Detrimental effects of lead contamination in zinc and zinc-nickel alloy electroplating.

Bruno CAUWE, Lucien RENARD and Alain WEYMEERSCH,
R.D.C.S. Research and Development of the Cockerill Sambre Group

Abstract

Zinc and zinc-nickel electrolytes are contaminated by lead coming from different origins (raw materials and anodes).

This lead affects both the electroplating process (current efficiencies, mechanisms) and the quality of the deposit (composition, corrosion resistance and adherence after heat treatment).

Those detrimental effects have been studied and explained by laboratory scale trials (circulating cell and pilot line) and samples caracterisations.

The solution adopted for the new E.G.L. of the Cockerill Sambre Group is presented.

The origin of lead in the electrolyte

Lead found in the electrolyte is brought there in two different ways: raw materials and lead-silver anodes.

The raw materials consist of the zinc and nickel necessary for electrolyte regeneration. The quality of raw materials used on the zinc-plating lines of the Cockerill Sambre Group is on average 10 to 20 ppm of lead in proportion to zinc or nickel. In other words, for each kilogram of zinc or nickel dissolved into the electrolyte, 10 to 20 mg of lead are simultaneously introduced. Much smaller quantities of lead are brought with given additions of H_2SO_4 or possibly Na_2SO_4.

When insoluble lead-silver anodes are used, much greater quantities of lead are introduced into the electrolyte. Lead concentration measured out in the electrolyte is then close to its saturation limit.

Description of the experimental systems

Circulating cell simulation trials were carried out in order to assess the effects of lead contamination both on the electroplating process and on the quality of the product.

Samples of cold-rolled steel 0.7 mm thick, with a surface area of 1 dm^2 first underwent surface treatment similar to that used on industrial lines:

- Electrolytic cleaning in an alkaline solution kept at 80°C. Current density is set at 11 A/dm^2 and applied in the following sequence: anodic (1 sec), cathodic (1 sec) and anodic (1 sec).
- Rinsing in hot distilled water (80°C).
- Electrolytic pickling in a sulfuric acid solution maintained at 20°C. A 10 A/dm^2 current density is applied in the following sequence: cathodic (1 sec), anodic (0.5 sec) and cathodic (1 sec).
- Rinsing in distilled water.

The surface preparation installation is shown in figure 1.

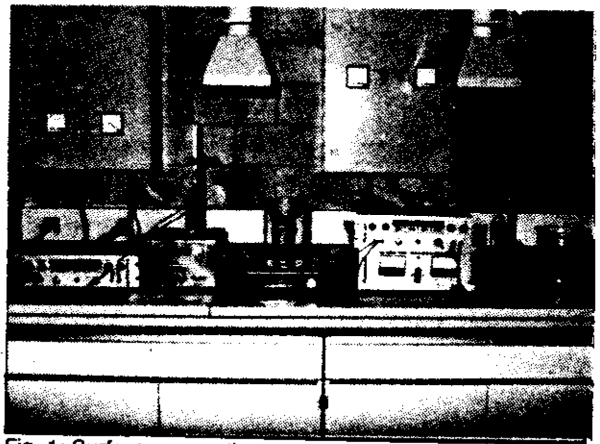

Fig. 1: Surface preparation treatment

Following pre-treatment, the samples are placed in a circulating electrolysis cell. This fixed electrodes cell is designed so as to obtain turbulent flow of the electrolyte parallel to the electrodes. Cathode-anode distance is 5 mm. Type Ti-IrO_2 anode is used. A photograph of the installation is given in figure 2 and a principles diagram given in figure 3.

Electrolyte lead contamination was artificially produced by the controlled addition of lead acetate.

