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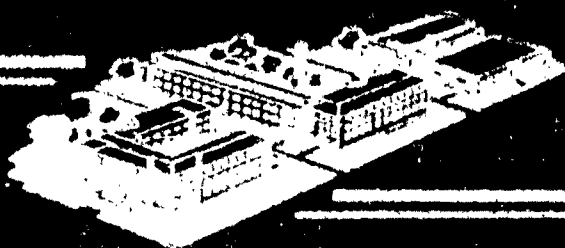
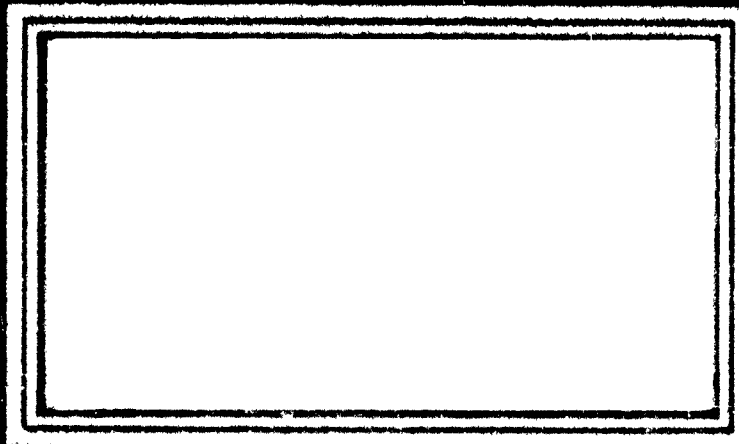
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PROGRESS REPORT



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INTERIM TECHNICAL REPORT

on

A RESEARCH INVESTIGATION OF POSSIBILITIES
FOR OBTAINING HOT-HARD ELECTRODEPOSITED
CHROMIUM OR CHROMIUM-BASE ALLOYS FOR
CANNON

to

WATERTOWN ARSENAL

October 1, 1952

by

William H. Safranek, J. Edwin Bride, George M. Scanlon,
Cloyd A. Snively, and Charles L. Faust

Contract No. DA-33-019-ORD-766

W. A. L. File No. 691.1/25-51

O. O. Project No. TR3-3003B

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INTERIM TECHNICAL REPORT

Contractor: Battelle Memorial Institute

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Ordnance District: Cleveland, Ohio

Contract Number: DA-33-019-ORD-766 W. A. L. File No. 691.1/25-51

O. O. Project Number: TR3-3003B

R. A. D. No. TR3-3003B

Priority: War Department 2B

Title of Project: "A Research Investigation of Possibilities for Obtaining Hot-Hard Electrodeposited Chromium or Chromium-Base Alloys for Cannon".

Authors: William H. Safranek, J. Edwin Bride, George M. Scanlon, Cloyd A. Snively, and Charles L. Faust.

Object: To investigate possibilities for an erosion-resistant chromium or chromium-alloy electroplate for lining gun tubes.

Summary: The properties and plating characteristics of hot-hard, chromium-iron alloy plate were improved by modifying the plating conditions. A reduction in stress in the plate and better bridging of the plate over machining scratches in cannon steel were the principal improvements. The bore of an erosion-gage weapon insert was plated with the improved type of deposit. A new procedure, including electropolishing, and excluding the chromium-strike plate, was used to adhere the alloy plate to the bore surface. The insert will be forwarded to Watertown Arsenal for firing tests. Laboratory tests on plates produced with the same procedure indicate that the alloy was bonded to cannon steel.

Another erosion-gage weapon insert was plated with chromium-iron alloy several months before the development of the plating conditions for reducing stress in the plate. Under the conditions of the firing tests at Watertown Arsenal, the chromium-iron alloy did not adhere to the chromium-strike plate.

The wear resistance of chromium-iron plate was improved by adding addition agents to the plating bath for modifying the plate structure. The deposit with the better wear resistance is banded, whereas the plate with the lesser wear resistance is columnar. The columnar structure is free

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of stress cracks, but, so far, the banded structure has contained cracks caused by excessive stress.

Conclusions

The progress on improving the properties of the chromium-iron alloy plate presages an ultimate successful development of an erosion-resistant electroplated lining for gun tubes. The outlook is encouraging for obtaining the banded plate with excellent wear resistance. To achieve this objective, further research is required.

Report Period

This report covers the period from February 10, 1952, to October 1, 1952.

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**A RESEARCH INVESTIGATION OF POSSIBILITIES
FOR OBTAINING HOT-HARD ELECTRODEPOSITED
CHROMIUM OR CHROMIUM-BASE ALLOYS FOR CANNON**

to

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BATTELLE MEMORIAL INSTITUTE

by

**William H. Safranek, J. Edwin Bride, George M. Scanlon,
Cloyd A. Snavely, and Charles L. Faust**

October 1, 1952

INTRODUCTION

This is an interim report on the continuation of the research program for the development of an improved erosion-resistant plating for gun tubes. Previous reports described the development of a process for plating chromium-iron alloy with certain properties that were superior to the properties of conventional hard chromium plate.*

The chromium-iron alloy, containing approximately 94 per cent chromium and 6 per cent iron, was deposited without the crack system

*The previous reports were as follows:

- (1) Final Technical Report on "A Research Investigation of Possibilities For Obtaining Hot-Hard Electrodeposited Chromium or Chromium-Base Alloys For Cannon", Battelle Memorial Institute, February 9, 1952 (Contract No. DA-33-019-ORD-9);
- (2) Interim Technical Reports on "A Research Investigation of Possibilities For Obtaining Hot-Hard Electrodeposited Chromium or Chromium-Base Alloys For Cannon", Battelle Memorial Institute, September 1, 1950, September 15, 1951, and January 15, 1952 (Contract No. DA-33-019-ORD-9);
- (3) Final Technical Report on "A Research Investigation of Possibilities For Obtaining Hot-Hard Electrodeposited Chromium or Chromium-Base Alloys For Cannon", Battelle Memorial Institute, November 15, 1949 (Contract No. W33-019-ORD-6397).

