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**SOME RECENT DEVELOPMENTS IN THE
ZINC-PLATING OF STEEL CARTRIDGE CASES
IN CANADA**

by

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EXTRACTION METALLURGY DIVISION

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ABSTRACT

For some time high-quality electroplated zinc has been specified as a suitable coating for protecting drawn-steel cartridge cases of the 105 mm and 3 inch, 70 calibre, types. The present report outlines a recent Canadian investigation that has shown how to improve the quality of the zinc which is being applied by present processes. In particular, the following improvements are dealt with:

- (1) An alkaline anodic treatment to remove zinc phosphate coatings from steel surfaces, particularly coatings that have undergone heat treatment.
- (2) A rapid and effective method of removing ferrous iron and nickel, and probably other similar impurities, from the cyanide zinc plating bath.
- (3) A rapid and effective method of removing the same contaminating materials from the surfaces of zinc anodes used in the same type bath.

In addition a hydrochloric acid corrosion test has been developed, which has enabled the detection of metal contaminants in the zinc coatings and thus in the cyanide plating baths.

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Int. Report

INTRODUCTION

1. In 1956 the Canadian Department of National Defence agreed to accept drawn-steel cartridge cases of the 3 inch, 70 calibre type for the Navy, and of the 105 mm type for the Army. Each case was to be zinc-plated in accordance with Federal Specification QQ-Z-325a of the U. S. A. , in which a Type II, Class 2 zinc coating was specified for the exterior surfaces and a Type II, Class 3 zinc coating for the interior surfaces. ~~Those parts of this specification which are pertinent to this investigation are given in Appendix I.~~

2. By the early part of 1958 cases of both types were being produced, inspected, placed in cardboard cartons and shipped to the Filling Division for storage until required. This storage was in unheated buildings where, due to the temperature fluctuations, a certain amount of moisture condensation must have taken place. In other words, for at least part of the time, the zinc coatings on the cartridge cases must have been covered with a thin film of condensed water which somewhat resembled distilled water except that it doubtless contained carbon dioxide dissolved from the atmosphere.

3. In December 1958, tiny black spots were observed on the surfaces of several cases of each type. The manufacturer then made certain process changes which he believed would improve the zinc coatings and prevent the development of spots on future cases. However inspection during the following months revealed that spots

had developed on some of the newer cases soon after they had been placed in storage; also that there had been an increase in the number of older cases with spots, and in the number and size of the spots on each case. This corrosion would not have been considered particularly serious in wartime when the cartridges probably would have been used a few months after they had been manufactured. However under present-day conditions they might remain in storage for many years. Also at some time in the future the plated cartridge cases might have to be stored under tropical conditions which would be much more corrosive than the present storage conditions.

4. This Division was requested by both the manufacturer and the user of the cases to make a thorough investigation of the causes of this deterioration and recommend a remedy.

5. The complex manufacturing procedure used at that time in producing the cases is outlined in Appendix II. Although the changes which were made during the investigation have been included in the list, these have been placed in "boxes" to enable the reader to obtain a clearer understanding of the situation.

6. The investigation is described under the main headings:

- I Examination of materials involved in the problem
- II Laboratory corrosion testing
- III Improvement of the surfaces of the cases prior to zinc plating
- IV Improvement of the zinc plating procedure.

INVESTIGATION

I Examination of Materials Involved in the ProblemMaterial under same heading in Electroplating Report
Metallographic Examination

7. Metallographic examinations by D. E. Parsons⁽¹⁾ and J. J. Sebisty⁽²⁾, both of the Mines Branch staff, revealed that the surfaces of the drawn steel were smooth and covered with a uniform grey coating of zinc phosphate 0.0005 inch thick, prior to the tempering treatment (Step ix). After this treatment the steel was slightly rough and covered with temper oxides and the remains of the zinc phosphate coating. These formed a rough dull-black film containing numerous tiny, severely-cracked areas. Following the sulphuric acid pickle, which was supposed to remove this film, the surface of the steel was severely pitted and covered with an adherent smutty, black coating. Many of the pits were between 0.001 and 0.0015 inch in depth and partially or completely filled with black material. The abrasive treatment (Step xvii), adopted by the plant management, improved the surface appearance but increased the amount of material in the pits.
8. It further was found that the black spots, seen on the zinc-plated cartridge cases in storage, were mounds of corrosion product covering a tiny uncoated pitted area of steel. Apparently the zinc was plated on the adherent smutty, black coating resulting from the sulphuric acid treatment, instead of being plated directly on the steel.

Thickness of Zinc Coating

9. Using a chemical stripping method it was found that the average thickness of the zinc coatings on the exterior surfaces of the cartridge cases varied between 0.0003 and 0.0006 inch.

Analysis of the Zinc Coatings on the Cases

10. Iron was found to be the major impurity in the zinc coatings; however nickel, chromium and copper were present as trace elements.

Analysis of Zinc Plating Bath

11. The plating bath used for plating the cartridge cases contained sodium cyanide, sodium hydroxide and zinc cyanide as the major constituents. In addition there was a considerable amount of iron, small amounts of nickel and chromium, and a trace of copper.

Nature of Smutty Black Coating

12. It was shown by the X-ray diffraction method that the smutty, black coating, remaining after the sulphuric acid pickling, consisted largely of zinc phosphate and an unidentified material.

Nature of Corrosion Product on Zinc Coatings

13. It was shown by the same method that the dark spots, found on the cartridge cases in storage, consisted largely of basic zinc carbonate ($4 \text{ ZnO} \cdot \text{CO}_2 \cdot 4\text{H}_2\text{O}$). The material causing the color in the spots remained unidentified.

II Laboratory Corrosion Testing

14. The laboratory corrosion testing was done

- Use material under same heady - Electro paper*
- (a) to attempt to determine the reason for the formation of the black spots found on the zinc-plated cartridge cases in storage.
 - (b) to indicate the purity of the zinc coatings produced under various conditions during the investigation.

Salt Spray and Humidity Tests

15. Investigation showed that the finished zinc-plated cartridge cases passed the 96-hour salt spray test required by the Federal Specification. If the test was continued beyond this length of time white corrosion products eventually appeared. However this material bore no apparent resemblance to the black spots that were observed on the plated cartridge cases in storage. Accordingly it was decided that the salt spray test would be of no assistance in the present investigation.

16. It is interesting to note that for some time specialists in this field have regarded the salt spray test as inadequate for determining the quality of zinc coatings. For this reason the American Society for Testing Materials has ceased to use it for this purpose.

17. Black corrosion spots, similar to those observed on cases in storage, were not produced during tests in the humidity cabinet. This is another corrosion test for zinc required in some specifications.

Distilled Water Tests

18. As stated above, the zinc-coated cartridge cases must be covered with a film of water, probably somewhat resembling distilled water containing dissolved carbon dioxide, during part of the time they are in this particular kind of storage. Accordingly samples cut from zinc-coated cartridge cases were immersed in distilled water, which had been exposed to the air, at 70°F (21°C). In this way black spots, similar in appearance to those already observed on cartridge cases in storage, were produced on chromate-treated zinc coatings in 10 to 14 days and on unchromated ones in 2 to 3 hours. Unfortunately this test was unsuitable for use in evaluating the plating on cases in production because of the length of time required.