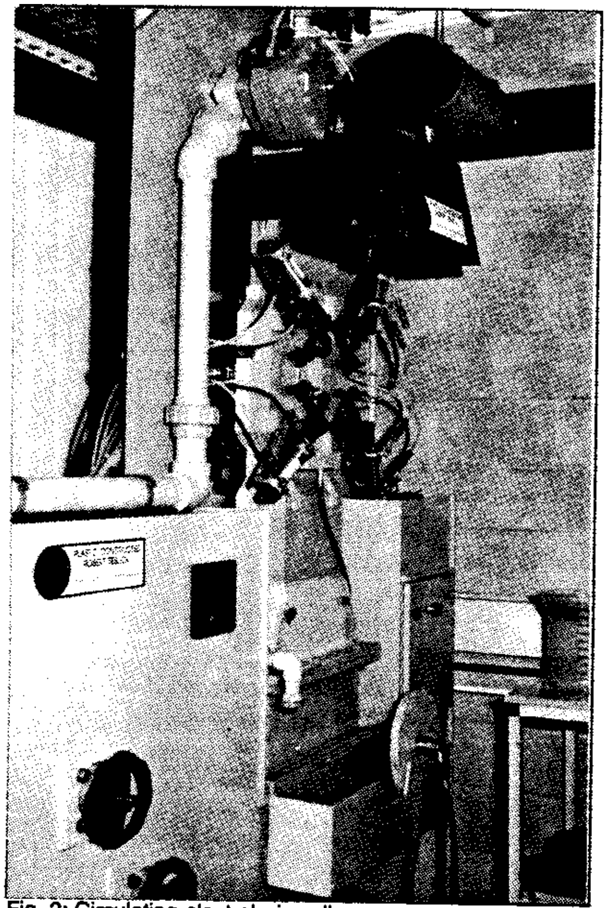

Fig. 2: Circulating electrolysis cell

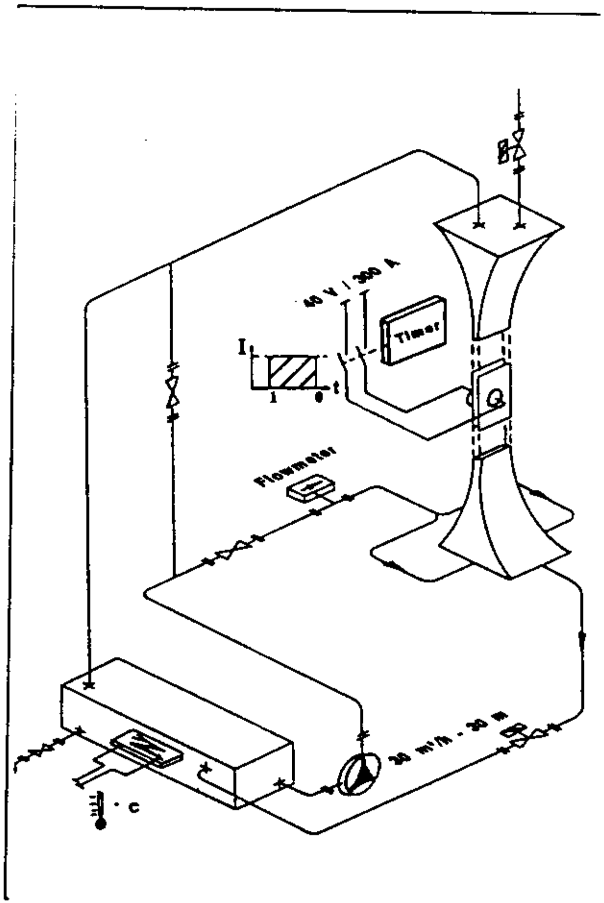

Fig. 3: Principles diagram of circulating electrolysis cell

Effect of lead contamination on electroplating processes

Lead codeposition

Lead codeposition takes place during electrolytic deposition of zinc or zinc-nickel alloy on steel. Lead is deposited at its limiting current density. This codeposition process, clearly described in the references[1] was confirmed during tests. Indeed, all other parameters remaining constant, lead concentration as measured in the deposit is directly proportional to electrolyte lead contamination. This was noticed in the electrodeposition of both pure zinc (figure 4) and zinc-nickel alloy (figure 5). An increase in electrolyte stirring must help induce lead codeposition. This was confirmed for pure zinc electrodeposition in figure 6.