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characteristic of conventional hard chromium and did not soften appreciably after heating to at least 1200 F. The alloy-plating bath comprised principally trivalent chromium, instead of the hexavalent chromium contained in the conventional chromium bath. The plating efficiency and the rate of deposition were much greater in the trivalent-chromium solution.

Bore surfaces of sections of 40-mm gun tubes and erosion-gage weapon inserts plated successfully with the chromium-iron alloy. However, the adherence was not satisfactory under the conditions imposed in firing an erosion-gage weapon. The firing-test results also indicated a need for improving the properties of the plate, because, as a result of the firing test, cracks appeared in the plate over circumferential machining scratches in the bore surface.

New work during the interim covered by this report was aimed at improving the properties of the chromium-iron plate and its adherence to cannon-bore surfaces. Modifications in plating conditions were established for improving the properties of the plate. These modifications were adapted to plating the bore surfaces of seamless tubes and, subsequently, the bore surfaces of erosion-gage weapon inserts.

EXPERIMENTAL DATA*

Properties of Chromium-Iron Plates Produced in the Chromic Sulfate Bath Operated With Lead-Tin-Alloy-Coated Anodes

Results of Plating Brass Tubes

A previous report described the development of a plating bath prepared with basic chromic sulfate and operated with lead-tin-alloy-coated anodes.** The effect of changing the pH of the bath on the properties of the chromium-iron alloy plate was determined by plating smooth-bore brass tubes and increasing the pH by increments of about 0.3 unit. The

*The data were recorded in Laboratory Record Books Nos. 6526, pages 91 to 100, 6995, pages 1 to 62, and 7121, pages 14 to 23.

**Final Technical Report (Contract No. DA-33-019-ORD-9), February 9, 1952, Battelle Memorial Institute, on "A Research Investigation of Possibilities For Obtaining Hot-Hard Electrodeposited Chromium or Chromium-Base Alloys For Cannon".

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results, detailed in Table 1, showed that increasing the pH of the bath to 1.6 improved the properties of the plate. Previously, the pH of the bath was 1.15 for plating erosion-gage Weapon Insert 68X, which failed in the firing test.

Results of Plating Erosion-Gage Weapon Insert 67X

Erosion-gage Weapon Insert 67X was plated with chromium-iron alloy with the pH of the chromic sulfate bath adjusted to 1.6. The other plating conditions are detailed in Appendix I. The thickness of the plate was about 0.0035 inch.

A cross section of the plate one inch from one end of the tube is shown in Figure 1. It was crackfree, as plated. The plate on the one-inch section appeared to be satisfactorily adherent, judging by chisel testing*, after heating three hours at 750 F and cooling in the furnace. However, cracking of the plate was evident after the heat treating. The cracking was particularly noticeable over the circumferential machining scratches in the surface of the steel left by the reamer or side-cutting tool. The scratches apparently caused the defect in the plate.

Under the conditions imposed by the firing test, the adherence of the plate was unsatisfactory. The first round caused blistering and the second round caused spalling of a part of the chromium-iron alloy plate from the chromium-strike plate. The failure has been attributed to the passivation of the surface of the chromium-strike plate when the insert was submerged in the chromium-iron plating bath before plating was started. Ferric iron and hexavalent chromium were the passivating agents in the plating bath.

Hot-Hardness Data

Vickers hardness measurements at elevated temperatures on a chromium-iron-alloy electrodeposit containing 87 per cent chromium and 13 per cent iron (a flat panel) are given in Table 2. The data confirm the previous expectation that the chromium-iron plate would retain its hardness while being heated. Very little softening occurred during heating to 930 F. The hardness remained about 200 Vickers during heating to 1300 F. The procedure for plating the 87 per cent chromium-13 per cent iron alloy was the same as that used to plate erosion-gage Weapon Insert 67X, except for the difference in agitation.

*The chisel test consists of cutting chips out of the plated surface with a round-nosed cold chisel. The absence of flaking or peeling of the plate from the steel surface denotes good adherence.

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TABLE 1. PROPERTIES OF CHROMIUM-IRON ALLOY PLATES —
EFFECT OF CHANGING THE pH OF THE CHROMIUM
SULFATE BATH⁽¹⁾ ON PLATES IN SMOOTH-BORE
BRASS TUBES⁽²⁾

Bath, pH	Cathode Current Density, amp/sq ft	Properties of the Plates
1. 15	240	Cracked and peeling from the chromium-strike plate
1. 15	200	Ditto
2. 0	240	Blistered and flaking from the chromium-strike plate
1. 6	240	Crackfree and blisterfree; gray mat; smooth except for a few scattered nodules
1. 8	240	Blistered and flaking from the chromium-strike plate
1. 7	240	Ditto
1. 45	240	Crackfree and blisterfree; gray mat; smooth except for a few scattered nodules and pits.

