EFFECTS AND CONTROL OF

NICKEL AND IRON IMPURITIES IN

CYANIDE ZINC PLATING BATHS

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ABSTRACT

Spots of dark corrosion product appeared on steel cartridge cases of 105 mm and 3 inch, 70 calibre types after they had been cyanide zinc plated, chromated and stored in an unheated building for from one to eight months. In searching for the cause of and remedy for these spots, the plating bath was analyzed and shown to contain small amounts of nickel, copper and chromium, and much larger amounts of ferrous iron. These same metals were found in the zinc on the cases.

Experimental steel coupons plated in this bath gave spots of dark corrosion product after immersion in distilled water exposed to the atmosphere. In similar experiments with a plating bath made from pure chemicals the plated coupons did not give dark spots. Accordingly it was concluded that the dark spots on the cases were due to the presence of nickel and the other metals found in the plant bath and in the zinc coatings produced in the plant.

A quick hydrochloric acid test was developed to determine semi-quantitatively the amounts of these contaminating metals present in zinc coatings. With the aid of this test it was found possible to determine the source of the contaminants in the coatings, how to reduce the amount of them entering the plating bath and thus the zinc coating, and how to remove the contaminants which had succeeded in entering the plating bath.

Cartridge cases are now being zinc plated on an industrial scale using decontaminated baths. The freedom of the bath from nickel, iron and similar impurities is being checked periodically by subjecting plated samples to the hydrochloric acid test.

INTRODUCTION

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., the exterior surface being plated with a Type II, Class 2 coating and the interior surface with a Type II, Class 3 coating.

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.

In December 1958, tiny dark 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 require storage

under tropical conditions which would be much more corrosive than the present ones.

The Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada, was requested by both the manufacturer and the user of the cases to make a thorough investigation of the causes of this deterioration and to recommend a remedy.

The investigation is described under the main headings: 1) Examination of materials involved in the problem, 2) Laboratory corrosion testing, 3) Improvement of the zinc plating procedure.

INVESTIGATION

1. Examination of Materials Involved in the Problem

Metallographic Examination of Plated Cartridge Cases

A metallographic examination by J. J. Sebisty[1] revealed that the dark spots seen on the zinc-plated cartridge cases in storage, were mounds of corrosion product each covering a tiny uncoated pitted area of steel.

Analysis of Zinc Plating Bath

The bath used for plating the cartridge cases contained sodium cyanide, sodium hydroxide and zinc cyanide as the major constituents. In addition, chemical analysis showed the presence of 1.4 g/l iron, 0.015 g/l nickel, 0.03 g/l chromium, and 0.004 g/l copper.

The Corroded Zinc Coatings

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. In the spectrographic analysis of a typical zinc coating iron was found to be the major impurity (1.3 per cent); however, 0.1 per cent nickel and 0.06 per cent copper were present, as
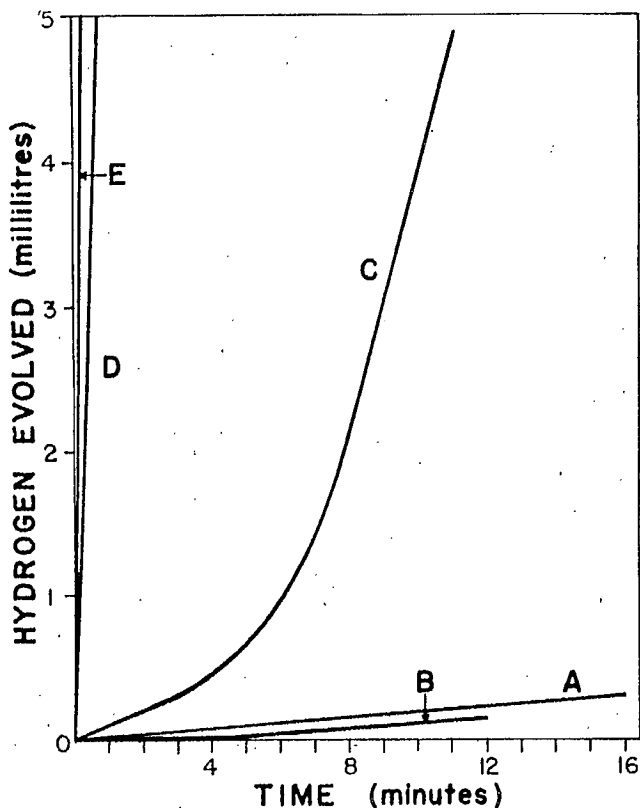
Fig. 1. Dissolution rates of laboratory-produced and plant-produced electroplated zinc coatings: A—laboratory-produced coatings on mild steel, from a purified cyanide plating bath; B—plant-produced coating on mild steel, from a commercial cyanide plating bath; C—plant-produced coating on mild steel, 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 non-Canadian cartridge case, from a commercial cyanide plating bath.