Hydrochloric Acid Tests

19. According to U. R. Evans⁽³⁾, many investigators have found that relatively pure zinc is attacked comparatively slowly by dilute acids, and very little smut remains on the surface after the attack. They also have found that small percentages of other metals in zinc increase or decrease its rate of dissolution. Although analysis had shown certain other metals to be present in the zinc coatings of interest in this investigation, the amounts of these metals were very small, and their analyses very complicated and time-consuming; also the accuracy of analyses was not of a high order. In view of this, a test for determining the rate of dissolution of electroplated

zinc coatings in dilute hydrochloric acid was adopted to give an indication of the amount of metallic impurities present in the coatings. The rate was determined by measuring the rate of evolution of hydrogen (Such a test, using dilute sulphuric acid, was used by F. W. Harris⁽⁴⁾ in testing cast zinc specimens). The required apparatus and the procedure used in the hydrochloric acid test are described in Appendix III.

20. A large number of electroplated zinc coatings from laboratory experiments and plant production were subjected to this test. Samples from other plants, including that of a British manufacturer, also were tested. In these tests the gas evolution rate varied from 0.05 to 17 ml/minute, and the time required to completely dissolve coatings of 0.6 mil thickness varied from 2 to 160 minutes. The dissolution rates shown in Figure 1 illustrate graphically the great differences which were found in electroplated zinc coatings on steel. It may be added that, although not included in the graph, zinc coatings on cases produced in the U. S. A. were found to dissolve as rapidly as those on cases produced in Canada and Great Britain. It is of interest to note that by far the greatest dissolution rates were obtained from zinc coatings on cartridge cases.

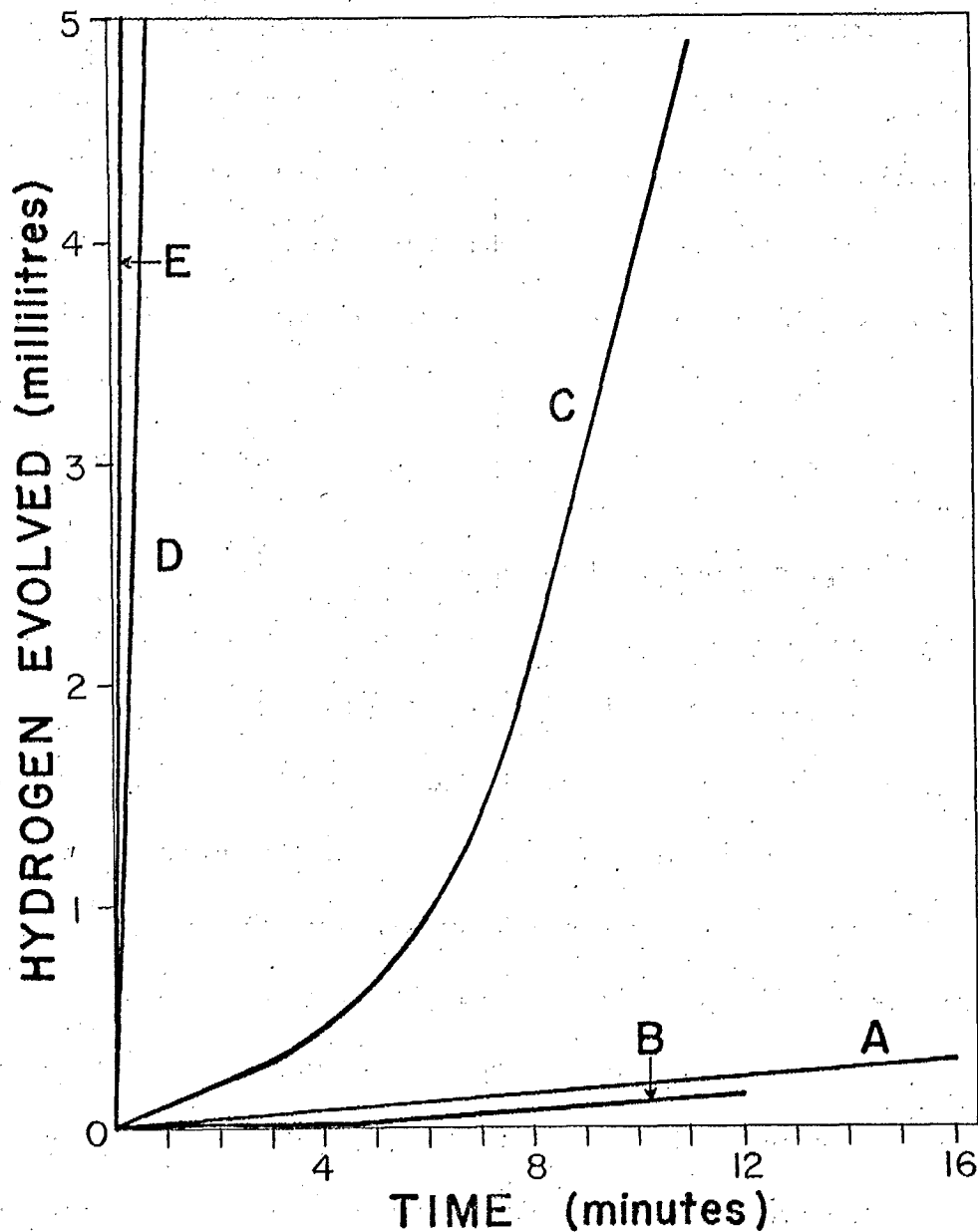


Figure 1. Dissolution rates of laboratory-produced and plant-produced electroplated zinc coatings.

- A-laboratory-produced coating on mild steel, from a purified cyanide plating bath (see para. 44).
- B-plant-produced coating on mild steel, from a commercial cyanide plating bath.
- C-plant-produced coating on mild steel, from an acid-sulphate plating bath.
- D-plant-produced coating on a Canadian 105 mm cartridge case, from a commercial cyanide plating bath.
- E-plant-produced coating on a British cartridge case, from a commercial cyanide plating bath.

III Improvement of the Surfaces of the Cases Prior to Zinc Plating

21. As stated earlier under the heading "Metallographic Examination", the steel was covered with a film of temper oxides and the remains of the zinc phosphate coating after the tempering treatment (Step ix) had taken place. This film contained numerous tiny severely-cracked areas. During the pickling (Step xii) a considerable part of the film remained unattacked by the acid; however the latter did reach the steel through the cracks, and pits were produced in such locations.

22. Since it would be difficult to electroplate a zinc coating of good quality on such a surface, the writer attempted to remove all nonmetallic material so that the steel would be entirely exposed prior to plating. Various acid treatments, both chemical and electrochemical, were entirely unsuccessful. Alkaline solutions had some effect but the rate was prohibitively slow. Cathodic treatment in 5 to 10% sodium hydroxide solution removed the original nonmetallic material but at the same time deposited another material which was insoluble in acid. Finally it was found that a one-minute anodic treatment in a similar solution would remove all undesirable material and leave an active steel surface.

23. Further experimental work by the manufacturer of the cases showed that anodic treatment in his alkaline cleaner solution removed the nonmetallic material completely provided that the

cleaner contained at least 3% of sodium hydroxide (Step xxiv). The use of this solution, instead of one containing sodium hydroxide alone, had the additional advantage that objectionable fumes were reduced to a minimum.

24. The manufacturer also showed that anodic pickling in 60% (by volume) commercial sulphuric acid was superior to ordinary pickling in a 10% solution (by volume) of the same acid (Step xxvi) because it tends to open up the pits in the steel so that their interiors can be plated more effectively. The writer suggested the use of water sprays for rinsing in Step xxvii.

25. It will be noted that during this investigation emphasis was placed on the removal of the phosphate coating after the steel had been subjected to heat treatment. It should be pointed out that the removal of this material prior to the heat treatment would be the most desirable procedure.