(1) The 4-gallon plating bath was prepared with 3.78 lb/gal basic chromium sulfate (manufactured by Mutual Chemical Company and designated MSO), 0.42 lb/gal $(\text{NH}_4)_2\text{SO}_4$, 0.107 lb/gal $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and 0.085 lb/gal $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. It contained 74 g/l trivalent chromium, a trace of hexavalent chromium, 2.0 g/l ferric iron, 35 g/l sodium, 9 g/l ammonium, and 2 g/l magnesium, and was operated at 140 F.

(2) The brass tubes were 5/8-inch ID x 12 inches long. The plating procedure was as follows:

- (a) Brushed with powdered pumice
- (b) Cleaned by soaking 5 minutes in solution of 8 oz/gal of Anodex at 180 F
- (c) Rinsed in hot water
- (d) Dipped in 10 per cent solution of hydrochloric acid
- (e) Rinsed in cold water
- (f) Chromium plated for 10 minutes at 140 amp/sq ft in chromic acid bath at 110 F
- (g) Rinsed in cold water
- (h) Plated in chromium-iron bath, after immersion for 2 minutes. The tubes were plated vertically with copper anodes plated with about 0.010 inch of lead-tin-alloy plate.

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TABLE 2. HOT-HARDNESS MEASUREMENTS ON A CHROMIUM-IRON-ALLOY PLATE*

Temperature, F	Load, kg	Hardness at Temperature, DPHN	Hardness After Holding at Temperature for 21 Hours, DPHN
Room	5.0	439	--
Room	1.0	426	--
930	0.5	402	372
1300	0.5	203	189
Room	5.0	391	--

*Data from the Fourth Progress Report to the Navy Department, Bureau of Aeronautics, on "Research and Development of Electrodeposition of New Chromium and Chromium-Alloy Plate", Battelle Memorial Institute, April 1, 1952. The alloy contained 87 per cent chromium and 13 per cent iron. It was deposited from a bath prepared with basic chromium sulfate and contained 1.6 g/l ferric iron and a trace of hexavalent chromium.

Properties of Chromium-Iron Plates Produced in the Chromic Ammonium Sulfate Bath Operated With Iron-Silicon-Alloy or Platinum Anodes

Stress Data

The chromium-iron-alloy plates obtained in the bath prepared with basic chromium sulfate and operated with lead-tin-alloy-coated anodes were highly stressed, according to stress measurements with a spiral contractometer.* The chromium-iron alloy applied to erosion-gage Weapon Insert No. 67X was such a highly stressed deposit.

Substituting chromium ammonium sulfate** for the basic chromium sulfate, increasing the pH of the bath to 2.0, and operating with iron-silicon-alloy or platinum anodes resulted in a considerable decrease in the stress,

*The design and use of the spiral contractometer was described by A. Brenner and S. Senderoff in the February, 1949, issue of the Journal of Research, National Bureau of Standards.

**Technical grade, purchased from the Mutual Chemical Company of America.

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from 24, 100 to 15, 100 psi. The stress data are detailed in Table 3. The composition of representative plates was 94 per cent chromium and 6 per cent iron.

Data on Covering Machining Scratches in the Cathode Surface

Plates produced previously in the bath containing sodium sulfate, introduced by preparing the bath with basic chromic sulfate, were defective because of discontinuities propagated from machining scratches in the steel. For example, Figure 2 shows discontinuities over a scratch in the bore surface of erosion-gage Weapon Insert 67X.

Such discontinuities apparently were eliminated as a result of excluding the sodium sulfate by substituting chromic ammonium sulfate for the basic chromic sulfate plus treating the bath with activated carbon. Cross sections of several representative plates produced in the chromium ammonium sulfate bath contained no discontinuities propagated from scratches in the cathode surface. A typical section of a chromium-iron plate on scratched steel is reproduced in Figure 3, showing complete coverage of the scratches by the plate. The scratches were introduced in the surface by polishing the steel with a polishing belt coated with 180-grit abrasive. Appendix II details the conditions used to produce this and similar chromium-iron-alloy plates on flat steel cathodes.

Anode Data

The operation of the chromium-iron plating bath with lead-base-alloy anodes previously resulted in oxidation of the ferrous iron and trivalent chromium to ferric iron and hexavalent chromium, respectively. A hexavalent-chromium concentration of 3.4 g/l caused a 17 per cent decrease in the cathode efficiency. The hexavalent chromium necessitated operation with a higher current density than the minimum current density required for plating in a bath containing no hexavalent chromium. Hydrogen peroxide was added to the plating bath to reduce the hexavalent chromium when its concentration exceeded 3.4 g/l, to prevent a further reduction in the cathode efficiency. However, the ferric iron was not reduced by the hydrogen peroxide. The hexavalent chromium and the ferric iron are undesirable oxidizing agents that can passivate the cathode surface submerged in the plating bath before plating is started. Such passivation has been observed for chromium and chromium-iron-alloy-plated surfaces.