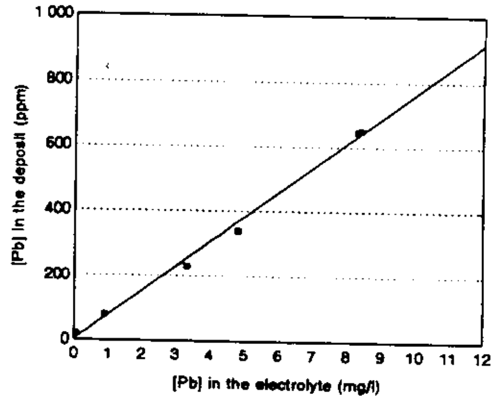

Fig. 4: Pure zinc coating - Lead content in the deposit versus lead contamination in the electrolyte - [Zn] = 32 g/l [H_2SO_4] = 83 g/l - 50°C - 100 A/dm² - 2 m/sec

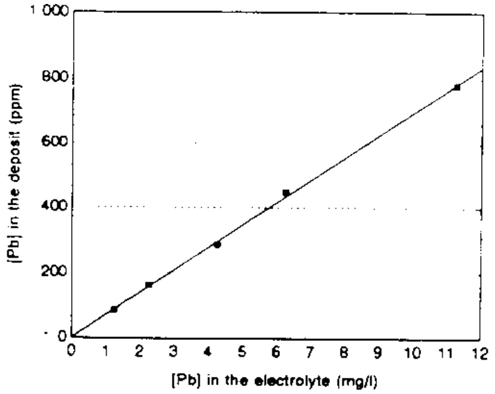

Fig. 5: [Ni] in the deposit = 12 % - Lead content in the deposit versus lead contamination in the electrolyte - [Zn]+[Ni] = 85 g/l [H_2SO_4] = 40 g/l - 50°C - 100 A/dm² - 2 m/sec

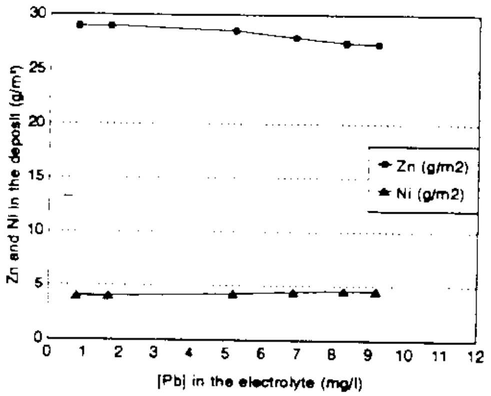

Fig. 7: Zinc and nickel values in the deposit versus lead contamination in the electrolyte - [Zn] = 65 g/l - [Ni] = 88 g/l [H_2SO_4] = 18 g/l - 50°C - 100 A/dm² - 2 m/sec

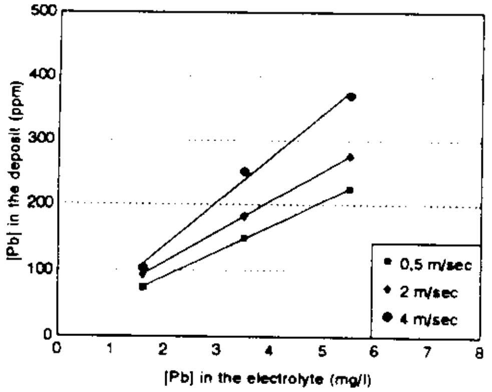

Fig. 6: Pure zinc coating - Lead content in the deposit versus lead contamination in the electrolyte and flow velocity [Zn] = 64 g/l - [H_2SO_4] = 86 g/l - 50°C - 100 A/dm²