well as a trace of chromium. It was shown by X-ray diffraction that the dark spots found on the cartridge cases in storage, consisted largely of basic zinc carbonate (4 ZnO · CO_2 · $4H_2O$). The material causing the color in the spots remained unidentified.

2. Laboratory Corrosion Testing

Investigation showed that dark corrosion spots similar to those observed on cases in storage, were not produced during salt spray testing. Corrosion tests of this kind are in some specifications for zinc coatings.

As already stated, it was believed that zinc-coated cartridge cases must be covered with a film of water, probably somewhat resembling distilled water containing dissolved carbon dioxide, during at least 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 exposed to the air at 70F. In this way dark 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 two to three hours.

Mild steel coupons plated in the plant plating solution in the laboratory, and tested in the same way, developed similar dark spots. On the other hand, similar coupons plated in a solution made from reagent grade chemicals did not develop dark spots in this test.

Mild steel coupons plated in solutions made from reagent grade chemicals, but containing in addition 0.09 and 10.45 mg/l of nickel as sulfate, developed dark spots in the distilled water test. The spots in the zinc coating from the solution of

lower nickel content, were fewer and the pits underneath were shallower than those in the coating from the solution of higher nickel content.

3. Improvement of the Zinc Plating Process Contamination of Plating Baths

It soon became obvious that the present investigation would require numerous tests of zinc coatings to determine the extent of their contamination by small traces of other metals. Ordinary chemical and spectrographic analyses would have been very time-consuming and the results might not have been accurate. Therefore a different method of testing the coatings was developed.

Many investigators have found that relatively pure zinc is attacked comparatively slowly by dilute acids, and that small proportions of other metals in the zinc increase or decrease its rate of dissolution.[2] In view of this, a test for determining the rate of dissolution of electroplated zinc coatings in dilute hydrochloric acid was developed on the assumption that it would give an indication of the amount of metallic impurities present in the coatings. The results of chemical and spectrographic analyses showed that by far the greatest proportion of contamination was due to iron and nickel. The rate of dissolution was determined by measuring the rate of evolution of hydrogen. (Such a test, using dilute sulfuric acid, was used by F. W. Harris[3] in testing cast zinc specimens.) The apparatus and procedure used in this hydrochloric acid test are described in the Appendix.
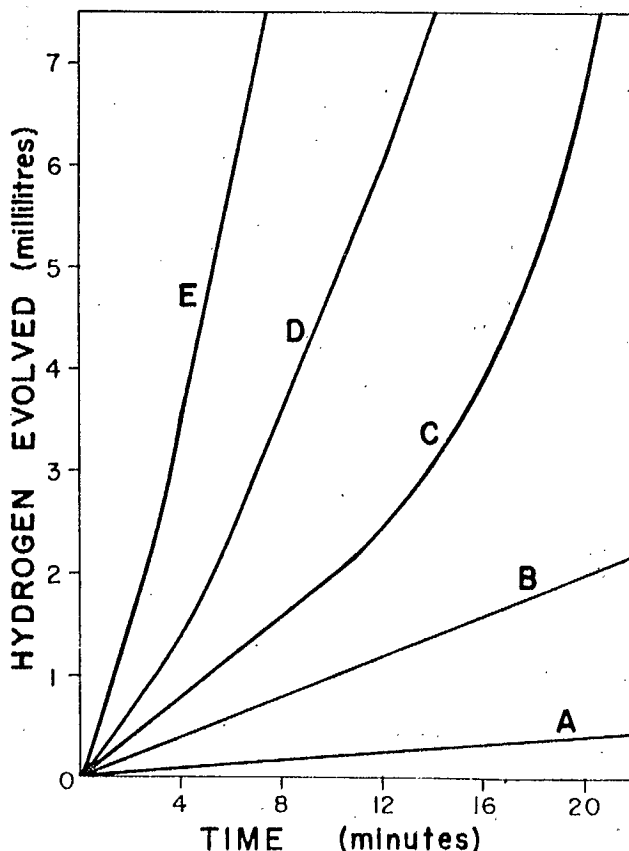