IV Improvement of the Zinc Plating Process

Nature of Plating Bath Contaminants

26. As stated earlier, small amounts of iron, nickel, chromium and copper were found in the zinc coatings on the cartridge cases in storage. Then, as expected, it was found that small amounts of these same metals were present in the zinc plating bath at the plant.

Accordingly the first phase of this part of the investigation was to replace the old bath by a new one produced from commercially-pure

chemicals, and use the latter for plating cartridge cases having clean and active metal surfaces.

27. A piece of cartridge-case steel was plated in a sample of the new bath in the laboratory. The resulting coating was subjected to the hydrochloric acid test.

28. Cartridge cases were plated continuously in the plant, starting with the same bath. Plated cases Nos. 5, 686 and 1276 were removed and subjected to the hydrochloric acid test (1276 cases were approximately 1 1/2 days' production).

29. For comparison, a piece of mild steel was plated in the laboratory in a bath purified as in paragraph 44, the resulting sample being subjected to the hydrochloric acid test.

30. As shown in Figure 2, none of the zinc coatings produced in the plant gave as low a rate of hydrogen evolution as did the one plated in the purified bath in the laboratory, ie, under the most nearly ideal conditions. However the rate of hydrogen evolution increased considerably as the number of cases plated in the plant increased. The difference in rates between B (the first sample plated in the laboratory using commercial materials) and C (the fifth case plated in the plant using commercial materials) is particularly noteworthy. The result obtained with the coating on case No. 1276 approached that obtained with the coating on a case which had corroded in storage.

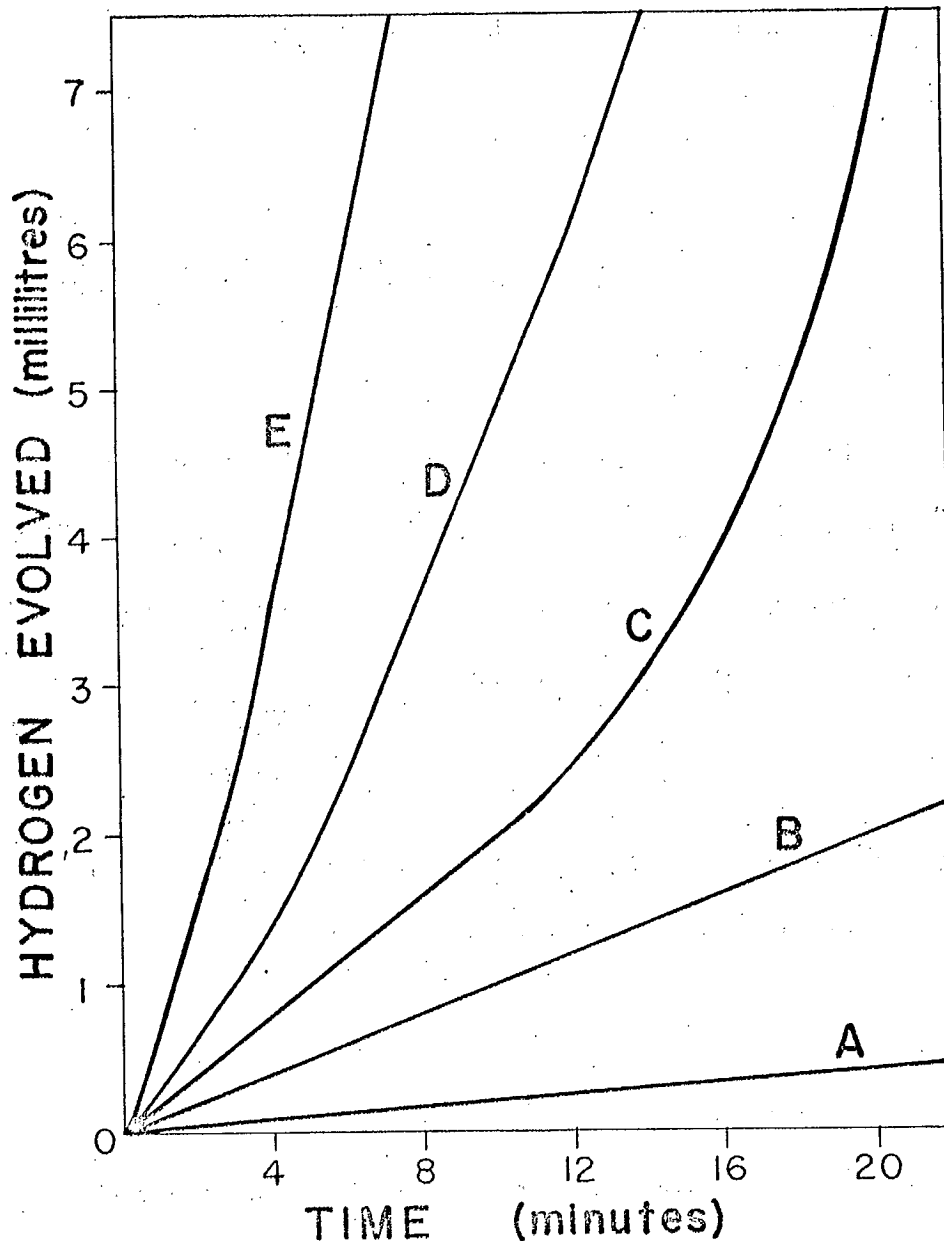


Figure 2. Variation of dissolution rates of electroplated zinc coatings on cartridge cases with the number of cases plated. The dissolution rate of a laboratory-produced coating on mild steel is included for comparison.

- A- laboratory-produced coating on mild steel, from a purified cyanide plating bath.
- B- laboratory-produced coating on cartridge-case steel; from freshly prepared commercial cyanide plating bath.
- C- plant-produced coating on the 5th cartridge case electroplated from a bath similar to that used in plating B.
- D- plant-produced coating on the 686th cartridge case plated from the same bath as C.
- E- plant-produced coating on the 1276th cartridge case plated from the same bath as C.

31. These results strongly indicated that the original bath was comparatively free from contamination, but that the concentration of one or more contaminants increased as the plating proceeded.

32. It was recalled that iron and nickel had been found in the original plating bath used at the plant; so one or both of these was immediately suspected of being the contaminant (or contaminants) which produced such a great change in the rate of corrosion of the zinc in the hydrochloric acid test.

33. To obtain actual proof of this a series of laboratory experiments was performed. Zinc coatings were plated from solutions containing impurities as follows:

No appreciable impurities

.05, 0.31 and 1.25 grams/litre of iron in the ferrous state

0.09 ~~grams~~_{mg}/litre of nickel.

The results of the hydrochloric acid tests on these coatings are shown in Figure 3. It is quite evident that after iron or nickel is introduced into the plating bath, the hydrogen evolution rates of the resulting plated samples become greater (sometimes much greater) than they would be in the absence of these two contaminants; also a much larger amount of iron than of nickel is required to produce the same result.

