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**CANADA**

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**METALLURGICAL EXAMINATION  
OF GALVANIZED TUBING**

by

**J. J. SEBISTY**

**PHYSICAL METALLURGY DIVISION**

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METALLURGICAL EXAMINATION OF GALVANIZED TUBING

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J. J. Sebisty \*

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SUMMARY OF RESULTS

An examination was made of galvanized tubing samples which represented material that was found to exhibit peeling of the outer zinc layer on inspection after galvanizing.

It was concluded that the peeling deterioration was primarily caused by inadequate cooling between the galvanizing operation and racking of the tubes into bundles.

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

CONTENTS

	<u>Page</u>
Summary of Results . . . . .	i
Introduction . . . . .	1
Pretreatment . . . . .	1
Galvanizing Conditions . . . . .	1
Steel Composition . . . . .	2
Bath Composition . . . . .	2
Coating Weight . . . . .	2
Metallurgical Examination . . . . .	2
Visual Inspection. . . . .	2
Metallographic Examination . . . . .	3
Iron Content Determinations . . . . .	3
Discussion . . . . .	4
Conclusions . . . . .	5
Figures 1 to 3 . . . . .	6-7

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## INTRODUCTION

In connection with the hot-dip galvanizing research being conducted at the Physical Metallurgy Division under the auspices of the Canadian Zinc and Lead Research Committee, a request was received through Dr. S.F. Radtke, Director, International Lead Zinc Research Organization, Inc., for assistance in metallurgical examination of galvanized tubing which was found to show peeling of the outer zinc layer when the bundled tubes were examined about 24 hr after galvanizing. Representative samples and manufacturing data were received from Mr. W. Tunney, Technical Service Manager, St. Joseph Lead Company, Monaca, Pennsylvania (letters of October 29 and December 3, 1965). The manufacturing details were summarized as follows:

### Pretreatment

The 1.315 in. x 14 gauge tubing was produced on a Yoder Electric Weld mill from hot rolled, pickled and oiled skelp. The tubing was degreased at 180°F in an alkaline cleaner, rinsed and pickled for 30 minutes in 8% inhibited sulphuric acid at 140°F, rinsed and dipped in 22° Bé zinc-ammonium-chloride solution and fed to the galvanizing bath through a top flux layer.

### Galvanizing Conditions

Bath temperature	840°F
Immersion time	about 1.5 minutes
Withdrawal speed	175 ft/min
Production rate	fifteen 20-ft pieces/min
Outside air wiper	40 lb gauge, 5.5 ft from surface of bath
Air wipe temperature	ambient
Inside blow	100 lb gauge, superheated steam at 650°F
Time from zinc surface to inside blow	15 seconds
Tube temperature at inside blow	close to 787°F

Tubing was air cooled on a chain conveyor to approximately 500°F and then racked into bundles. Tubing in the centre of the racked bundle which periodically exhibited peeling of the outer zinc layer was found to be 140 to 150°F 24 hr after galvanizing.

Steel Composition (%)

	<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Cu</u>	<u>Ni</u>	<u>Cr</u>	<u>Mo</u>	<u>Sn</u>	<u>Al</u>
Adherent coating	.16	.43	.011	.031	.010	.03	.016	.042	Tr	.004	-
Non-adherent coating	.18	.46	.012	.034	.012	.04	.015	.036	Tr	.002	-
" " "	.18	.46	.008	.035	nil	.02	.01	.03	.01	-	.009

Bath Composition

Prime Western zinc was used with 0.21% Al (Zn-7% Al) added per ton of zinc. This quantity of aluminum added in the withdrawal area was stated to have no influence on the iron-zinc alloy growth in the coating or on the flux characteristics. (It is suspected that the quoted aluminum content is in error, being too high).

Coating Weight

Outside	0.90 oz/sq ft of surface
Inside	1.18 " " " "

METALLURGICAL EXAMINATION

Visual Inspection

A photograph of the samples provided after sectioning longitudinally to show inside and outside surfaces is given in Figure 1. Although not stated, these were presumably taken from a tube which was positioned at or near the centre of a racked bundle. The sample 0.5 ft from the tube end, as shown on the right of Figure 1, had a bright metallic finish on the inside and a whitish-grey crystalline deposit (not identified) on the exterior surface. There was no evidence of separation of the zinc layer on either surface, even by vigorous scratching with a scribe. In contrast, bonding of the bright zinc layer on the interior of the 4 ft sample was completely destroyed and the thick layer present could be readily peeled away as shown on the left of Figure 1. The exterior coating on the same sample had a discoloured appearance varying from patches and bands with a black finish to brighter areas broken up by a black network pattern.