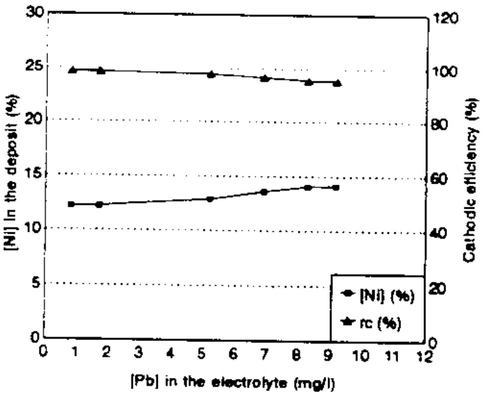

Fig. 8: Cathodic efficiency and [Ni] in the deposit versus lead contamination in the electrolyte - [Zn] = 65 g/l - [Ni] = 88 g/l [H_2SO_4] = 18 g/l - 50°C - 100 A/dm² - 2 m/sec

The effects of lead on cathode efficiency

Whereas nothing regarding the effect of lead on the cathodic efficiency of pure zinc electrodeposition was noticed, in the case of zinc-nickel electrodeposition things were quite different. All other conditions remaining equal, an increase in electrolyte lead concentration leads to zinc coating weight loss, weight of the nickel coating remaining constant (figure 7). This is expressed by a weakening of global cathodic efficiency and an increase of nickel concentration in the deposit, when lead levels in the electrolyte increase (figure 8).

Hence it is necessary to take electrolyte lead pollution levels into account in order to determine production parameters. Figure 9, for instance, shows the way in which zinc-nickel electrolyte composition must be adapted according to lead levels, thus guaranteeing nickel concentration in the deposit close to 12%.

Lead profile in the deposit

By interrupting electrolysis after a short time span (0.1 sec), then after 2 sec, 4 sec and so on up to 20 secs, lead distribution throughout the coating could be determined (figures 10 and 11).

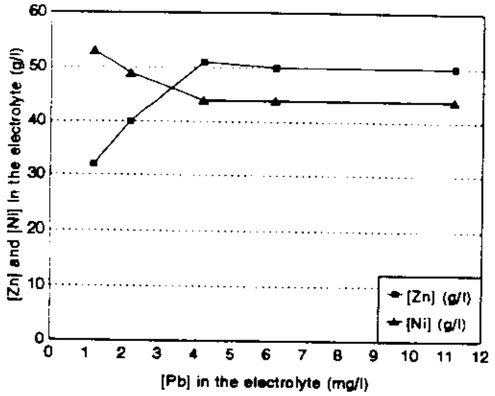

Fig. 9: Zinc and nickel concentrations to obtain 12 % of nickel in the deposit versus lead contamination in the electrolyte $[H_2SO_4]$ = 40 g/l - 50°C - 100 A/dm² - 2 m/sec

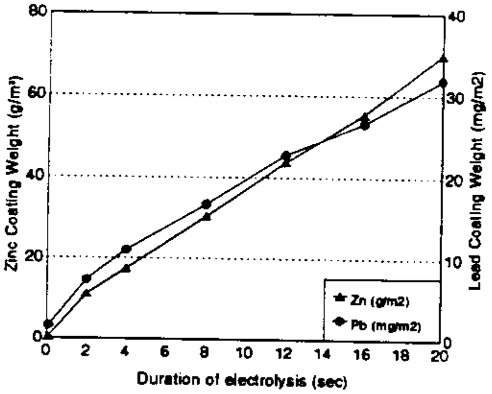

Fig. 10: Pure zinc coating - Zinc and lead codeposition [Zn] = 65 g/l - $[H_2SO_4]$ = 83 g/l - [Pb] = 8.4 mg/l - 50°C 100 A/dm² - 2 m/sec

On these diagrams, lead can be observed to have been evenly codeposited throughout the coating except at the steel-zinc interface where lead concentration is locally very high. Figure 10 shows that lead settles on the substrate before zinc deposition. This lead is certainly reduced through a process of cementation when the steel is put into contact with the electrolyte before start of electrolysis. On the circulating cell used, several seconds pass from the switching on of the circulation pump to the closing of the electrolysis circuit. The time is necessary to establish a stationnary flow in the electrolysis cell.

Events however take on a wholly different turn in our industrial cell where the steel strip is put into contact with the electrolyte simultaneously with the start of electrolysis.