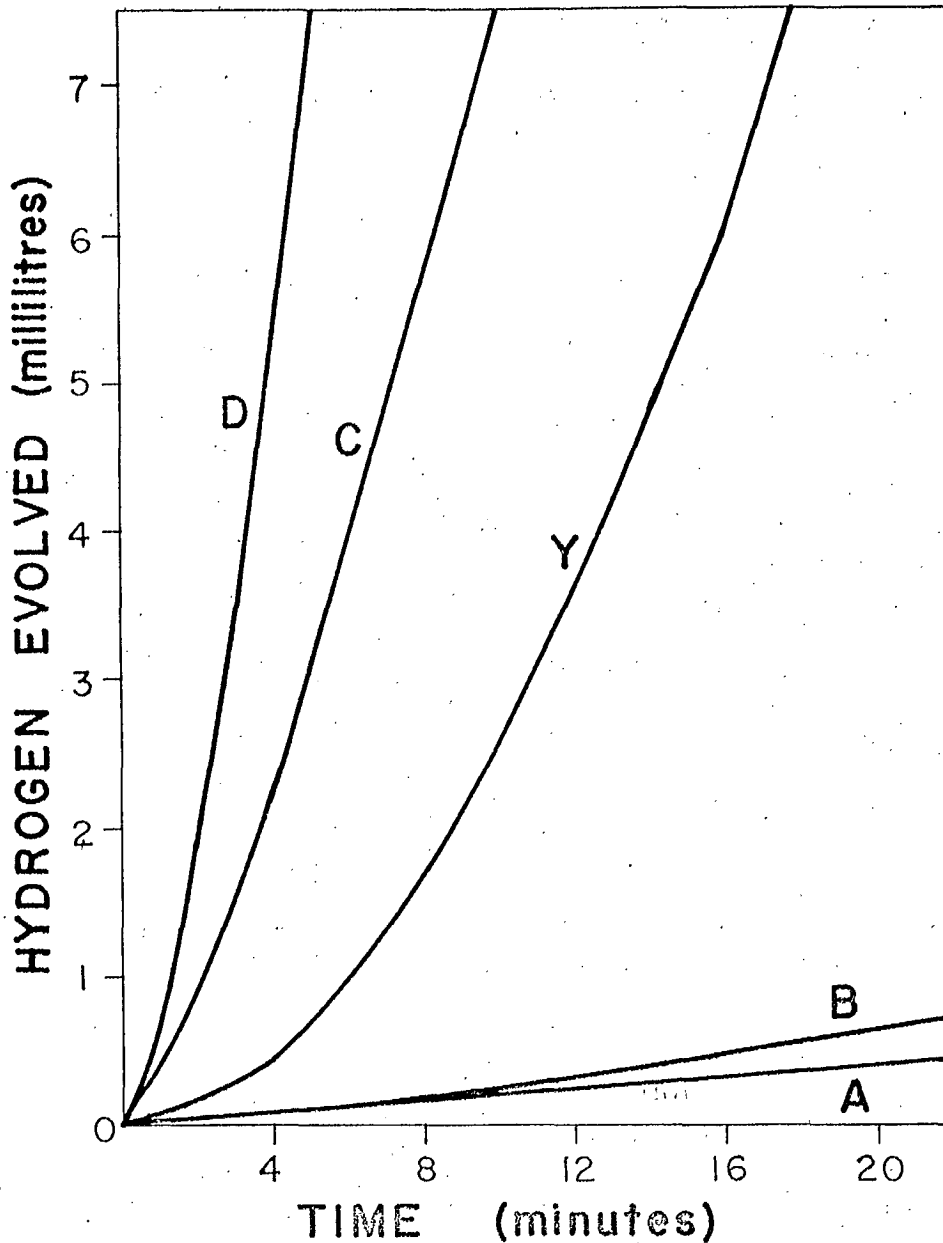


Figure 3. Dissolution rates of laboratory-produced zinc coatings on mild steel, from purified zinc-plating baths containing ferrous iron or nickel as impurities.

- A - bath with no appreciable impurities.
- B - bath containing 0.05 grams/litre iron.
- C - bath containing 0.31 grams/litre iron.
- D - bath containing 1.25 grams/litre iron.
- Y - bath containing 0.09 ~~grams~~ mg/litre nickel.

34. In view of the analytical results obtained, it is possible that chromium and copper also are highly undesirable contaminants. These will be investigated later.

Source of Plating Bath Contaminants

35. The next problem was to determine the source of these contaminants which apparently continued to enter the plant plating bath while it was in use. As indicated in Appendix II, the internal anodes used in zinc plating the cartridge cases consisted of a nickel tube with a flared piece of mild steel fastened to one end by means of a nut and bolt of 18-8 stainless steel. The stainless steel contains about 8% of nickel. It appeared that the bath could have been contaminated by the very slow but continuous solution of these metals.

36. Zinc-plating experiments were performed using pairs of anodes, each pair consisting of a zinc anode connected electrically to an anode of one of the following materials: mild steel, nickel, 18-8 stainless steel (containing 8% nickel and about 70% iron) and inconel (containing 76% nickel and 7.5% iron, as well as 15% chromium). The samples for the hydrochloric acid test were not plated until each pair of anodes had been used in its plating bath for from 20 minutes to 2 hours and then the non-zinc anode removed. All baths had been purified before use, and all cathodes were of mild steel.

37. The results of the hydrochloric acid tests on the plated samples are given in Figure 4. These are due to the nickel and/ or

