersion at 465°C (869°F).
0.60% Sn, 0.15% Cd, 0.60% Cu, 0.0016% Sb,
0.15% Al, 0.5% Pb, 0.03% Fe.

Figure 1. Microstructures of 0.15% Al coatings galvanized under the conditions indicated. X500, nitramyl etch.

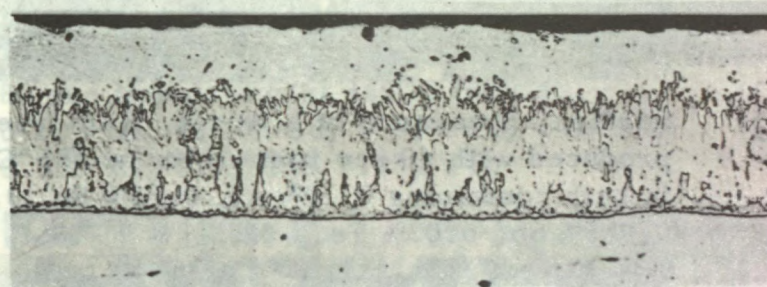


(a) 40 sec immersion at 455°C (851°F).
0.60% Sn, 0.30% Cu, 0.008% Sb,
0.10% Al, 0.03% Fe.



(b) Galvanizing conditions as for (a) except for addition
of 1.0% Pb to the bath

Figure 2. Microstructures of 0.10% Al coatings showing the relative
thickness of the eta layer in lead-free (a) and lead-
containing (b) coatings. X500, nitramyl and picral etch.



(a) 80 sec immersion at 445°C (833°F).
0.15% Sn, 0.15% Cd, 0.15% Cu, 0.04% Sb,
0.05% Al, 0.5% Pb, 0.03% Fe.



(b) Galvanizing conditions as for (a) except for copper and
antimony which were 0.60% and 0.0016%, respectively.

Figure 3. Microstructures of 0.05% Al coatings showing a more
or less normal structure in (a) and the modification (b)
produced by increasing the copper content of the bath.
X500, nitramyl and picral etch.

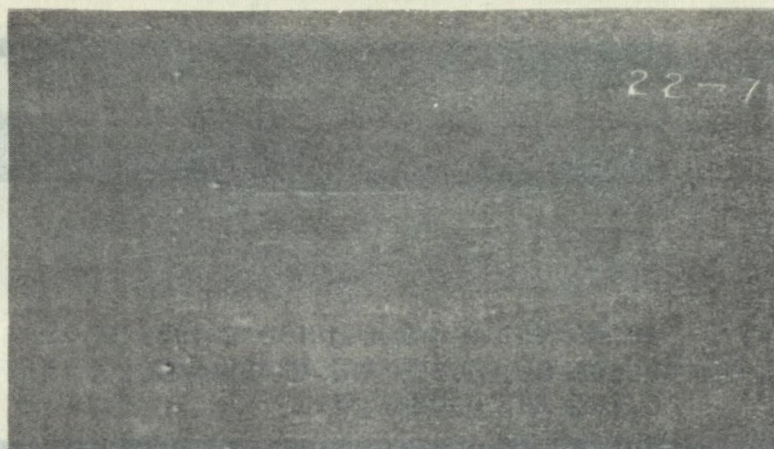


Figure 4. Spangle-free coating produced with 40 sec immersion at 455°C (851°F) in lead-free bath containing 0.10% Al, 0.15% Cd, 0.30% Cu, 0.008% Sb, 0.03% Fe. X1.

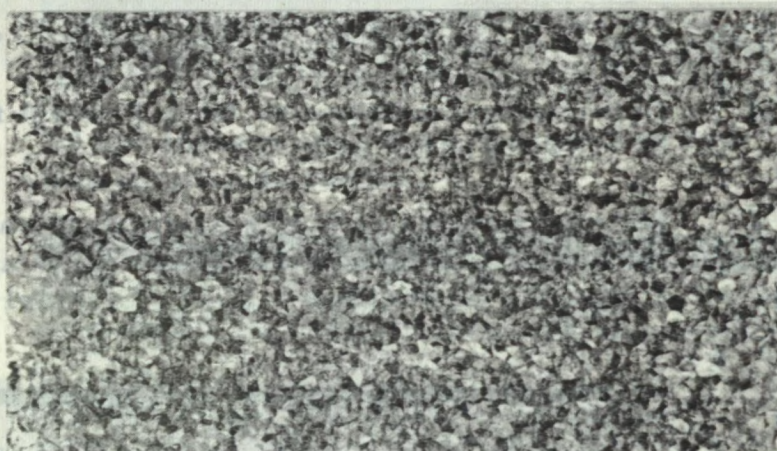


Figure 5. Surface appearance of high-tin, lead-free coating produced with 40 sec immersion at 455°C (851°F) in bath containing 0.10% Al, 0.60% Sn, 0.30% Cu, 0.008% Sb, 0.03% Fe. X1.



Figure 6. Surface appearance of high-lead coating prepared under the same conditions as for sample in Figure 5 except for presence of 0.15% Sn and 1.0% Pb. X1.