Fig. 2. Variation of dissolution rates of electroplated zinc coatings on cartridge cases with the number of cases plated: A—laboratory-produced coating on mild steel, from a purified cyanide plating bath (included for comparison); B—laboratory-produced coating on cartridge-case steel, from freshly-prepared 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.

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This procedure was first used for obtaining a measure of the metal contamination in various zinc coatings from laboratory experiments and plant production. Samples from other plants were also 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 Fig. 1 illustrate graphically the great differences which were found in electroplated zinc coatings on steel. It is of interest to note that by far the greatest dissolution rates were obtained from zinc coatings on cartridge cases.

The next phase of this part of the investigation was to replace the contaminated bath at the plant by a new one produced from commercially pure chemicals, and to use the latter for plating cartridge cases. 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. Cartridge cases were plated continuously in the plant, starting with the same new bath. Plated cases No. 5, 686 and 1276 were removed and subjected to the hydrochloric acid test (1276 cases were approximately one and one-half days' production). For comparison, a piece of mild steel was zinc plated in a purified* bath in the laboratory and the resulting coating was subjected to the hydrochloric acid test. The results of the tests performed on the various coatings are shown in Fig. 2.

As shown in Fig. 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, i.e., under the most nearly ideal conditions. However, the rate of

*Purification by the "zinc-dust electrolysis" process is described later.

Fig. 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 per cent 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 2 hr with 2 zinc anodes (for comparison); B—coating plated after bath had been used for 20 min with stainless steel (18-8) and zinc anodes; C—coating plated after bath had been used for 2 hr with stainless steel (18-8) and zinc anodes; D—coating plated after bath had been used for 2 hr with mild steel and zinc anodes; E—coating plated after bath had been used for 2 hr with nickel and zinc anodes; F—coating plated after bath had been used for 35 min with Inconel and zinc anodes.

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. 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.