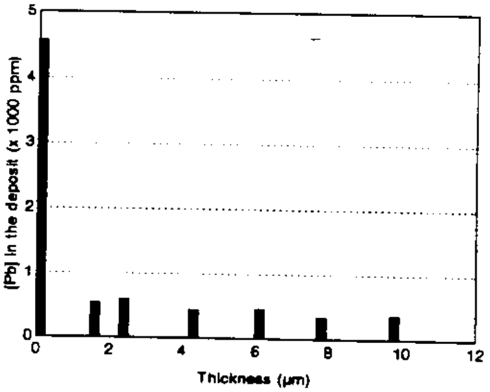

Fig. 11: Pure zinc coating - Lead profile - [Zn] = 65 g/l $[H_2SO_4]$ = 83 g/l - [Pb] = 8.4 mg/l - 50°C - 100 A/dm² - 2 m/sec

Similarly, after interrupting electrolysis current and prior to rinsing, the cementation process takes place on the surface of the zinc and leads to local lead enrichment[2].

Effect of lead contamination on product properties

Coating adherence following heat treatment

When lead contaminated zinc-plated coating is subjected to heat treatment, a loss of coating adherence to the substratum may occur, to the extent that coating may peel away entirely (see figure 12).

Delamination occurs at the interface of the zinc-iron alloy formed during heat treatment and the pure zinc. It only happens under certain time and temperature heat treatment conditions[1]. One of the most critical combinations is heat treatment at 300°C for 30 minutes. Besides, these are the conditions of a test imposed by certain car manufacturers. Following this treatment, simply folding the sample brings adherence loss to light.

This test carried out on samples with different lead contamination levels demonstrated that zinc-plating should not have a lead content above 150 ppm. If the concentration is higher, loss of adherence will be observed.

In the case of zinc-nickel coating, during heat treatment, interdifusion phenomena between steel and coating are much slower and no coating delamination has ever been noticed.

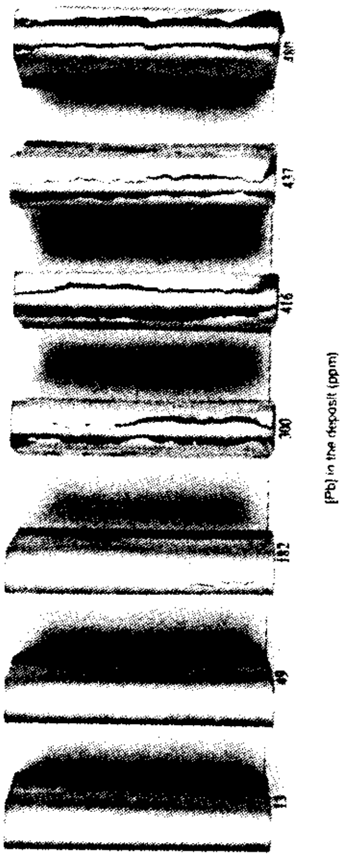

Fig. 12: Delamination of lead contaminated zinc-plated coating, after heat treatment at 300°C for 30 min

Corrosion resistance

Zinc-plated steel samples with different lead contents were subjected to the salt spray test (A.S.T.M. B117 standard). Figure 13 shows that lead contamination of the zinc-plated coating has no effect on the latter's resistance to corrosion.

In the case of zinc-nickel coated steel, results are totally different and very slight lead contamination of the coating leads to a substantial reduction in corrosion resistance. This was discovered with experimental samples carried out in a circulating cell (see figure 14).

