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**METALLURGICAL EXAMINATION OF
GALVANIZED REFRIGERATION
UNIT SAMPLES**

by

J. J. SEBISTY

PHYSICAL METALLURGY DIVISION

FOR REFERENCE IR 63-105

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METALLURGICAL EXAMINATION OF GALVANIZED
REFRIGERATION UNIT SAMPLES

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SUMMARY OF RESULTS

An examination was made of samples from a galvanized refrigeration unit, which showed extreme variations in thickness of the zinc coating on the spiral-wound fins of individual tubes in the unit.

It was found that accidental or intentional fabrication of parts of the spiral fin from strip material with a high carbon content, which is prone to aggressive attack by molten zinc, was responsible for the abnormal coating formation encountered during galvanizing.

*Senior Scientific Officer, Non-Ferrous Metals Section,
Physical Metallurgy Division, Mines Branch, Department of Mines
and Technical Surveys, Ottawa, Canada.

CONTENTS

	Page
Summary of Results.	i
Introduction.	1
Sample Description.	1
Composition and Microstructure of Fin Steel.	2
Composition and Microstructure of Coating.	3
Galvanizing Tests	4
Discussion.	4
Conclusions	5
References.	5
Table 1	2
Figures 1 to 9.	6-9

INTRODUCTION

In connection with the hot-dip galvanizing research being conducted by the Physical Metallurgy Division under the auspices of the Canadian Zinc and Lead Research Committee, a request was received from Dr. S.F. Radtke, Director, International Lead Zinc Research Organization (letter of September 25, 1963), for metallurgical examination of three galvanized samples taken from an ammonia refrigeration unit. An explanation was required for the extreme variations in thickness of the zinc coating on the spiral-wound fins of individual tubes in the unit. The samples were received on October 7, 1963.

SAMPLE DESCRIPTION

The overall size of the refrigeration unit is 18 ft x 27 in. x 16 in. Within a channel and angle framework and end header units, seventy 18-ft lengths of 1 in. OD steel tubing are stacked ten high and seven wide. A continuous spiral-wound fin fabricated from 0.015 in. tin plate is wrapped around each tube giving an overall OD of $2\frac{1}{4}$ in. From the approximate unit dimensions given, it would appear that the spacing of the finned tubes on the 27-in. side is $\frac{1}{2}$ in. and is practically nil on the 16-in. side. No details of the galvanizing conditions employed were given other than the fact that the assembled unit was vented during galvanizing to provide for free connection of the individual tubes to the atmosphere. Sulphuric acid pickling was used in pretreatment.

Photographs of the submitted samples showing normal and abnormal galvanizing behaviour of the finned tubes are given in Figures 1 to 3. Figure 1 represents a piece from a tube (Sample 3) which had developed an abnormally thick coating on the fins throughout the full 18-ft tube length. On another tube (Sample 1) there was a sudden transition from normal (A-end) to abnormal (B-end) coating formation on the fins as shown in Figure 2. In the longitudinal cross section in Figure 3 (Sample 2), the abnormally thick coating on the fins can be seen; this exceeded $1/16$ in. Affected tubes were stated to be located without any definite pattern as to position within the unit or to position of the unit during the galvanizing operation.

COMPOSITION AND MICROSTRUCTURE OF FIN STEEL

The sudden transition from normal to abnormal coating formation on Sample 1 in Figure 2 was of particular interest and this area was stripped for further examination. The change from thin to thick coating was found to coincide exactly with a spot-welded joint in the spiral-wound fin as illustrated by the lower sample in Figure 4. Pieces of the fin steel from either side of this joint were analysed by the Analytical Chemistry Subdivision of the Mineral Sciences Division, Mines Branch and the reported results are given in Table 1. For comparison the composition limits for tin plate steel⁽¹⁾ are also given.

Although of otherwise acceptable composition, both materials exceeded the accepted maximum of 0.12% C. In the one case the carbon was slightly high only but was more than double the above figure in the material that galvanized abnormally. This difference in composition was reflected in the steel base microstructure and hardness. The low carbon material had a larger grain size and, as illustrated in Figure 5, a scattered dispersion of spheroidized cementite particles indicated it to be more or less typical of normal tin plate steel; the Rockwell hardness was 69 (30-T scale). In contrast, the high-carbon steel had a very fine grain structure combined with an excessive and uniform dispersion of spheroidized cementite as shown in Figure 6; the Rockwell hardness was 76 (30-T scale). Of particular significance is the fact that the latter type of spheroidized structure is known to exhibit very aggressive attack after lengthy immersion in molten zinc, even at normal galvanizing temperatures⁽²⁾.