Since it was recalled that iron and nickel had been found in the original plating bath used at the plant, one or both of these was immediately suspected of being the contaminant which produced the great change in the rate of dissolution of the zinc in the acid test. To investigate this a series of laboratory experiments was performed. Zinc coatings were plated from solutions containing impurities as follows: (a) no appreciable impurities, (b) 0.05, 0.31 and 1.25 g/l iron in the ferrous state, (c) 0.09 mg/l nickel. The results of the hydrochloric acid tests on these coatings are shown in Fig. 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
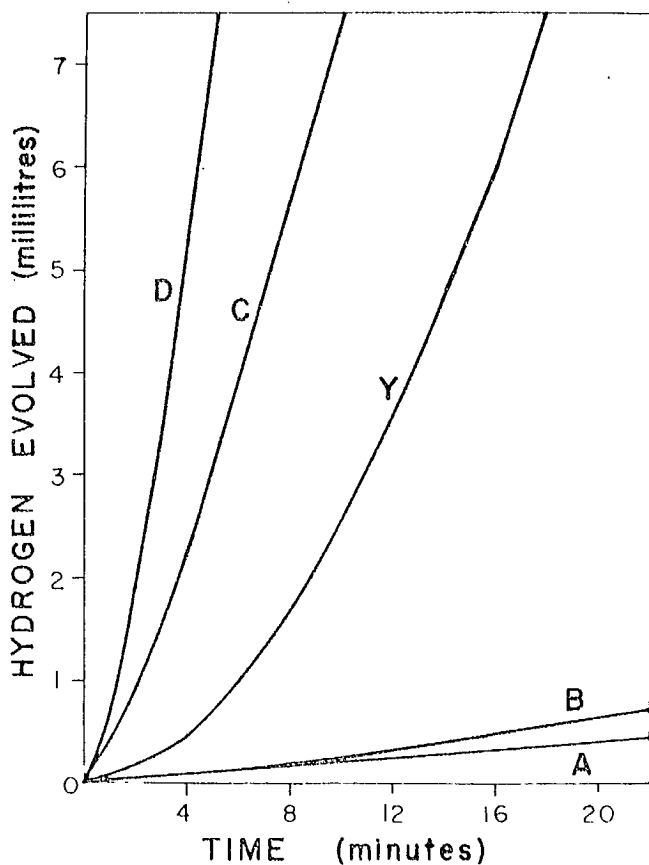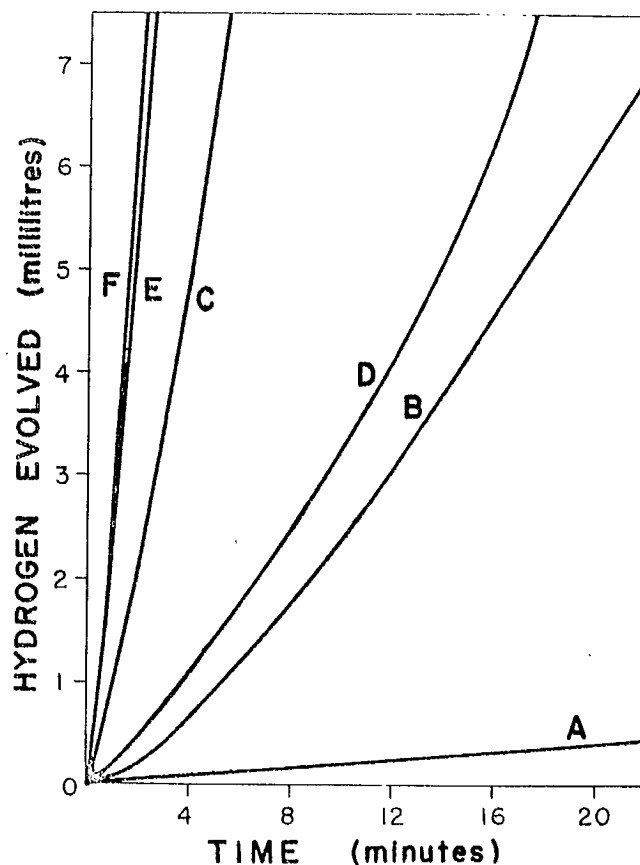

Fig. 3. Dissolution rates of laboratory-produced zinc coatings on mild steel, from purified zinc-plating baths containing ferrous iron or nickel as impurities: A—bath with no appreciable impurities; B—bath containing 0.05 g/l iron; C—bath containing 0.31 g/l iron; D—bath containing 1.25 g/l iron; Y—bath containing 0.09 mg/l nickel.

a much larger amount of iron than of nickel is required to produce the same effect. In view of the fact that copper and chromium were found in the zinc coatings and the plating bath it is possible that these elements also are undesirable contaminants. However, the effect of their presence was not studied during the present investigation.