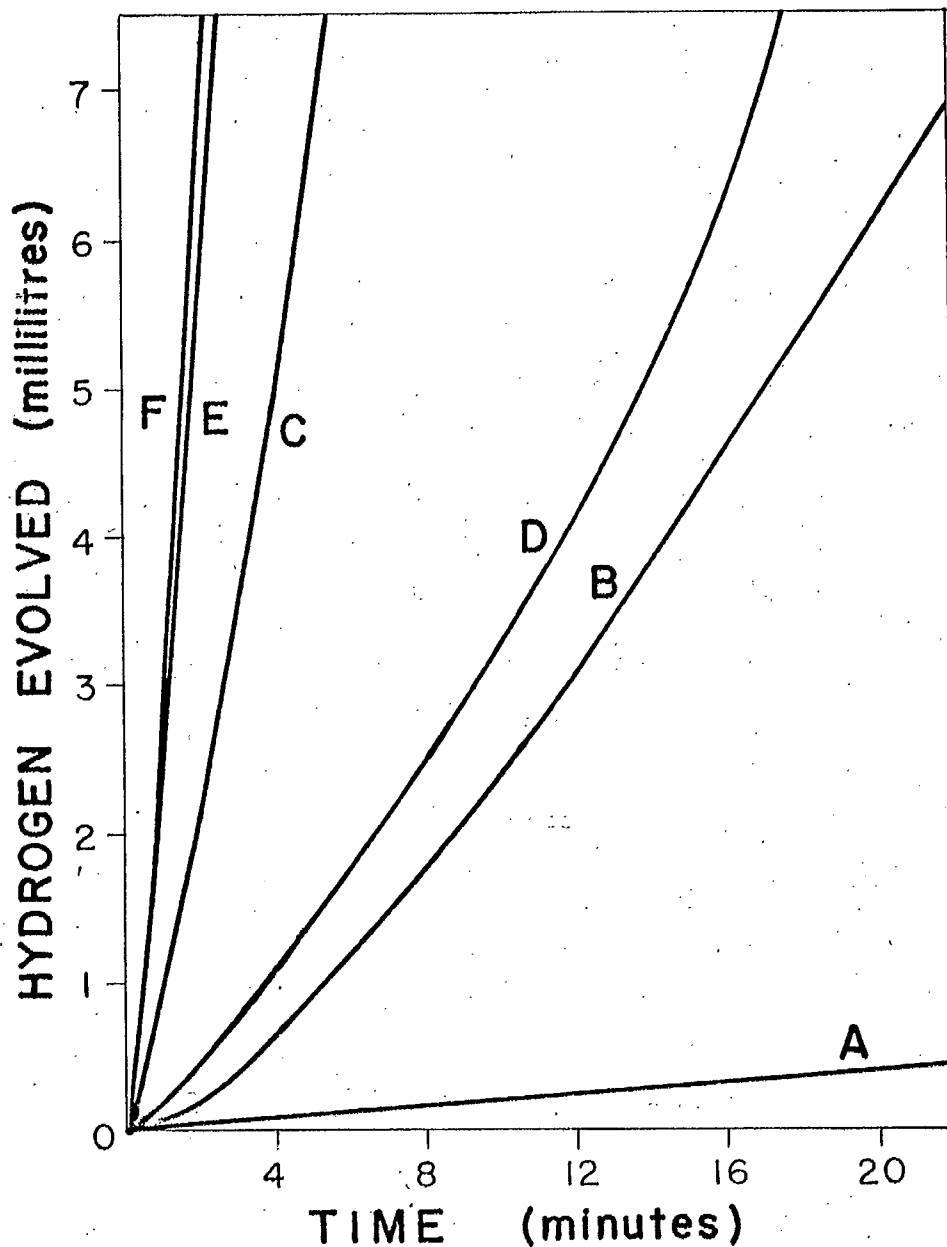


Figure 4. Dissolution rates of laboratory-produced zinc coatings on mild steel, from purified zinc plating-baths in each of which an anode of zinc (99.99% purity) and one of a different metal had been used. Prior to plating each sample the non-zinc anode was removed from the bath.

- A- coating plated after bath had been used for two hours with 2 zinc anodes (for comparison).
- B- coating plated after bath had been used for 20 minutes with a stainless steel (18-8) anode and a zinc anode.
- C- coating plated after bath had been used for 2 hours with a stainless steel (18-8) anode and a zinc anode.
- D- coating plated after bath had been used for 2 hours with a mild steel anode and a zinc anode.
- E- coating plated after bath had been used for 2 hours with a nickel anode and a zinc anode.
- F- coating plated after bath had been used for 35 minutes with an inconel anode and a zinc anode.

iron dissolved in the baths from the various anodes containing these metals. The zinc-plated samples from the resulting baths gave a much greater hydrogen evolution rate than did those from baths which did not contain nickel or iron. Here again it was shown that nickel is a much more serious contaminant than iron. Since the inconel (76% nickel) had an even greater effect than pure nickel it is possible that chromium also is a highly undesirable contaminant.

38. Experiments also were conducted in a zinc-plating pilot plant where it was possible to plate individual cartridge cases in racks similar to those used in the continuous production line. It was found that an ordinary internal anode of nickel and mild steel, when connected to the electric circuit, caused the dissolution rates of the zinc coatings to increase rapidly. If this internal anode was disconnected from the circuit but allowed to remain in the bath during plating, the same results were obtained but a longer time was required. When the internal anode was removed from the bath the dissolution rates remained low; however, of course, the interior surfaces were not plated. The rates continued to be low, and the interior surfaces were plated, when internal anodes of zinc were used.

39. During these experiments the hydrochloric acid test proved to be an important tool in detecting the presence of contamination in the plating baths and pointing to the major source of this contamination.

Prevention of Plating Bath Contamination

40. In view of these results, it has been suggested that the internal anodes of nickel and mild steel formerly used in production be replaced by zinc anodes. This would keep the contaminant content of the plating bath at a desirably low level; however the shape of the zinc anode would change due to dissolution of the zinc and this, in turn, would cause an undesirable change in the thickness of the internal zinc coating.

Removal of the Contaminants from the Plating Bath

41. Zinc coatings from a purified plating bath may have a hydrogen-evolution rate as low as $\frac{0.12}{1.2}$ ml/hour in the hydrochloric acid test. Even a plating bath produced from reagent-grade chemicals would not give a zinc plate having such a low evolution rate. Accordingly the next stage of the investigation consisted of a search for a method of purifying zinc cyanide plating baths which have been contaminated by elements such as nickel and iron.

42. Several procedures which have been proposed in the literature were first investigated, the first being the preliminary electrolysis of the plating bath using zinc anodes and mild steel cathodes at a low current density for 16 hours. Such a procedure is commonly called "dummying". In some of these experiments the anodes were cleaned in acid, which gave some improvement as shown by the hydrochloric acid test; however none of the experiments involving the use of "dummying" were particularly successful, as shown in Figure 5.

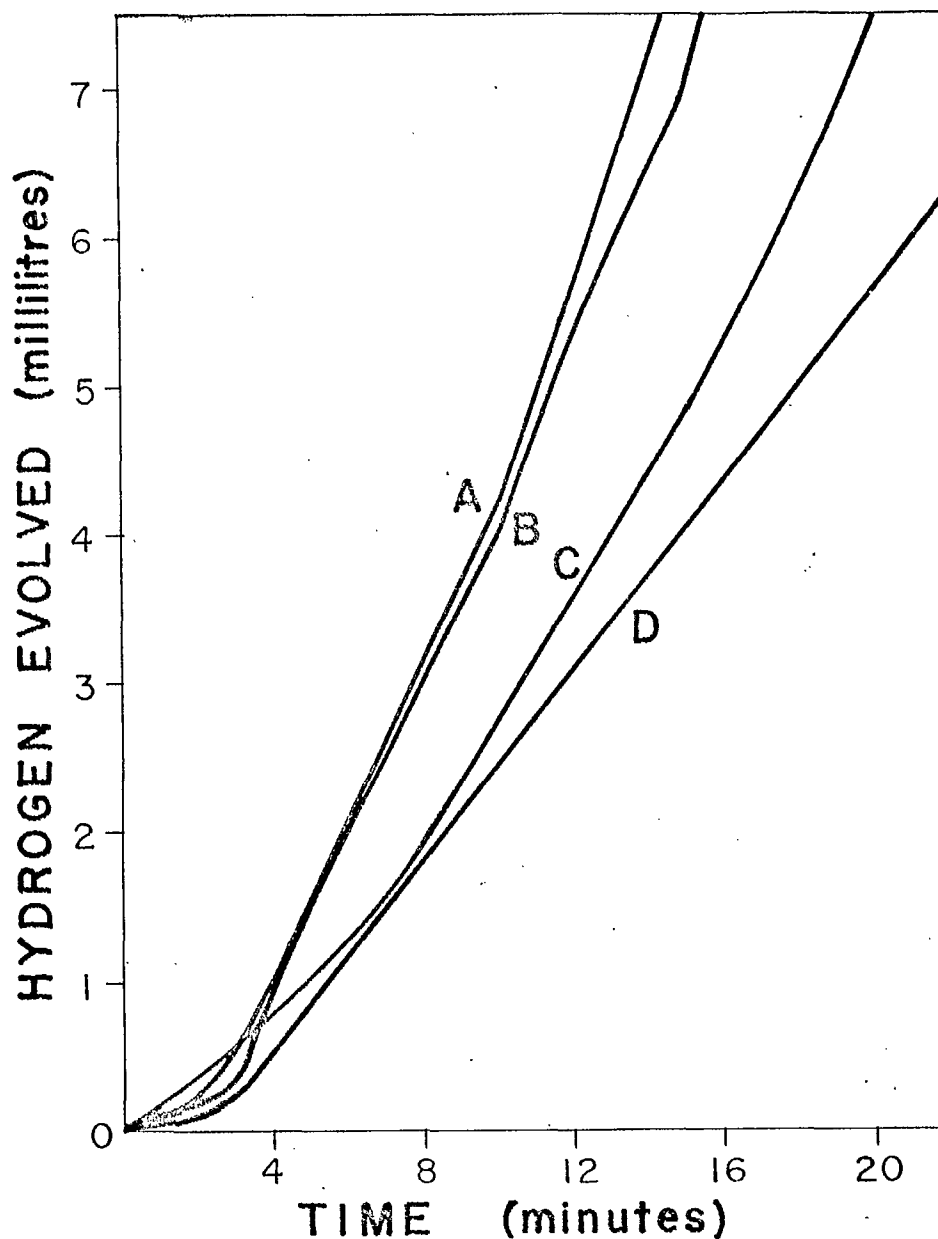


Figure 5. Dissolution rates of laboratory-produced zinc coatings on mild steel, from commercial plating baths some of which had been purified by preliminary electrolysis using zinc anodes and mild steel cathodes (dummying).