These peeling and blackening effects are typical of so-called conventional galvanized coatings in which the iron-zinc reaction has been prolonged by slow-cooling or subsequent heating. Depending on the time, temperature and local stress conditions, the zinc layer initially separates,

but may retain sufficient point contact that it eventually disappears by continued reaction to form more of the underlying zeta iron-zinc phase. The black oxidized surface of this phase can be seen in Figure 1. The exterior coating on the 4 ft sample represented an apparently advanced stage in this sequence, principally because the zinc layer was initially thin as a result of wiping. The black network pattern on this surface corresponds to zinc grain boundaries and is explained by the inherently higher diffusion rate, and thus earlier depletion of zinc, in such areas. Similar zinc diffusion effects were not evident on the peeled interior coating of this sample because of the much heavier zinc deposit, which appeared to have separated from the base metal more completely when the interface bond was broken.

#### Metallographic Examination

Photomicrographs of coating cross sections are given in Figures 2 and 3. Apart from the more irregular iron-zinc alloy growth on the interior surfaces, and the consequent heavier zinc drag-out, there were no basic differences in the microstructures of the coatings on the two samples. However, insofar as deterioration due to slow cooling was concerned, each of the four structures shown represents a different stage of failure.

Complete separation of the thick zinc layer from the interior coating of the 4 ft sample is illustrated in Figure 2(a). The degree of separation apparent was unavoidably exaggerated since the zinc layer pulled free on cutting of the specimen and had to be cemented in place. This accounts also for its lack of register with the adjacent alloy phase. In Figure 2(b) it can be seen that much of the initially thin zinc layer in the outer coating has disappeared locally, having reacted to form iron-zinc alloy. Patches of zinc remaining were apparently unbonded but presumably retained some adherence because of mechanical keying along the irregular interface. These patches correspond to the brighter surface areas of the exterior coating in Figure 1.

As noted earlier, neither of the zinc layers on the 0.5 ft sample could be induced to peel. However, Figure 3 confirms that here also some destruction of the zinc-zeta interface bond had taken place, particularly in the exterior coating. Separation in this case was almost continuous in the area examined as shown in Figure 3(b) but, again, the good adherence would presumably be accounted for by interface keying. Minimal bond failure was evident on the interior coating of the 0.5 ft sample and local areas only were affected as shown in Figure 3(a).

#### Iron Content Determinations

Duplicate determinations of the iron content of the coatings were made and the results are given in Figure 1. These substantiate the metallographic effects noted and confirm the higher reaction activity on the 4 ft sample, as

well as the reaction variation on the exterior and interior of the 0.5 ft sample.

## DISCUSSION

From the various observations discussed above, it is apparent that maximum zinc reaction effects occurred in the sample remote from the end of the tube and, even in the end sample, variable deterioration was observed, being minimal in the interior coating. Thus, it must be concluded that the primary cause of bonding and appearance deterioration of the zinc layer was insufficient cooling of the tubes because of racking in bundles too soon after galvanizing. Such failure is not uncommon when galvanized products are stacked or nested together without first being adequately cooled. The prolonged exposure at elevated temperatures results in continued growth of iron-zinc alloy and particularly to reaction dissolution of the zinc around the zeta crystals forming the outer boundary of the zeta phase layer. The interface bond is thereby destroyed permitting the zinc to be peeled away. As suggested by the exterior coating on the 4 ft sample, the separated zinc layer will eventually be consumed by reaction to form zeta as long as it is not induced to lift out of place.

Although steel composition can influence the rate of iron-zinc alloy growth at elevated temperatures, it is not considered that this was a factor in promoting peeling in the present case. The difference in chemistry of the three steels defined is negligible and the variable adherence quoted for the different grades is most probably related to location in a bundle of the particular tubes inspected. Differences in the production time interval between galvanizing and racking may also have been responsible for the adhesion effects mentioned, and, to some extent, variations in surface roughness could have had an indirect effect on the amount of mechanical keying between the zinc and the underlying alloy layers.

As a matter of interest, it is questionable whether the tubes could have cooled to the estimated temperature of 500°F before racking. Experimental work previously done at these laboratories on 1 in. O.D. galvanized tubing established that peeling of the outer zinc layer required heating for about 4 days at 480°F and about 8 hours at 570°F. It can therefore be appreciated that the tubes were probably somewhere above this latter temperature when racked, particularly in view of the fact that extensive zinc layer separation was found on the tube end sample where relatively rapid cooling could be expected.

## CONCLUSIONS

It is suggested that peeling and other deterioration of the coating on the samples of galvanized tubing submitted was primarily caused by inadequate cooling after galvanizing and before racking of the tubes into bundles. Standard practice to avoid such deterioration, particularly with heavy-wall products, is to water quench. However, when air cooling is used, any stacking or bundling of the products should be delayed until a temperature considerably below the galvanizing temperature, and preferably approaching ambient conditions, is reached. Close proximity contact as would occur with tubing on a run-out table should not be harmful during this cooling period.

Alternatively, if space considerations preclude extensive air cooling racks, some other form of forced cooling of the bundles could be adopted provided this was done soon enough, and was effective in rapidly reducing the temperature at all points in the stack.