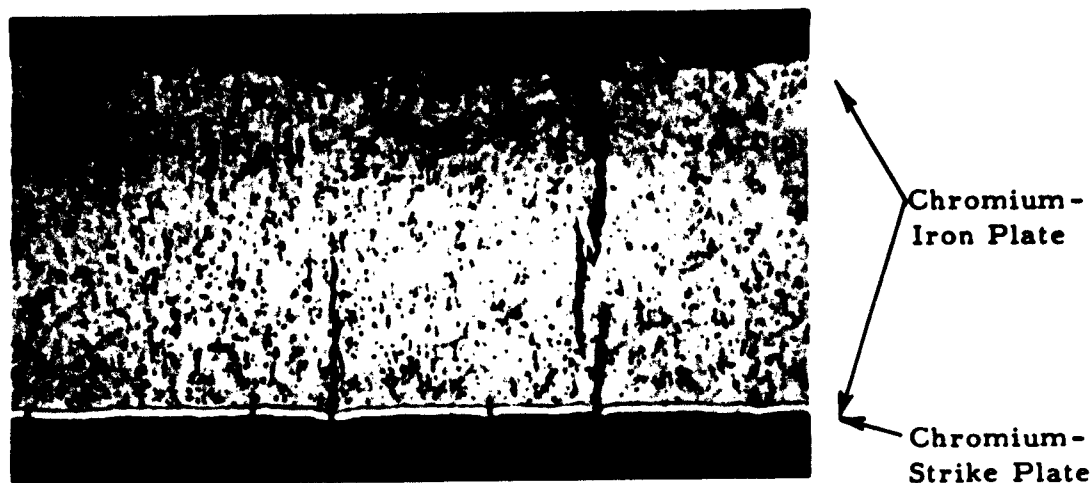
Improved anode materials were discovered recently. Platinum and iron-silicon-alloy anodes containing 14.5 per cent silicon are insoluble and do not oxidize ferrous to ferric iron, or trivalent to hexavalent chromium.

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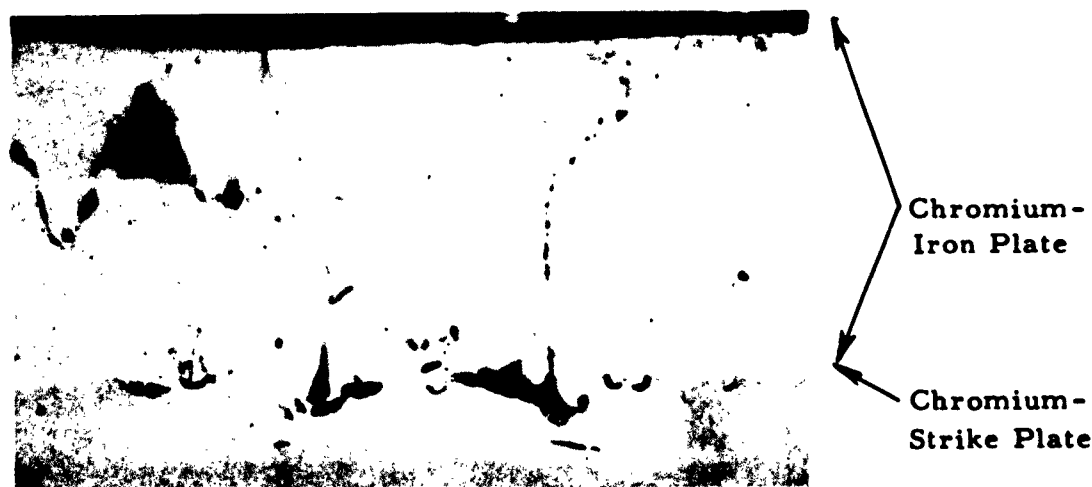
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500X Two-second electrolytic etch in 91554
10% oxalic acid at 3 volts and 80 F

FIGURE 1. DISCONTINUITIES IN CHROMIUM-IRON PLATE IN CIRCUMFERENTIAL CROSS SECTION OF EROSION-GAGE WEAPON INSERT 67X AFTER 3-HOUR 750 F HEAT TREATMENT



500X As plated 96110

FIGURE 2. DISCONTINUITIES IN CHROMIUM-IRON PLATE OVER CIRCUMFERENTIAL MACHINING SCRATCHES IN BORE SURFACE OF EROSION-GAGE WEAPON INSERT 67X

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TABLE 3. STRESS IN CHROMIUM-IRON-ALLOY PLATES(1)

Chromium Salt	Plating-Bath Composition		Other Salts	Bath, pH	Cathode Current Density, amp/sq ft	Temperature, F	Tensile Stress in Plate, psi
	Iron Concentration, g/l	Iron					
450 g/l basic chromium sulfate(2)	0.6 Fe 3+		50 g/l (NH ₄) ₂ SO ₄	1.8	230	130	18,000
Ditto	0.6 Fe 3+		Ditto	1.4	230	130	31,600
-	1.2 Fe 3+		-	1.4	230	130	31,200
-	1.9 Fe 3+		50 g/l(NH ₄) ₂ SO ₄ plus 20 g/l MgSO ₄ ·7H ₂ O	1.4	230	130	24,100
300 g/l Cr(NH ₄)(SO ₄) ₂ ·12H ₂ O	0.7 Fe 2+		100 g/l(NH ₄) ₂ SO ₄	2.1	200	115	11,400
Ditto	0.7 Fe 2+		Ditto	2.1	200	115	15,100

(1) Stress measurements were made with a spiral contactometer.

(2) MSO, purchased from the Mutual Chemical Company of America.