- A- coating from commercial plating bath with no preliminary electrolysis.
- B- coating from commercial plating bath which had been "dummied" at a low current density for 16 hours.
- C- coating from commercial plating bath which had been "dummied" as in B. Anodes cleaned once in acid during the "dummy" treatment.
- D- coating from commercial plating bath which had been "dummied" as in B. Anodes cleaned several times in acid during the "dummy" treatment.

43. Little improvement also was obtained when using the standard method of treating the plating bath with zinc dust. The treatment recommended by H. J. Backe and R. F. C. Robinson⁽⁵⁾, in which the bath was treated with zinc dust at 113°F (45°C), gave a major improvement but required at least 24 hours.

44. Much better results were obtained by a new procedure developed by the writer in which zinc dust was added to the plating bath either in the plating cell or in a purifying tank equipped with zinc anodes and a steel cathode. The solution, at room temperature, was vigorously agitated while being electrolyzed at a current density of 75 to 85 amp/sq. ft. The quantity of zinc dust and the length of time required depended on how badly the bath was contaminated. Five to 10 grams of zinc dust per litre of solution and 1/2 to 2 hours appear to be adequate for most baths. The cathodes were scraped several times during treatment to remove the zinc sponge that formed on their surfaces. During the process the zinc particles gradually adhered to one another and became sufficiently heavy to settle to the bottom. At the end of the treatment the plating bath was filtered and returned to the plating tank.

45. The results obtained in experiments with these different zinc dust treatments are shown in Figure 6.

46. It has been shown in Figures 3 and 4 that a very small amount of nickel is a serious contaminant when present in a zinc cyanide

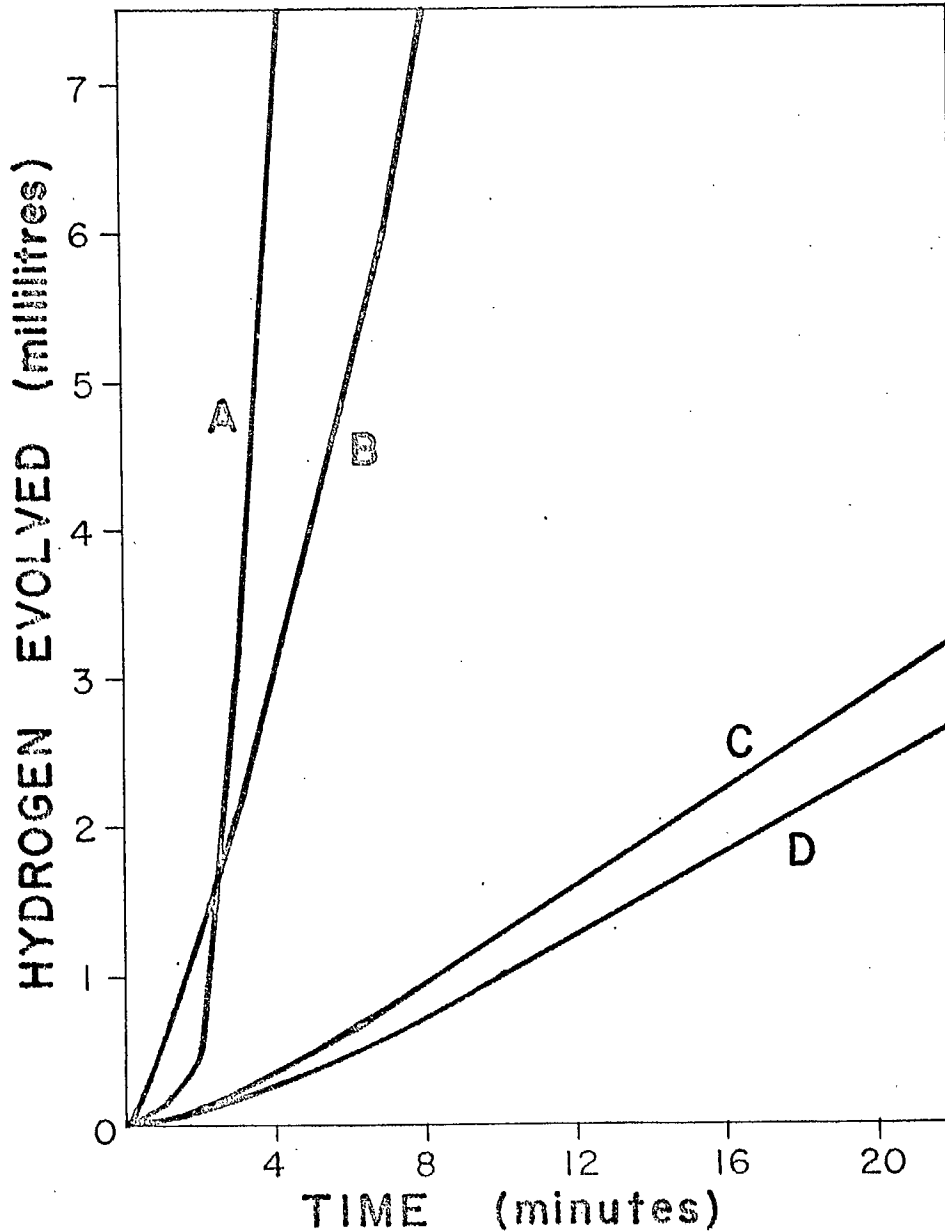


Figure 6. Dissolution rates of laboratory-produced zinc coatings on mild steel, from plating baths purified by various zinc-dust treatments. The results obtained with an unpurified bath are included for comparison.

- A- coating from a severely contaminated bath.
- B- coating from the same bath as A after it had been given the standard zinc-dust treatment at 70°F.
- C- coating from the same bath as A after it had been given a zinc-dust treatment at 113°F for 24 hours.
- D- coating from the same bath as A after it had been given a zinc-dust treatment at 70°F accompanied by electrolysis, for one hour.

plating bath. This contamination can be avoided by using internal anodes of comparatively pure iron, which is much cheaper than nickel or nickel alloys such as 18-8 stainless steel or inconel. The iron also dissolves slowly in the bath, but it can be removed by means of the electrolytic zinc-dust treatment.

47. It is important to add that the current efficiency of zinc plating is greater in cyanide baths purified by the electrolytic zinc dust treatment described above than in cyanide baths containing impurities such as nickel and ferrous iron. Ferric iron is not considered to be a contaminant.

Decontaminating Zinc Anodes

48. On some occasions, during the present investigation, it was observed that a purified plating bath produced zinc coatings having high dissolution rates. This appeared to happen when the zinc anodes had been used previously in a contaminated plating bath and had not been cleaned sufficiently afterward. Pickling the anodes in various strengths of hydrochloric, sulphuric or nitric acids failed to remove all of the contaminants from the zinc.