(a) 80 sec immersion at 465°C (869°F).
0.60% Sn, 0.60% Cd, 0.15% Cu, 0.04% Sb,
0.05% Al, 0.5% Pb, 0.03% Fe.



(b) 80 sec immersion at 465°C (869°F).
0.60% Sn, 0.15% Cd, 0.60% Cu, 0.04% Sb,
0.05% Al, 0.5% Pb, 0.03% Fe.



(c) 20 sec immersion at 445°C (833°F).
0.15% Sn, 0.60% Cd, 0.60% Cu, 0.04% Sb,
0.05% Al, 0.5% Pb, 0.03% Fe.

Figure 7. Surface appearance of typical low-aluminum (0.05%) coatings galvanized under conditions indicated. X1.

APPENDIX

INDIVIDUAL ADDITIONS OF TIN, CADMIUM, ANTIMONY AND COPPER

This was a limited-scale study involving additions of tin, cadmium, antimony and copper separately to iron-saturated zinc baths. Two series of baths were run. The basic composition was Zn + 0.03% Fe in one series, and Zn + 0.03% Fe + 0.15% Al + 0.5% Pb in the second. Two levels of each element were selected to represent impurity and alloying concentrations. These were: 0.01% and 2.50% Sn, 0.05% and 1.25% Cd, 0.01% and 0.25% Sb, and 0.05% and 1.25% Cu. A constant bath temperature of 455°C (851°F) and immersion times of 0.25, 1 and 2 min were employed. Test panels were cut from commercial low-carbon, 24 swg, rimmed steel sheet representing two different degrees of surface roughness (average roughness 45 and 110 micro-inches). The experimental galvanizing and coating test procedures were similar to the methods used in the investigation described in the main body of this report.

The results obtained for the experimental conditions used are summarized below. The designation "aluminum-free" refers to coatings prepared with no aluminum and lead in the bath. Where these elements were present, the designation "aluminum-containing" applies.

Aluminum-free Coatings

Coatings in this series were characteristically thick, with well-defined iron-zinc alloy layers. As a result, ductility and adherence behaviour was inferior throughout. Such variations in these properties as were observed were thus of minor significance.

(a) At low (impurity) concentration, none of the additions had any apparent effect, except in the case of 0.05% Cd which appeared to improve the reflectivity of the semi-bright, spangle-free coatings otherwise obtained.

(b) In the presence of high (alloying) concentration of each element, the following observations were made:

With 2.50% Sn, the coatings assumed a frosty appearance with low reflectivity. Spangles were well defined but small, which supports the claim that tin without lead will not produce large spangle crystals. Other minor effects, including reduction in coating weight, iron-zinc alloy formation and coating ductility, were also apparent.

Antimony produced gross spangles and reduced coating ductility and adhesion.

Cadmium promoted heavier alloy growth at longer immersion times. This was accompanied by an increase in iron content and coating weight, as well as a loss in ductility. In contrast to the improved surface brightness obtained with 0.05% Cd, the higher addition of 1.25% was harmful to surface appearance, as indicated by the rough matte sheen of the spangle-free coatings.

Copper tended to reduce iron-zinc alloy formation and coating weight at immersion times up to 1 min, but these effects were reversed at 2 min. Staining of the coatings indicated this high level of copper to be detrimental to surface appearance.

(c) The rougher steel generally yielded thicker coatings having slightly poorer ductility and adherence. The behaviour of the two materials was not greatly dissimilar as far as coating surface appearance was concerned.

Aluminum-containing Coatings

In this series, the presence of aluminum was in most cases the principal factor controlling the thickness and other properties of the coating. The bath additions investigated were of secondary or

negligible importance, and most of the coatings remained characteristically thin with excellent ductility and adherence.

(a) The low (impurity) concentration of tin, antimony and copper had little or no effect, but 0.05% Cd tended to increase iron-zinc alloy formation and coating weight at the longer immersion times, particularly with the rougher steel. The reliability of the results with this low cadmium addition is, however, questionable in view of the findings of the main investigation.

The typical surface defects normally associated with high aluminum were not significantly altered by the various additions, nor was there any improvement in spangling behaviour.

(b) At high (alloying) concentration, the influence of tin and antimony was negligible except with respect to surface appearance. Both caused formation of medium to large spangles, with moderately good contrast. Of particular interest was the detrimental effect of copper at longer immersion times. More or less complete neutralization of aluminum inhibition was reflected in pronounced iron-zinc alloy formation and in heavy coatings which had poor ductility and adherence. Cadmium showed a similar but less pronounced response.

The dull flat sheen of copper-containing coatings indicated a further harmful effect of this element.

(c) The difference in surface roughness between the two grades of steel used had a negligible influence apart from the moderately rougher texture of coatings on the rougher steel. This tended to mask simple defects occurring at the sites of local steel attack, so that these were more prominent with thin coatings on the smoother steel.

(b) At high (alloying) concentration, the influence of tin and antimony was negligible except with respect to surface appearance. Both caused formation of medium to large sponges, with moderately good contrast. Of particular interest was the detrimental effect of copper at longer immersion times. More or less complete neutralization of aluminum inhibition was reflected in pronounced iron-zinc alloy formation and in heavy coatings which had poor detail.

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