TABLE 1

Chemical Composition of Fin Steel (Per Cent)

	Carbon	Sulphur	Phosphorus	Manganese	Silicon	Copper
Sample 1 (A-end) (Normal coating)	0.15	0.024	0.006	0.34	0.04	0.05
Sample 1 (B-end) (Abnormal coating)	0.25	0.027	0.010	0.41	0.07	0.07
Ingot steel for tin plate (1)	0.04- 0.12	0.015- 0.05	0.015- 0.14	0.2- 0.6	0.08 max	0.02- 0.2

COMPOSITION AND MICROSTRUCTURE OF COATING

Pieces of the thick coating were chipped from Sample 3 and chemical analysis revealed the following composition: 0.25% Pb, 3.77% to 4.03% Fe, 0.016% Cu, <0.01% Al, <0.005% Cd, <0.005% Sn. Apart from the very high iron content, which is referred to below, the results suggest that the composition of the bath in which the refrigeration unit was galvanized was satisfactory and not responsible for the unusual coating behaviour encountered.

Specimens cut from Sample 3 and from the A- and B-end of Sample 1 were mounted, polished, etched and examined microscopically. As expected, the fin steel on the A-end of Sample 1 exhibited a "normal" coating with a typical layered structure of iron-zinc alloy phases as in Figure 7. All of the individual phases were present including a thin gamma iron-zinc layer adjacent to the steel base. From the thickness and structure of the duplex delta-prime phase above the gamma layer, it would appear that an extended immersion time was used.

It was also confirmed that the abnormal coating on Sample 3 and the B-end of Sample 1 was related to extremely aggressive zinc attack of the high-carbon fin steel. Pronounced growth of the zeta iron-zinc phase in the form of a loose to densely-packed mass of small crystals embedded in a zinc matrix accounted for the thick coating formed. This also explains the high and variable iron content.

Typical microstructures found near the outer edge of the heavily-coated fin are shown at low and high magnifications in Figures 8(a) and 8(b). The absence of a gamma iron-zinc layer adjacent to the steel base is to be noted, as is also the similarity in structure and uniformity of the delta-prime phase in this coating and the coating on the low-carbon steel in Figure 7. This appears to conflict with a high iron-zinc reaction rate in the case of the high-carbon steel but is, however, consistent with the high rate of formation of the delta prime phase under such conditions, and the rapid reaction of this phase with zinc to form the zeta iron-zinc phase. Supporting evidence for the pronounced galvanizing activity of the high-carbon steel was provided by the irregular cross-section thickness of the steel base in the microstructures. This was reflected in marked unevenness of the steel surface, which was observed in prior stripping tests.

GALVANIZING TESTS

As a matter of interest, laboratory dipping tests were made with sections cut from the A- and B-end of Sample 1 in an iron-saturated zinc bath alloyed with 0.002% Al and 1% Pb. The original coating was removed by acid stripping and the sections regalvanized for 1/2 hr at 450°C (840°F) and also at 470°C (880°F). At the lower temperature, only moderate differences in coating build-up on the low- and high-carbon fin steels was apparent. The higher temperature produced much more exaggerated build-up on the high-carbon steel as illustrated in Figure 4, but this was still considerably less than on the submitted samples in Figures 1 to 3. The coating microstructure in this case also reflected a less advanced stage of steel attack and iron-zinc alloy growth. As would be expected from the geometry of the crimped fin, most severe attack was concentrated on the maximum-radius surface of each crimp as illustrated in Figure 9.

It will be appreciated that these tests were not made with the original steel surface intact, i.e., as applicable when the refrigeration unit was initially galvanized. Despite this difference, the results of the laboratory galvanizing tests strongly suggest that the immersion time and/or bath temperature conditions employed in the plant galvanizing operation contributed significantly to the gross coating formation encountered.

DISCUSSION

The variable galvanizing behaviour of the spiral fins in the refrigeration unit samples submitted was traced to use of tin plate or steel sheet having an excessively high carbon content. The steel base microstructure was characteristic of material that is known to exhibit aggressive attack on lengthy immersion in molten zinc, even at normal galvanizing temperatures.