49. Fortunately it was found that anodes which had been used during the purification of a plating bath by the new zinc-dust treatment were quite free from contamination, and always gave a good hydrochloric acid test when used in a purified plating bath. Experimental

data comparing the various methods of decontaminating anodes are given in Figure 7.

50. To produce zinc coatings that are satisfactory on the basis of the hydrochloric acid test it appears to be necessary to decontaminate both the plating bath and the anodes.

Present Status of the Zinc-Plating of Steel Cartridge Cases in Canada

51. The new purifying treatment just described was used successfully to purify the 100 gallons of plating bath in the zinc-plating pilot plant. Following that, equipment was installed in the continuous production plant to treat 500 gallons at a time, on a continuous basis if required.

52. As this paper is being written the plant, employing the new purifying treatment, comparatively pure iron internal anodes and the other improvements referred to, has been in operation for some days. During the first two days 1307 cartridge cases were plated and, on the cases tested, the maximum dissolution rate was 0.3 ml/minute and the average was 0.15 ml/minute.

53. Although the immediate production problems seem to have been solved, a number of interesting new ideas have developed during this investigation which will be pursued in the Division laboratories as opportunity permits.

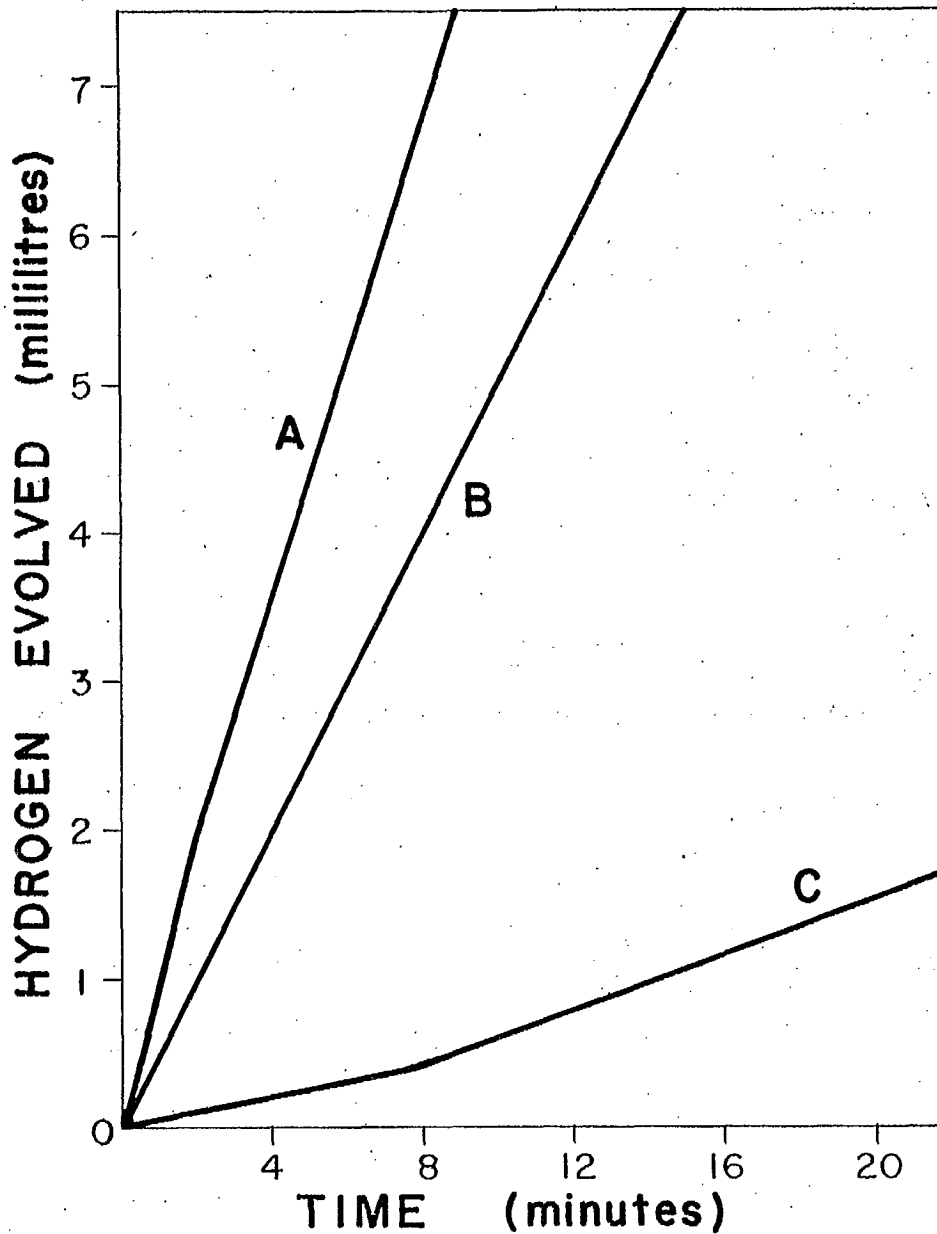


Figure 7. Dissolution rates of laboratory-produced zinc coatings on mild steel, from purified plating baths having zinc anodes which had been used in a contaminated bath and then subjected to various cleaning treatments. The results obtained with an uncleaned anode are included for comparison.

- A- from a bath having anodes which previously had been used in a contaminated bath.
- B- from a bath having anodes which had been acid-cleaned, after use in a contaminated bath.
- C- from a bath having anodes which had been cleaned by the new electrolytic zinc-dust treatment after use in a contaminated bath.

CONCLUSION

54. This report deals with recent Canadian developments in zinc plating the exteriors and interiors of steel cartridge cases. It is believed that these developments will be of considerable interest to other manufacturers of ammunition, and indeed to the whole electroplating industry.

55. The following improvements have been adopted as a result of the writer's experiments:

- (1) An anodic alkaline cleaning treatment for the removal of zinc phosphate coatings from steel, particularly after the coatings have been heat treated.
- (2) A new zinc-dust treatment that will adequately remove iron, nickel and probably other impurities from zinc-cyanide plating baths in much less time than previous methods.
- (3) A new method of removing iron, nickel and probably other impurities from the surfaces of the zinc anodes used in zinc-cyanide plating baths.

The writer also has developed a hydrochloric acid corrosion test for zinc coatings, which has proven to be a rapid and accurate method of detecting the presence of contaminants such as iron and nickel in the coatings, and thus in cyanide zinc plating baths.

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APPENDIX I

ZINC ELECTROPLATING SPECIFICATION

56. The following requirements are quoted from Federal Specification QQ-Z-325a, "Zinc Plating (Electrodeposited)":

3.2.1 Basis metal--The basis metal shall be substantially free from defects that will be detrimental to the appearance or the protective value of the plating. It shall be subjected to such cleaning, pickling and plating procedures as are necessary to yield deposits as hereinafter specified.

3.2.2. Plating--The zinc deposit shall be smooth, fine-grained, adherent, and free from blisters, pits, nodules, indications of burning, and other defects. Superficial staining which has been demonstrated as resulting from rinsing as specified hereinafter, shall not be cause for rejection. All details of workmanship shall conform to the best practice for high quality plating.

3.4.2 Salt-spray requirements--Type II plating (Supplementary chromate treatment) shall show no white corrosion products of zinc as defined in 3.4.2.1 when separate test specimens are subjected to continuous exposure to the salt spray for 96 hours in accordance with 4.5.3.

3.4.2.1 For type II plating the appearance of white corrosion products, visible to the unaided eye at normal reading distance, at accidental scratches through the chromate film to the zinc plate or unscratched areas of the chromate film shall be cause for rejection, except that white corrosion products at edges shall not constitute failure.