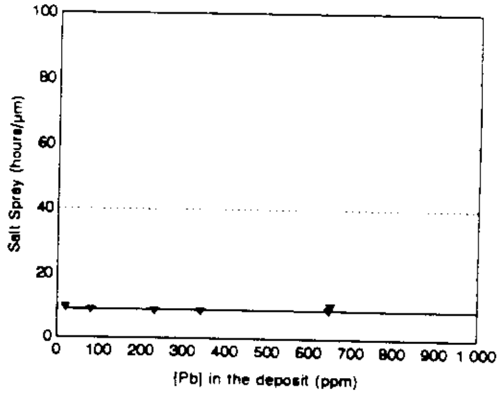

Fig. 13: Pure zinc coating - 20 g/m² - Effect of lead contamination in the deposit on the corrosion resistance in the salt spray test

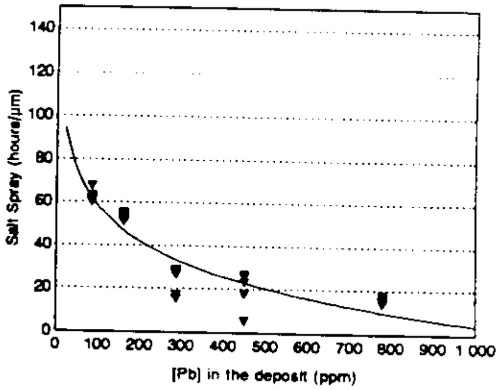

Fig. 14: [Ni] in the deposit = 12 % - 20 g/m² - Effect of lead contamination in the deposit on the corrosion resistance in the salt spray test - experimental products

Industrial application

Pilot line trials

Initial validation of results obtained in the simulation cell was carried out on an electrolysis pilot line. The line's main features are listed in table 1. Figures 15 and 16 give an overall view of the line and of the electrolytic deposition radial cell. The radial cell used within the context of the trials is equiped with insoluble Ti-IrO$_2$ anodes. Anode to steel strip distance is 6 mm.

Table 1: Pilot line - main features

Steel sheet:	maximum width: 350 mm
	thickness: 0.1 to 0.4 mm
Speed:	0 to 400 m/min
Treatment:	electrolytic cleaning
	rinsing
	electrolytic pickling
	rinsing
	single channel radial cell
	current density: 10 to 300 A/dm^2
	repeated rinsing
	post-treatments
	drying

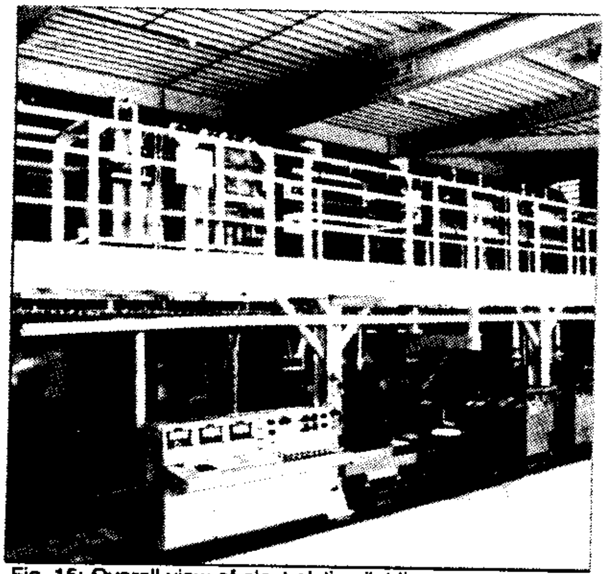

Fig. 15: Overall view of electrolytic pilot line

Electrolyte circulation is counter-flow, speed being adjustable between 0 and 4 m/sec. Maximum tested strip speed during trials in the radial cell was 150 m/min.

The relation between lead content in the zinc and zinc-nickel electrolytes and lead concentrations in the coatings, based on the process of lead deposition at its limiting current density, was confirmed. For lead contents, in the deposit below 50 ppm, zinc and zinc-nickel samples match the requirements:

- Good coating to zinc adherence after heat treatment.
- Correct zinc-nickel corrosion resistance.