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500X

93018

Three-second electrolytic etch in 10%
oxalic acid at 3 volts and 80 F

FIGURE 3. CROSS SECTION OF CONTINUOUS
CHROMIUM-IRON PLATE ON
SCRATCHED STEEL SURFACE

Furthermore, any iron in the bath that is oxidized by air to ferric iron during idle periods is reduced to ferrous iron rapidly by a short "dummy" period of operation. Thus, the bath is freed easily and completely of oxidizing agents that might passivate cathode surfaces submerged in the bath before plating is started.

No weight loss of the platinum anode was detected after a long period of operation. A small weight loss of the iron-silicon-alloy anode was noted, equivalent to an anode efficiency of between two and three per cent, based on ferrous iron. At first, the weight loss was attributed to erosion by the oxygen released at the anode surface. Later, a slight increase in the ferrous-iron concentration in the bath indicated that the weight loss was a result of anodic dissolution during plating.

Adherence Tests

The plating of erosion-gage weapon inserts with chromium-iron alloy was preceded previously with a nickel or a chromium-strike plate, and the firing tests revealed unsatisfactory adherence of the chromium-iron alloy to the nickel or the chromium-strike plate. Heretofore, the adherence of the chromium-iron alloy to SAE 4140 cannon steel without a strike plate was unsatisfactory, according to the chisel tests. Those results relate to

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alloy plates produced in chromic sulfate baths containing at least a trace of hexavalent chromium and ferric iron.

Adherence tests were repeated using the new plating bath prepared with chromic ammonium sulfate, treated with activated carbon, and operated with iron-silicon-alloy or platinum anodes to prevent the formation of hexavalent chromium and ferric iron. Chromium-iron plates deposited on electropolished cannon steel without a strike plate resisted removal in the chisel testing. This good adherence was obtained after heating the plated steel for 2½ hours in air at 750 F. The results were reproduced several times, using the plating procedure detailed in Appendix II.

Chisel testing before heating at 750 F revealed unsatisfactory adherence of the chromium-iron plate to the cannon steel. Thus, the diffusion resulting from the heat treatment appears to be necessary for bonding the plate to the steel. No measurable diffusion was noted during metallographic examination, but it is assumed that some occurs under the conditions of heat treatment.

Wear and Hardness Data

The results of wear tests on chromium-iron plate using a Taber Abraser and 200-mesh silicon carbide abrasive are compared with hardness measurements in Figure 4.

As a result of the 750 F heat treatment used to bond the plate to cannon steel, the rate of wear of the chromium-iron-alloy plate was reduced greatly by comparison with the rate of wear before such heat treatment. However, the conventional hard chromium was superior in resistance to wear in this test. It is sometimes claimed that this test is a hardness test, rather than a true wear test.

Chromium-iron alloy and conventional chromium from the chromic acid bath were about equal in hardness and wear resistance after heating to 1200 F. As a result of the heat treatment at 1200 F, which may be reached at the bore surface of cannon in firing service, the chromium plate softened considerably more than the chromium-iron plate. No change in microstructure occurred in the chromium-iron electrodeposit. Recrystallization of the chromium probably resulted from the heat treatment, on the basis of earlier data.*

*Final Technical Report on Contract W33-019-ORD-6319, dated September 1, 1948, Battelle Memorial Institute to Cleveland Ordnance District.

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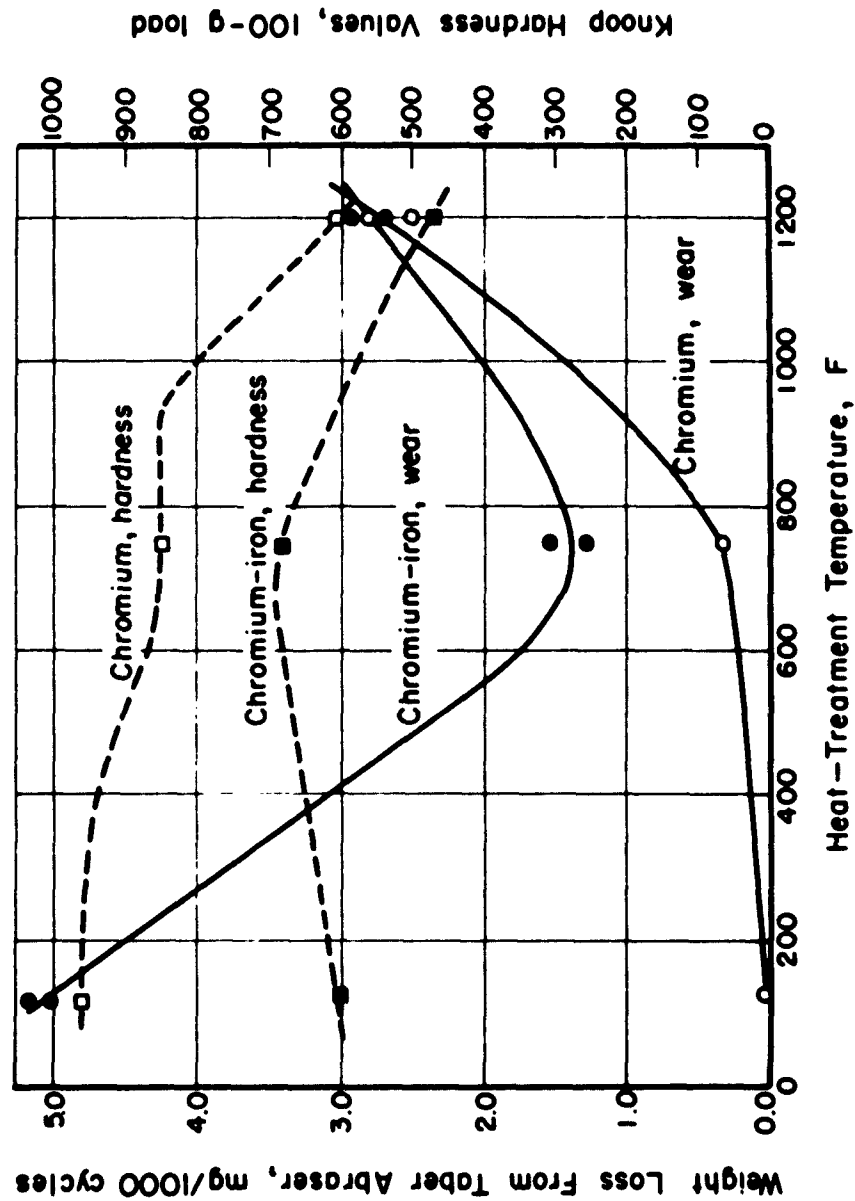