Information given stated that the spiral fins were entirely fabricated from tin plate. If this is correct, the only explanation for the high carbon strip material used is that some of the tin plate stock was off-composition. It is to be noted, however, that tin plate is normally subject to rigid composition and processing control and it is doubtful whether steel sheet with carbon content of double the accepted maximum of 0.12% would be processed to finished plate unless specially ordered. An alternative explanation is that the high carbon fin material was not tin plate but was, say, an unplated deep drawing grade of sheet of suitable temper and gauge that was substituted in the finning operation. Which of these two possibilities is correct could only be ascertained by tracing and/or analysing the original fin stock used.

Chemical analysis of coating samples suggested that the galvanizing bath composition was not a factor of any significance. On the other hand, laboratory dipping tests made gave strong indications that the immersion time and/or bath temperature conditions contributed directly to the gross coating formation encountered. Since no information on the galvanizing conditions or operation were provided, it is not possible to comment further in this direction.

CONCLUSIONS

The accidental or intentional fabrication of some parts of the spiral-wound fins from material with a high carbon content, and which is prone to aggressive attack by molten zinc, was responsible for the abnormal coating behaviour encountered in galvanizing of the refrigeration unit.

REFERENCES

1. W.E. Hoare - "Tin Plate Handbook" - Tin Research Institute, Middlesex, England (1956).
2. H. Bablik - "Hot Dip Galvanizing" - E. & F.N. Spon Limited, London, p. 250-262 (1950).

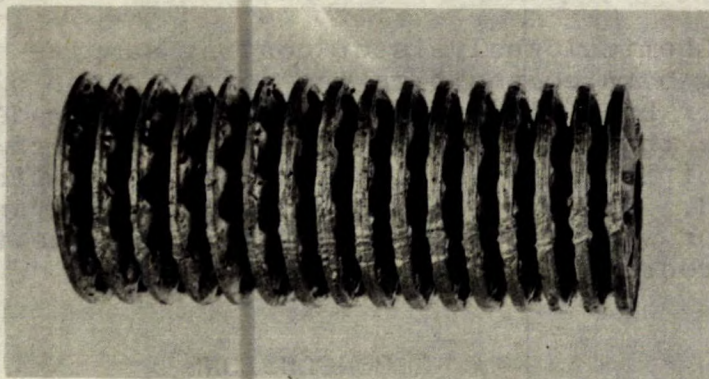


Figure 1. Sample 3 ($X_{\frac{1}{2}}$).

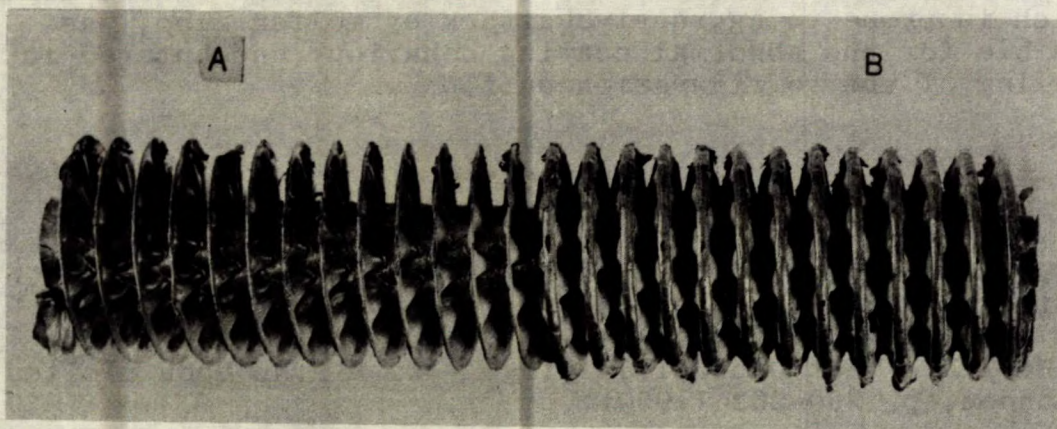


Figure 2. Sample 1 ($X_{\frac{1}{2}}$).



Figure 3. Sample 3 ($X_{\frac{1}{2}}$).



Figure 4. Upper samples represent regalvanized sections from Sample 1 (A- and B-end to left and right respectively). Lower sample shows fin joint in Sample 1 transition area. $X_{\frac{1}{2}}$



Figure 5. Microstructure of fin steel from A-end of Sample 1. Nital etch, X500.