Source of Plating Bath Contaminants

The next problem was to determine the source of the contaminants which apparently continued to enter the plant plating bath while it was in use. The internal anode used in zinc plating the interior surface of each cartridge case 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 contained about eight per cent nickel. It appeared that the bath could have been contaminated by the very slow but continuous solution of these metals.

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 per cent nickel and about 70 per cent iron) and Inconel (containing 76 per cent nickel and 7.5 per cent iron, as well as 15 per cent chromium). 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 two hours and the non-zinc anode had then been removed. All baths had been purified before use by the zinc-dust electrolysis process, and all cathodes were of mild steel.

The results of the hydrochloric acid tests on the plated samples are given in Fig. 4. It is believed that the increased dissolution rates shown by curves B, C, D, E and F, as compared to that of curve A, were due to nickel and/or iron dissolved from the anodes used in those baths. Here again it was shown that nickel is a much more serious contaminant than iron. Since the Inconel (76 per cent nickel) had an even greater effect than pure nickel it is possible that chromium also is a highly undesirable contaminant.

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. Here 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 in the hydrochloric acid to increase rapidly. When it was disconnected from the circuit but allowed to remain in the bath during plating, similar results were obtained but a longer time was required, and of course the internal surfaces were not plated. When the internal anode was removed from the bath the dissolution rates remained low, the interior surfaces again remaining unplated. The dissolution rates of the plated metal continued to be low, and the interior surfaces were plated, when internal anodes of zinc were used.

Prevention of Plating Bath Contamination

Even though the use of internal zinc anodes would keep the contaminant content of the plating bath at a desirably low level, the shape of the zinc anode would change due to dissolution of the zinc. This in turn would cause an undesirable change in the thickness of the internal zinc coating.

In the hope that electrolytic iron might perform more satisfactorily than mild steel as an internal anode material, labora-
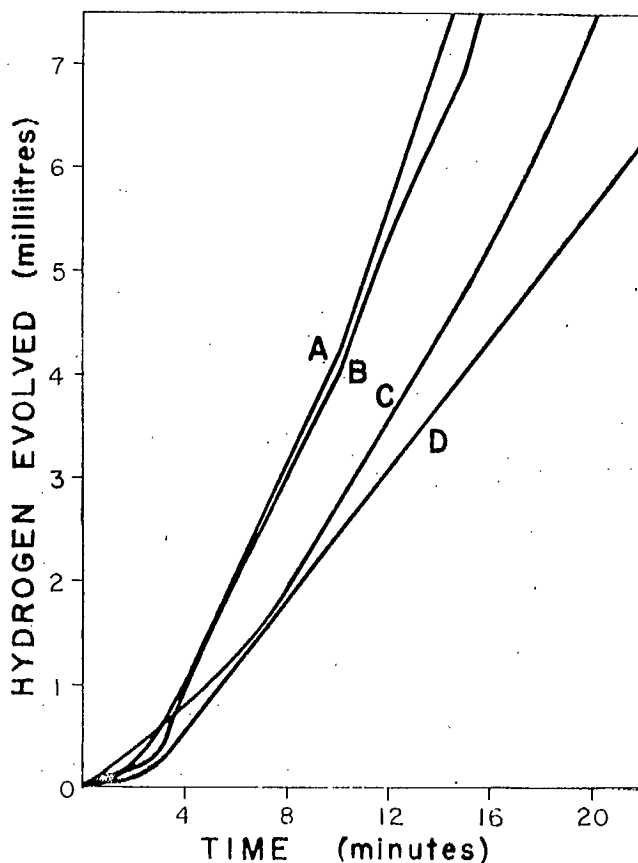