FIGURE 4. RELATIONSHIP BETWEEN WEAR-TEST DATA AND HARDNESS OF CHROMIUM AND CHROMIUM-IRON PLATES WITH AND WITHOUT HEAT TREATMENT FOR 2.5 HOURS

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Results of Plating Simulated Smooth-Bore Steel Tubes

The bore surfaces of simulated smooth-bore steel tubes 5/8-inch ID x 12 inches long were plated with chromium-iron alloy, using the procedure detailed in Appendix III. The results of plating 14 tubes are detailed in Table 4.

The plate was nonuniform in thickness on the tubes plated when iron-silicon-alloy anodes were used, due to a bow in the anode rods, which could not be straightened without breaking the brittle alloy. Blistering sometimes resulted at areas receiving less than the average current density, which was 100 amp/sq ft.

Substituting a platinum-sheathed silver anode for the iron-silicon-alloy anode resulted in improved uniformity of appearance and thickness of the plate. The plate on each tube was examined after sectioning the tube longitudinally. Plate that was 0.002 inch thick, or less, was satisfactory in smoothness. However, 0.003- to 0.004-inch-thick plate was slightly rough due to scattered nodules apparently caused by airborne dirt suspended in the plating bath.

Subsequently, a filtered solution was pumped through the tube being plated, eliminating the nodules. Nonuniform solution flow caused nonuniform plating thickness, but uniform flow at 0.3 gal/min resulted in plate with better thickness uniformity. Such plate, 0.0028 inch minimum and 0.0033 inch maximum, was smooth and free of discontinuities.

Plating Erosion-Gage Weapon Insert 69X

Erosion-gage Weapon Insert 69X was plated with chromium-iron alloy, using the procedure that previously gave satisfactory results for the simulated, smooth-bore steel tubes. The procedure is detailed in Appendix III.

The thickness of the plate was between 0.003 and 0.004 inch, corresponding to three hours of plating, at 100 amp/sq ft. Pumping filtered solution through the tube during plating resulted in smooth, nodule-free plate. The breech bore was plated nonuniformly, because the current density there was deficient owing to the larger circumference of the breech relative to the circumference of the tube. The plate within about 3/4 inch from the muzzle end was also nonuniform, probably owing to nonuniform solution flow near the muzzle. The greater part of the tube appeared to be uniform and free of defects.

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The erosion-gage weapon insert will be heat treated for bonding the plate to the bore surface, and forwarded to Watertown Arsenal for firing tests.

Properties of Chromium-Iron Plates Produced With Addition Agents

The wear resistance of chromium-iron plates was increased by modifying the structure of the deposit with the addition of silica and glycine to the basic chromium sulfate bath. Such plate has a banded structure, and is more resistant to wear than the plate with the columnar structure that was discussed in the preceding sections.* Taber Abraser measurements on plates with the banded structure were in the range of 0.00 to 0.03 mg/1,000 cycles. By comparison, plates with the columnar structure wore at the rate of about 5 mg/1,000 cycles. The measurements were made with 200-mesh silicon carbide abrasive embedded in CS17 wheels.

Stress cracks were evident in the plates produced to date with the banded structure. The plating conditions were as follows:

Temperature - 130 F
Current density - 200 to 260 amp/sq ft
Agitation (work bar) - 50 cpm, 1½-inch stroke
Anodes - Chromium-iron alloy or lead

The composition of the plating bath was as follows:

450 g/l MSO basic chromium sulfate
13.5 g/l ferrous ammonium sulfate, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
20 g/l magnesium sulfate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
100 g/l ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$
3.0 g/l water glass (29.5% SiO_2)
1.0 g/l glycine (aminoacetic acid)
Approx. 1.0 g/l chromic acid, CrO_3 , to oxidize the
ferrous to ferric iron, plus a trace of excess Cr^{6+}
1.4 pH

So far, the plate with banded structure has been deposited on flat panels. Since the uniformity of the thickness of such plate is better than the uniformity of the thickness of the columnar plate on flat panels, improved uniformity is expected to be attained on the bores of gun tubes by depositing plate with the banded structure.