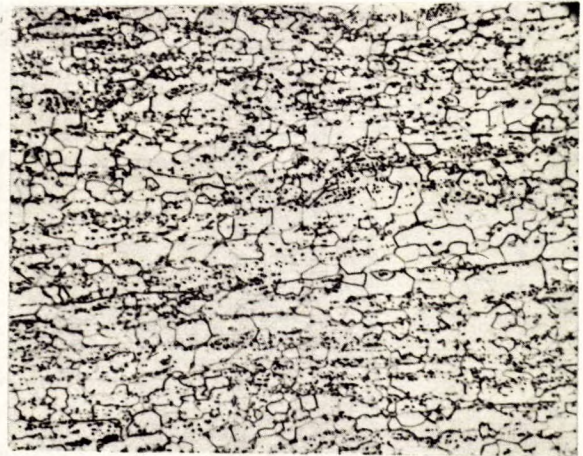
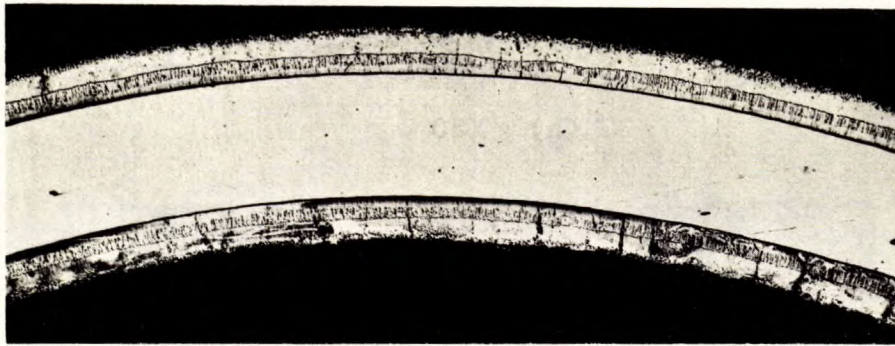
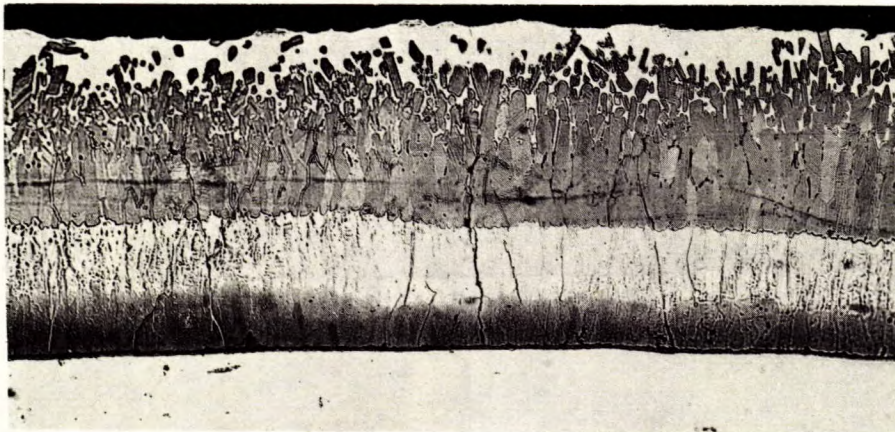


Figure 6. Microstructure of fin steel from B-end of Sample 1. Nital etch, X500.