Fig. 5. Dissolution rates of laboratory-produced zinc coatings on mild steel, from commercial plating baths some of which had been purified by preliminary electrolysis using zinc anodes and mild steel cathodes (dummying): A—coating from commercial plating bath with no prelim. electrolysis; B—coating from commercial plating bath "dummied" at a low current density for 16 hr; C—coating from commercial plating bath "dummied" as in B. Anodes cleaned once in acid during "dummy" treatment; D—coating from commercial bath "dummied" as in B. Anodes cleaned several times in acid during "dummy" treatment.

tory zinc plating experiments were conducted in which mild steel and electrolytic iron anodes of similar dimensions were used separately with zinc anodes. The compositions of the mild steel and the electrolytic iron are given in Table I. The results revealed that the anodes of electrolytic iron lost an average of 0.005 grams and those of mild steel an average of 0.059 grams during a plating time of three hours. It may be concluded, therefore, that electrolytic iron would be a more desirable material for internal anodes than mild steel and/or nickel.

Removal of the Contaminants from the Plating Bath

The next stage of the investigation consisted of a search for a satisfactory method of purifying zinc cyanide plating baths which had been contaminated by elements such as nickel and iron, and which would give good results on a large commercial

TABLE I

ANALYSES OF IRON INTERNAL ANODES (PER CENT)

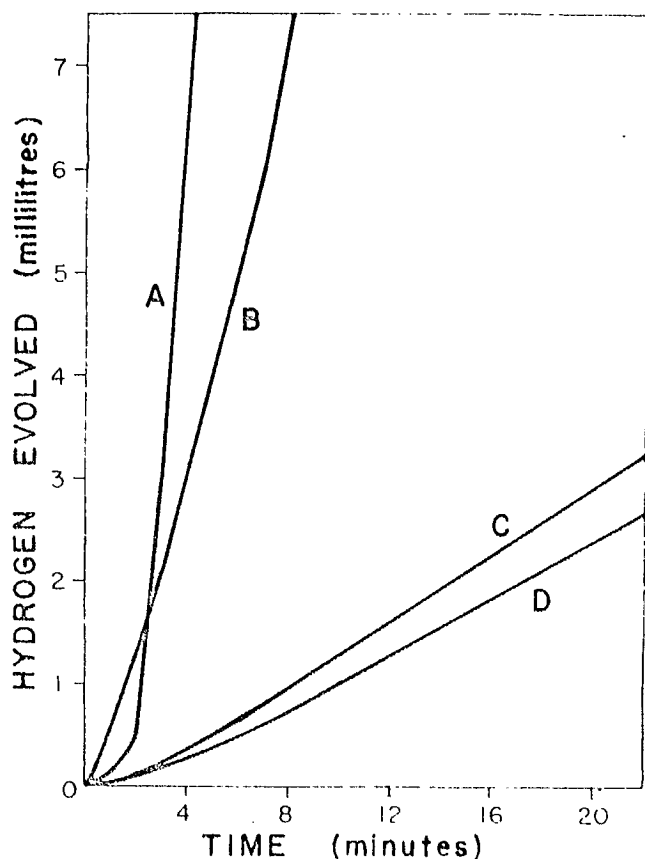| Anode Material	Carbon	Nickel	Manganese	Silicon	Sulphur	Phosphorus
Mild steel	0.16	0.066	0.65	0.14	0.045	0.034
Electrolytic iron	0.16	0.015	0.05	0.03	0.009	0.025

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Fig. 6. Dissolution rates of laboratory-produced zinc coatings on mild steel, from plating baths purified by various zinc-dust treatments: A– Coating from severely contaminated bath (for comparison); B– coating from same bath as A after zinc-dust treatment at 70F; C – coating from same bath as A after zinc-dust treatment at 113F for 24 hr; D - coating from same bath as A after zinc-dust treatment at 70F accompanied by electrolysis, for one hr.

scale. Several procedures which had 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 Fig. 5

The usual method of treating a contaminated bath with zinc dust at room temperature with thorough agitation, and then letting the dust settle in the bath for 48 hours, produced little improvement in the experiments. The treatment recommended by H. J. Backe and R. F. C. Robinson,[1] in which the bath was treated with zinc dust at 113F for 24 hours gave a major improvement. It should be noted that the treatment of a bath by either of these procedures necessitates a stoppage of the electroplating process.