*The plating and wear-test data were given in the Sixth Progress Report to the Navy Department, Bureau of Aeronautics, on "Research and Development of Electrodeposition of New Chromium and Chromium-Alloy Plate", Battelle Memorial Institute, August 1, 1962.

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TABLE 4. RESULTS OF PLATING THE BORE OF SIMULATED SMOOTH-BORE AMMONIUM SULFATE BATH⁽¹⁾ OPERATED WITH IRON-SILICON-

Tube No.	Bath Chromium Content, g/l	Bath Iron Content, g/l	Bath, pH	Anode	Plating Time, min
6995-34 ⁽²⁾	32	0.6	1.95	Duriron, contacts at top and bottom	60
6995-36A ^(3, 4)	32	0.6	1.95	Ditto	150
6995-36B	32	0.6	1.95	"	150
6995-37A	23	0.9	1.95	Duriron, contact at top only	60
6995-40A	33	0.9	1.8	Ditto	120
6995-40C ⁽⁵⁾	33	0.9	1.8	"	60
6995-40D	33	0.9	1.8	"	60
6995-42A	33	Not determined	1.8	Refinished Duriron	60
6995-42B	33	1.2	1.8	Ditto	120
6995-42C ⁽⁶⁾	33	1.2	1.8	"	190
6995-49A ⁽⁷⁾	32	0.6	1.8	Platinum-sheathed silver	60
6995-50	33	0.6	1.8	Platinum-sheathed silver	120

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STEEL TUBES WITH 100 AMP/SQ FT IN A CHROMIC
ALLOY OR PLATINUM-SHEATHED ANODES

Tube	Additions to Bath	Condition of Plate	Plate Thickness, inch
5/8-inch steel pipe	None	Completely covered except for about 1/2 inch at bottom; few blisters; many pits due to pits in steel; nonadherent	0.0012
Ditto	None	Partly gray and partly black; gray plate appeared to be adherent	0.0001 to 0.0003
"	None	Completely covered; few blisters; partly light and partly dark gray; flaked upon chisel testing before heat treatment	0.002 to 0.006
"	None	Completely covered; dark gray; did not withstand chisel testing before heat treatment	0.0005 to 0.0015
5/8-inch seamless tubing	10 g/l $\text{Cr}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	Completely covered; nonuniform thickness and appearance; many small blisters	0.0002 near top; 0.003 near bottom
Ditto	None	Completely covered; nearly uniform appearance; many small blisters on top 3 inches only	0.0007 top 0.0010 bottom
"	None	Completely covered; rough and pitted at top; smooth at center and bottom; flaked during chisel testing before heat treatment	0.0010 top 0.0013 bottom
"	None	Thin plate on one side of tube at top, apparently due to anode's being slightly off center	0.0006 top 0.0008 bottom
"	None	Ditto	0.0015 top 0.0028 bottom
"	None	Blistered at top; plate near bottom smooth on one side and slightly nodular on other side	0.0035 top 0.0048 bottom
"	New bath ⁽⁷⁾	Continuous, but nonuniform in appearance, due to nonuniform thickness of plate	0.0008 to 0.0025
"	None	Continuous, but rough and nodular in lower portion	0.003 to 0.004

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TABLE 4.

Tube No.	Bath Chromium Content, g/l	Bath Iron Content, g/l	Bath, pH	Anode	Plating Time, min
6995-51	33	0.6	1.8	Platinum-sheathed silver	120
6995-52	33	0.6	1.8	Ditto	120

(1) The 15-liter plating bath was prepared with the following:

300 g/l	$\text{Cr}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
100 g/l	$(\text{NH}_4)_2\text{SO}_4$
4.5 g/l	$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

The pH was raised to 2.0 with ammonium hydroxide solution; the bath was treated with 10 g/l activated carbon at 140 F and filtered.

The 12-inch-long tubes were plated with 16.5 amperes at 117 ± 2 F, corresponding to a cathode current density of 100 amp/sq ft.

The tubes were cleaned anodically in 10 oz/gal of "Anodex"^{*} solution, 250 amp/sq ft, 200 F, for 2 minutes; rinsed; electropolished for 3 minutes at 250 amp/sq ft., 90 F; rinsed; recleaned in "Anodex"; rinsed; dipped in 10 per cent by weight hydrochloric acid solution; and rinsed, before plating.

The 1/4-inch-diameter "Duriron"^{**} anodes, 14 inches long, were reduced from 3/8-inch-diameter "Duriron" welding rod by anodic dissolution in 48 per cent hydrofluoric acid solution at 90 F. Iron and chromium were not oxidized at the "Duriron" anode, which was essentially insoluble. The anode current density was about 200 amp/sq ft.

^{*} Cleaner purchased from MacDermid, Incorporated, Waterbury, Connecticut.

^{**} Iron-silicon alloy containing 14.5 per cent silicon, balance iron.

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(Continued)

Tube	Additions to Bath	Condition of Plate	Plate Thickness, inch
5/8-inch seamless tubing	Bath continuously filtered and pumped through tube	Smooth, continuous plate; nonuniform in thickness due to nonuniform flow on sidewall	0.0002 to 0.0066
Ditto	Solution filtered and pumped through tube at a reduced rate (0.3 gal/min)	Smooth, uniform, continuous plate	0.0028 to 0.0033

- (2) Current was reversed in the plating bath for 2 minutes before plating.
- (3) The electrical contact was completed before immersing this and the following tubes in the plating bath.
- (4) The steel anode contact at the bottom was partly dissolved.
- (5) The top of the tube was 1/4 inch above the solution level.
- (6) The weight loss of the anode was 1.77 grams, corresponding to an anode efficiency of 3.2 per cent.
- (7) A new plating bath was prepared for this tube, because the iron concentration was excessive in the other bath.