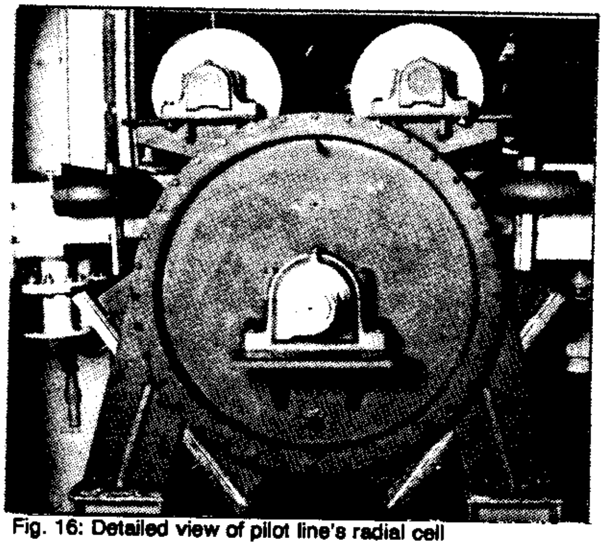

Fig. 16: Detailed view of pilot line's radial cell

Industrial line tests

A second validation of results was carried out on an industrial line. In April 1991, T.D.M., a subsidiary of the Cockerill Sambre Group, started a new electrogalvanizing line. The main features of this line are summarized in table 2. Figure 17 gives an overall view of the line. Figure 18 is a schematic diagram of the radial cell.

Table 2: T.D.M. - E.G.L. number 5 - main features

Steel sheet:	width: 950 to 1850 mm
	thickness: 0.4 to 1.5 mm
Max. speed:	140 m/min (central section)
Electrolysis:	12 radial cells,
	single channel,
	480 000 A installed

In July 1992, the insoluble lead-silver anodes, assembled when the line was opened, were replaced with Ti-IrO$_2$ anodes to improve the performance of zinc and zinc-nickel coated products.

After start-up time, lead concentration in the two electrolytes stabilised at an equilibrium value of the order of 1 mg/l. This concentration stems from a mass balance between lead inputs (raw materials) and lead outputs (coatings, driving due to rinsing).

In the case of zinc coatings, residual lead content in the deposit is of the order of 50 ppm, and the heat resistance tests confirmed our laboratory tests.

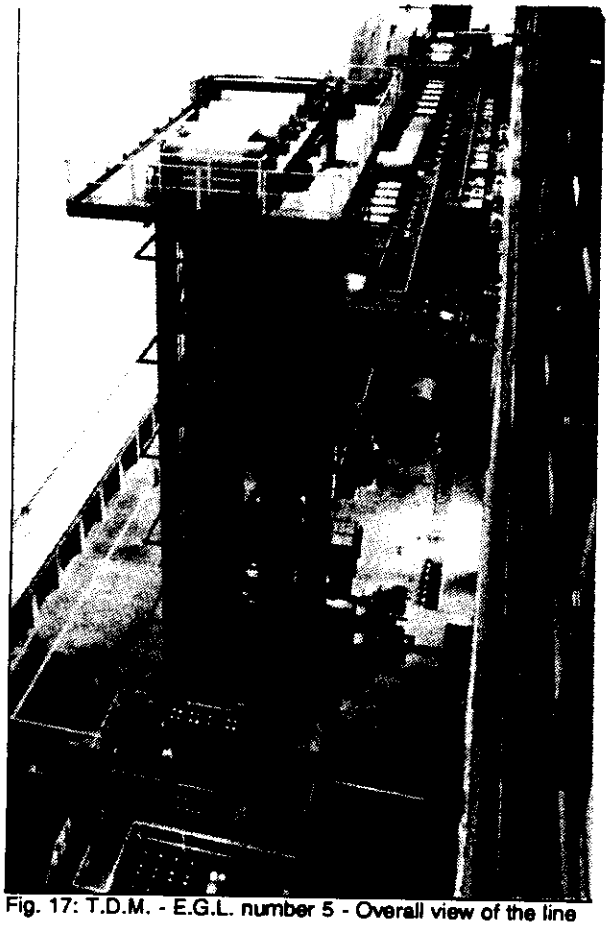

Fig. 17: T.D.M. - E.G.L. number 5 - Overall view of the line

- As regards zinc-nickel, co-deposited lead reaches the same 50 ppm value. The zinc-nickel coating with 12% nickel was produced at pH 1.3, with a cathodic efficiency above 85%. We compared our products' resistance to the salt spray test with industrial samples of various origins. All compared coatings have a coating weight of between 20 and 40 g/m².