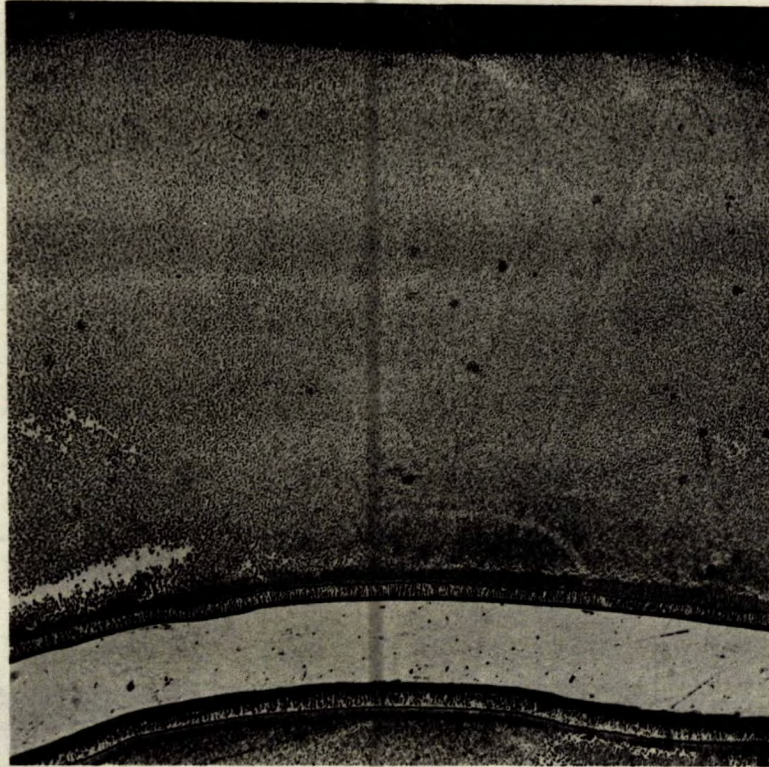


(a) X50

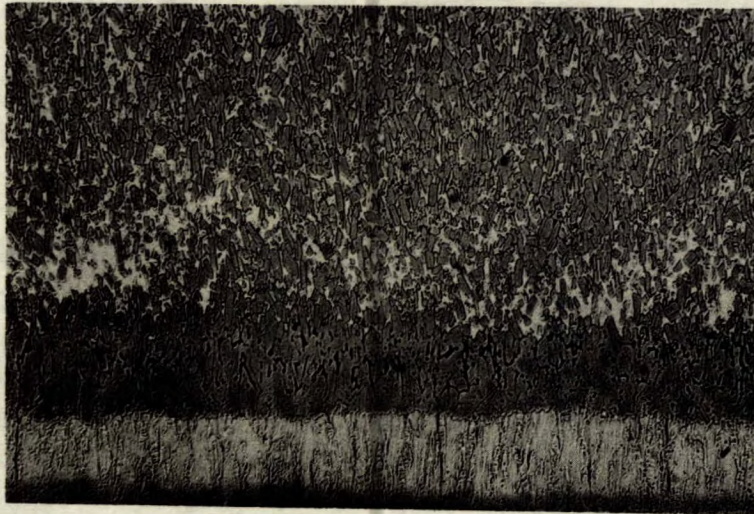


(b) X300

Figure 7. Microstructures of normal coating on A-end of Sample 1 at low and high magnifications. Picric etch.



(a) X50



(b) X300

Figure 8. Microstructures of abnormal coating on B-end of Sample 1 at low and high magnifications. Picric etch.

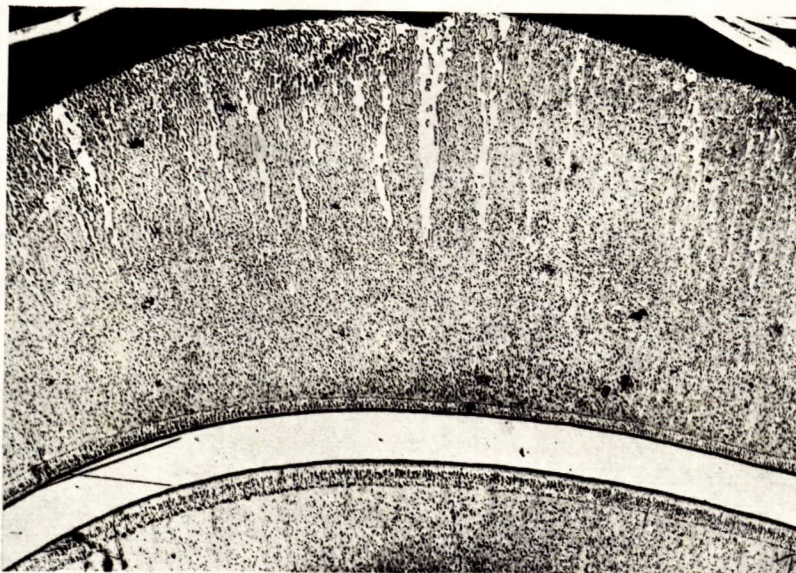


Figure 9. Microstructure of coating formed on B-end of Sample 1 by regalvanizing for 1/2 hr at 470°C (880°F).
Picric etch, X50.