APPENDIX II

MANUFACTURING PROCEDURE FOR CANADIAN ZINC-PLATED
CARTRIDGE CASES

57. A brief outline of the procedure used to manufacture Canadian zinc-plated drawn-steel cartridge cases is as follows:

58. A. Drawing and Machining

- (i) Early steps which are of little interest in the present investigation
- (ii) Hot water rinse, sulphuric acid pickle, zinc-phosphate application, soap coat, dry
- (iii) Fourth draw
- (iv) Last trim
- (v) Clean, rinse
- (vi) Heading
- (vii) First head turn and pierce primer hole
- (viii) Clean, rinse (via overhead conveyer)
- (ix) Salt bath tempering including:
 - (a) Barium and sodium chloride bath
 - (b) Brine quench
 - (c) Dry and heat over gas flame (city gas)
 - (d) Sodium nitrate bath
 - (e) Water rinse
 - (f) Dry
- (x) Clean, rinse
- (xi) Flange, primer hole and mouth anneal (induction heating)

- (xii) Hot water rinse, sulphuric acid pickle, zinc phosphate application, soap coat, dry
- (xiii) Tapering
- (xiv) Clean, rinse (via overhead conveyer)
- (xv) Second head turn
- (xvi) Clean, rinse (via overhead conveyer)
- (xvii) Abrasive cleaning with 60 to 120 grit paper on the outside and No. 50 steel grit and wire brush on the inside.

NOTE: This procedure was added to the process by the manufacturer after the corrosion spots were first observed.

- (xviii) Bead
- (xix) Mouth size
- (xx) Plug and ring gage
- (xxi) Primer hole rectifying
- (xxii) Clean, rinse (via overhead conveyer)
- (xxiii) Inspection before plating

NOTE: Cleaning and zinc-phosphate treatments were done in proprietary materials. Pickling was done in sulphuric acid (6 to 8% by volume commercial acid--Sp. G. 1.84) at 165 to 175°F (74 to 80°C). Soap-coating was done in an 11 to 12% soap-and-water mixture at 180 to 190°F (82 to 88°C). The soap is a proprietary product.

59. B. Electroplating

The cases are electroplated in an automatic machine with a single horizontal conveyer equipped with racks, each designed to hold one case in the mouth-up position. Each rack consists of an electrically-insulated outer frame which supports the case and provides the cathode contacts at the mouth and head. A one-inch nickel tube with a flared piece of mild steel securely fastened to one end with an 18-8 stainless steel nut and bolt, is attached to the frame by means of an electrical insulator and serves as an internal anode. Mechanical devices at convenient locations along the line tilt each rack slightly at right angles to the conveyer and then return it to the vertical position. This action drains the case and transfers it from one tank to the next. Each cycle consists of the following:

(xxiv) Cathodic cleaning in alkaline cleaner

NOTE: This has been changed to anodic cleaning in an alkaline cleaner containing at least 3% (4 oz/gal or 30 gm/litre) of sodium hydroxide as suggested partly by the writer and partly by the manufacturer.

(xxv) Rinse in water

- (xxvi) Pickle in sulphuric acid (10% by volume of commercial acid Sp.G. 1.84) at 160°F (71°C)

NOTE: This has been changed to an anodic pickle in sulphuric acid (60% by volume of commercial acid Sp.G. 1.84) at 70°F (21°C) to open up the pitted steel surface as suggested partly by the writer and partly by the manufacturer.

- (xxvii) Two separate rinses in water

NOTE: Sprays have been added. Suggested by the writer.

- (xxviii) Anodic cleaning in a solution containing 8 oz/gal (60 gm/litre) sodium cyanide and 4 oz/gal (30 gm/litre) sodium hydroxide.

- (xxix) Electroplate in a solution as follows:

Zinc	4 to 5 oz/gal (30 to 38 gm/l)
Sodium cyanide	12 to 13.5 oz/gal (90 to 100 gm/l)
Sodium hydroxide	10.5 to 12 oz/gal (79 to 90 gm/l)
Temperature	80°F (27°C)
Current density	74 amp/sq. ft. (8.0 amp/sq. dm) for exterior surfaces 54 amp/sq. ft. (5.8 amp/sq. dm) for interior surfaces

NOTE (1): Cases are tilted once during plating to replenish the electrolyte in the interior.

NOTE (2): The plating bath is being zinc-dust treated by the new electrolytic process suggested by the writer.

- (xxx) Three separate rinses in water
- (xxxi) Chromate treatment in proprietary solution
- (xxxii) Two cold and one hot water rinses
- (xxxiii) Dry in a stream of warm air, 140°F (60°C)
- (xxxiv) Final inspection
- (xxxv) Placed in cardboard cartons ready for shipment to the
Filling Division.

APPENDIX III
THE HYDROCHLORIC ACID CORROSION TEST FOR
ZINC COATINGS ON STEEL

Scope

60. This method is for determining the dissolution rate of electroplated zinc coatings on steel, in dilute hydrochloric acid.

Reagent

61. Hydrochloric acid (10 per cent solution by volume of 12N C. P. acid, Sp.G. 1.19, in distilled water).

Equipment

62. 1-2000 ml beaker
1-1500 ml beaker
1-60° glass funnel, 75 mm diameter and 70 mm stem
1-50 ml burette
1-burette support
3-steel panels (1 1/4" by 1 1/4") which have been electroplated with zinc.

Preparation of Test Panels

63. One square inch of electroplated zinc on each test panel is left exposed while the remaining surface areas, including the edges, are masked with electroplater's tape. The exposed area must not be scratched or soiled in any way.

Procedure

64. Place a masked panel horizontal on the bottom of the 1500 ml beaker, with the exposed surface uppermost. Cover the sample with the 60° funnel. Fill the burette with the prepared hydrochloric acid. Slowly pour sufficient acid into the 1500 ml beaker to cover the stem of the funnel. Cover the open end of the burette with a finger, then invert and immerse it in the acid. Keeping the end of the burette below the surface of the acid, place the open end over the funnel stem, and lower it down onto the tapered section. Clamp the burette in the support stand. Lower the top surface of the column of acid to the 50 ml mark on the burette.

65. The exposed zinc will be attacked immediately by the hydrochloric acid, and hydrogen will be produced. The hydrogen will rise into the burette displacing the acid. Each minute make a record of the total volume of gas collected until the steel has been exposed or the column of acid has been completely displaced with hydrogen. Freshly prepared acid should not be used more than three times, to ensure accurate results. (It should be pointed out that the rate of gas evolution increases materially as soon as the steel is exposed to the action of the acid).

66. The accepted dissolution rate of the electroplated zinc coating will be the average of the results obtained from three panels.

Modified Procedure for Use with Cartridge Cases

67. This modified procedure has been performed successfully on the exterior surfaces of finished cartridge cases with the aid of a plastic apparatus devised by the writer. This is in the form of a saddle which is clamped onto the case with "U" bolts and takes the place of the 1500 ml beaker. A hole is drilled through the plastic saddle to expose a zinc-coated area of one square inch. A plastic cylinder approximately 100 mm in diameter and 160 mm long is attached to the upper surface of the saddle in such a way that it surrounds the hole and retains the hydrochloric acid when the apparatus is clamped to a case. A rubber seal is used between the saddle and the coated surface of the case.

68. The test is performed by clamping the apparatus to the case at the desired location and placing the inverted funnel over the hole in the saddle. Continue the procedure as previously directed in the instructions. Cases used in this test can be stripped and replated without loss.