The relation between corrosion resistance, expressed by the test, and the coating's lead content was confirmed (see figure 19).

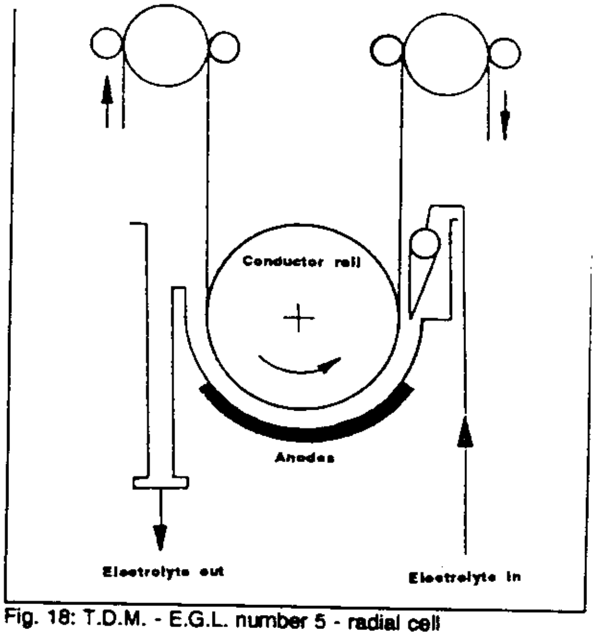

Fig. 18: T.D.M. - E.G.L. number 5 - radial cell

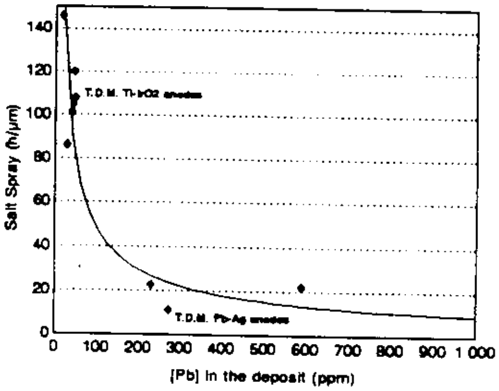

Fig. 19: [Ni] in the deposit = 12 to 13 % - 20 to 40 g/m²
Effect of lead contamination in the deposit on the corrosion resistance in the salt spray test - industrial products

Conclusions

Zinc and zinc-nickel electrolytes are liable to be polluted by lead in two ways: through lead contained in the zinc and nickel raw materials and through insoluble anodes of the lead-silver type.

This lead leads to a worsening of product performance. In the case of pure zinc coatings, lead leads to a loss of coating adherence following heat treatment. In the case of zinc-nickel coatings, lead contamination of the latter gives rise to a dramatic drop in resistance to corrosion.

To avoid these negative effects, we took the following measures:

- Replacement of insoluble lead-silver anodes with new type Ti-IrO_2 anodes.
- Strict purity control of the raw materials introduced in regeneration units.

These two precautions, crucial for guaranteeing product quality, were taken on the Cockerill Sambre Group's new electrogalvanizing line at Marchin, T.D.M. plant.

Références

1. SRINIVASAN V., CUZMAR J.S. and O'KEEFE T.J., *Metallurgical Transactions B*, 21B, 81-86 (February 1990)

2. KIKUCHI I., *CAMP-ISIJ*, 5, 680 (1992)

3. KIKUCHI I., *CAMP-ISIJ*, 5, 681 (1992)

4. WEYMEERSCH A., WINAND R. and RENARD L., *Plating and Surface Finishing*, 68, 56-59 (April 1981)

5. WEYMEERSCH A., WINAND R. and RENARD L., *Plating and Surface Finishing*, 68, 118-121 (May 1981)

6. WANG H.M., CHEN S.F., O'KEEFE T.J., DEGREZ M., WINAND R., *Journal of Applied Electrochemistry*, 19, 174-182 (1989)