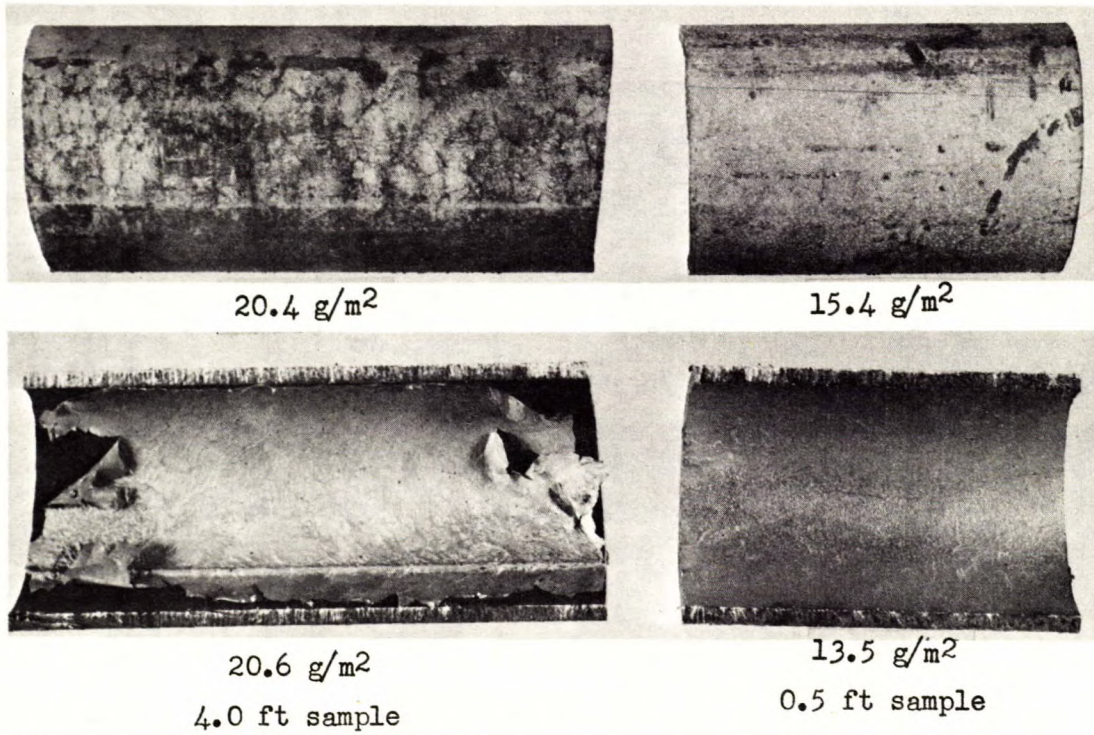
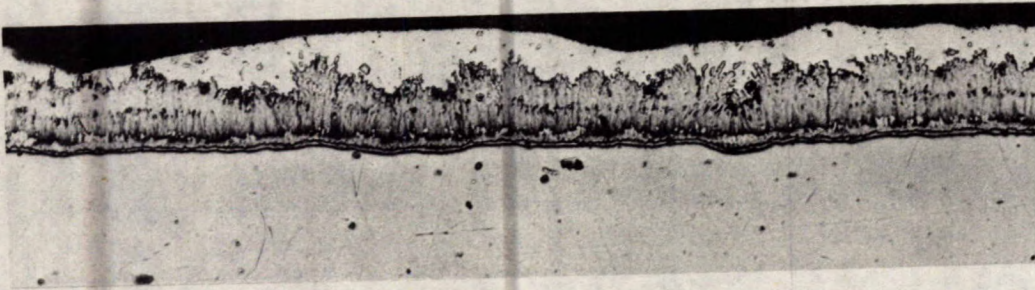


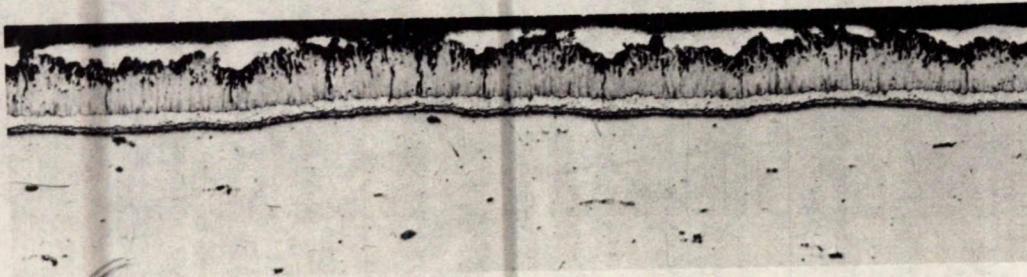
Figure 1 - Exterior and interior views of tubing samples with iron content of coating indicated in each case. X1



Figure 2 - Microstructures of coatings on 4 ft sample. X300



(a) Interior coating



(b) Exterior coating

Figure 3 - Microstructures of coatings on 0.5 ft sample. X300