Much better results were obtained by a procedure called in this paper the zinc-dust electrolysis process, 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; however, 5 to 10 grams of zinc dust/litre of solution and one-half to two hours appeared 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.

With this modification of the earlier zinc-dust process it is possible to purify the bath more thoroughly in considerably less time. When a purifying tank is used this process can proceed on a continuous basis without interruption in the plating. If it should be necessary to use the plating cell itself, a shut-down period of only two to three hours would be required for the whole procedure including the filtration. Although purification of baths with zinc dust has been proposed by a number of other investigators, it is believed that this particular modification has not been described in the literature. The results obtained in experiments with the different zinc dust treatments are shown in Fig. 6.

It has been shown in Figs. 3 and 4 that a very small amount of nickel is a serious contaminant when present in a zinc cyanide plating bath. This contamination can be avoided by using internal anodes of electrolytic iron, which are much cheaper than anodes of nickel or nickel alloys such as 18-8 stainless steel or Inconel. As shown above, this iron also dissolves slowly in the bath, but it can be removed quite rapidly by means of the zinc-dust electrolysis process described above.

It is important to add that the current efficiency of zinc plating is greater in cyanide baths purified by the zinc-dust electrolysis process than in cyanide baths containing impurities such as nickel and ferrous ions. Ferric ion is not considered to be a contaminant.

Decontaminating Zinc Anodes

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. On some occasions during the present investigation, it was observed that a plating bath purified by the zinc-dust electrolysis process 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, sulfuric or nitric acids failed to remove all of the contaminants from the zinc. It was found that anodes which had been used during the purification of a plating bath by the zinc-dust electrolysis treatment were quite free from contamination, and the resulting zinc coatings always gave a good hydrochloric acid test when produced in purified plating baths. Experimental data comparing the various methods of decontaminating anodes are given in Fig. 7.

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

The zinc-dust electrolysis process just described was used successfully several times, to purify both the 100 gallons of plating solution and the zinc anodes in a zinc-plating bath that was used to plate steel cartridge cases during pilot plant experiments.

The 6000-gallon bath and the zinc anodes in the manufacturer's automatic plating machine, which had previously been contaminated with nickel and iron, also were successfully treated in situ by the zinc-dust electrolysis process. However, suitable equipment was not available to install an auxiliary purification tank for continuous treatment by the new process while plating was in progress, so the following alternative procedure was used to keep the impurities at a low level:

The plating solution in the 6000-gallon bath was pumped continuously through a large filter which had been thoroughly coated with zinc dust. The filter was recoated when the zinc dust began losing its efficiency. This was indicated by an increase in the rate of hydrogen evolution obtained during
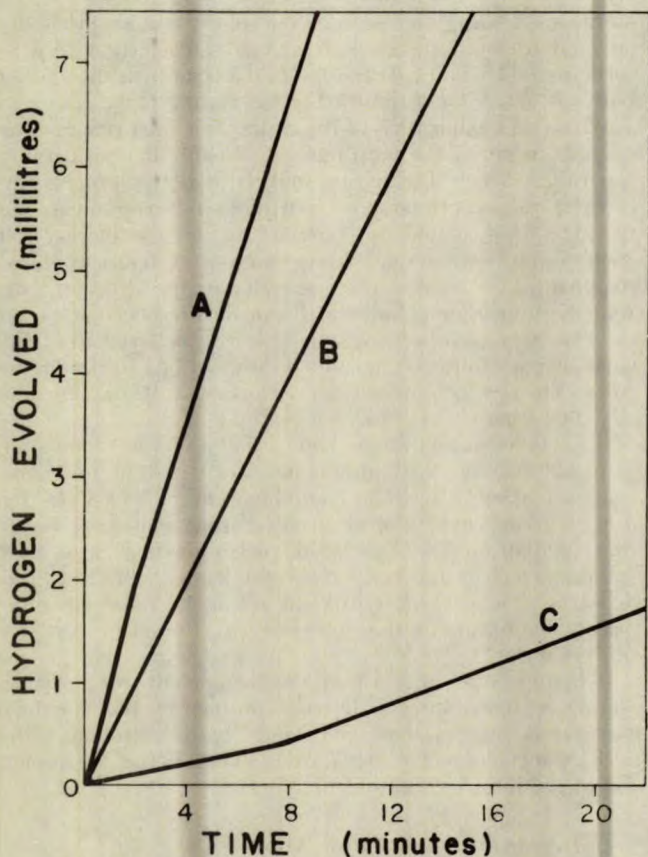
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Fig. 7. Dissolution rates of laboratory-produced zinc coatings on mild steel, from purified plating baths having zinc anodes which had been used in contaminated bath and then subjected to various cleaning treatments: A—from bath having anodes previously used in contaminated bath; B—from bath having anodes acid-cleaned after use in contaminated bath; C—from bath having anodes cleaned by zinc-dust electrolytic treatment after use in contaminated bath.

hydrochloric acid tests on a succession of zinc coatings produced on steel cartridge cases. The plant, employing the zinc-dust electrolysis process to purify the bath, followed by continuous filtration through zinc dust, and using electrolytic iron internal anodes, has been in operation for several months. During this time more than 35,000 cartridge cases have been plated and, on the cases tested by the hydrochloric acid test, the average rate of hydrogen evolution has been maintained at 0.15 ml/minute for at least the first 12 minutes. It is understood that in the commercial plant, equipment will be installed for continuous zinc-dust electrolysis treatment in view of the fact that more effective decontamination of the bath can be obtained by this method.

Prior to this investigation, corrosion spots had been observed on cases soon after they had been placed in storage; however, no spots have been reported on cases produced by the new procedure, after nine months in similar storage.

CONCLUSIONS

Zinc-electroplated steel cartridge cases in unheated storage had shown a tendency to corrode excessively, the deterioration being in the form of a localized attack of the coatings with the production of dark corrosion product consisting largely of basic zinc carbonate. This poor resistance to corrosion has been shown to be largely due to the contamination of the zinc plating baths with iron, nickel, and possibly copper and chromium, by far the worst offender being nickel.

It has been shown that this undesirable condition can be greatly reduced by an improved method of treating the zinc electroplating solution and the anodes. In addition it has been shown that, by a suitable choice of internal anode material for the electroplating process, the rate of bath contamination can be greatly reduced.

A hydrochloric acid dissolution test for zinc coatings, which has proven to be a rapid and accurate method of detecting the presence of contaminants such as nickel and iron in the coatings, has been developed.

APPENDIX
THE HYDROCHLORIC ACID DISSOLUTION TEST FOR ZINC COATINGS ON STEEL

Preparation of Test Panels

One square inch of zinc coating on each of three similarly electroplated test panels 1.25 by 1.25 in. is left exposed while the remaining surface, including the edges, is masked with electroplater's tape. The exposed area must not be scratched or soiled in any way.

Procedure

Place one of the masked panels horizontally on the bottom of a 1500 ml beaker with the exposed surface uppermost. Cover the panel with a 60° funnel. Fill a 50 ml burette with hydrochloric acid (10 per cent by volume of 12N CP acid in distilled water). Slowly pour sufficient acid of the same strength 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 a support stand. Lower the top surface of the column of acid to the 50 ml mark on the burette.

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

A procedure for the hydrochloric acid testing of plated cases, in which the cases are not destroyed, has also been developed by the author.

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