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APPENDIX I

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APPENDIX I

Procedure Used For Plating Erosion-Gage Weapon Insert No. 67X

Pretreatment

1. The bore was scrubbed with powdered pumice and a bristle brush.
2. The tube was rinsed in cold water.
3. The tube was cleaned by soaking for 30 minutes in a solution of 10 oz/gal of Anodex*, heated to 180 F.
4. The tube was rinsed in cold water.
5. After inserting the lead-tin-alloy-plated anode and attaching the Lucite fixtures for holding the anode in the center, the tube was dipped in a 10 per cent solution of hydrochloric acid.
6. The rinsing, after acid dipping, was in cold water.
7. In a chromic acid bath heated to 120 F and containing 400 g/l CrO_3 and 0.40 g/l H_2SO_4 , the tube was etched anodically for 30 seconds, at 100 amp/sq ft.
8. Chromium was plated for 10 minutes in the chromic acid bath with 240 amp/sq ft at 120 F.
9. The tube was rinsed in cold water.

Plating Procedure

After immersing the tube about 2 minutes in the chromium-iron bath, chromium-iron alloy was deposited at 240 amp/sq ft (40 amperes) for 60 minutes, at 140 F. The plating bath originally was prepared with the following:

*Alkaline cleaner mixture purchased from the MacDermid Company.

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3.78 lb/gal basic chromium sulfate*

0.42 lb/gal ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$

0.167 lb/gal magnesium sulfate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

0.0418 lb gal ferrous ammonium sulfate, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

0.378 g/gal sodium sulfite, $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$

0.425 lb/gal sulfuric acid, 95% H_2SO_4

At the time the tube was plated, the bath contained the following:

75 g/l trivalent chromium

Trace hexavalent chromium

0.7 g/l ferric iron

1.5 pH

Heat Treatment

After plating, the erosion-gage weapon insert was heated for 3 hours at 750 F and cooled slowly in the furnace.

*MSO, purchased from the Mutual Chemical Company of America.

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APPENDIX II

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APPENDIX II

Procedure Used for Plating Flat Steel Cathodes for Obtaining Adherence Data

Flat SAE 4130 steel panels, 0.065 x 1 x 3 inches, were placed in a 3-inch-thick x 1-inch-wide by 3-inch-long Lucite box with open sides, in order to equalize the distribution of current as much as possible, and were plated as follows:

1. Anodically cleaned in a solution of 10 oz/gal of Anodex* with about 100 amp/sq ft at 180 F for two minutes.
2. Rinsed in hot water.
3. Electropolished for 3 minutes at 240 amp/sq ft, 90 F, in a solution prepared with 80 volume per cent of 85 per cent phosphoric acid and 20 volume per cent of 95 per cent sulfuric acid. **
4. Rinsed in cold water.
5. Anodically cleaned for 1 minute in the Anodex solution.
6. Rinsed in hot water.
7. Immersed for a few seconds in a 10 per cent solution of hydrochloric acid.
8. Rinsed in cold water.
9. With the cathodic current lead connected before immersing the flat cathode in the plating bath, chromium-iron alloy was plated for 2 hours at 100 amp/sq ft, 115 to 118 F, in the following bath:

300 g/l chromium ammonium sulfate***, $\text{Cr}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

*Alkaline cleaner mixture purchased from the MacDermid Company.

**This electropolishing process is disclosed in United States Patent No. 2,334,699, assigned to Battelle Development Corporation.

***Technical grade, purchased from the Mutual Chemical Company of America.

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100 g/l ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$

4.5 g/l ferrous ammonium sulfate, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

10 to 15 ml/l ammonia solution, 29% NH_3 , to raise the pH to 2.0 ± 0.1

Prior to plating, the bath was treated with 10 g/l activated carbon* and filtered. Lead anodes were used in porous cups to prevent the oxidation of ferrous iron and trivalent chromium in the cathode compartment.

*Darco 51, purchased from the Darco Corporation.

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APPENDIX III

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APPENDIX III

Procedure Used for Plating Simulated Smooth-Bore Steel Tubes and Erosion-Gage Weapon Insert 69X

Assembly in Fixture

Lucite fixtures for holding the platinum-sheathed silver anode in the centers of the tubes were affixed to both ends of each tube. The outside of each tube was covered with stop-off tape. Each tube was 12 inches long.

Pretreatment

1. The bore surface of each tube was cleaned anodically in a solution of 10 oz/gal of Anodex* with about 100 amp/sq ft at 180 F for three minutes. The lead-sheathed silver rod was the cathode during the cleaning.
2. Rinsed in warm water.
3. Electropolished for 3 minutes at 240 amp/sq ft in a solution prepared with 80 volume per cent of 85 per cent phosphoric acid and 20 volume per cent of 95 per cent sulfuric acid.**
4. Rinsed in cold water.
5. Anodically cleaned for 1 minute in the Anodex solution.
6. Rinsed in hot water.
7. Immersed for a few seconds in a 10 per cent solution of hydrochloric acid.
8. Rinsed in cold water.

*Alkaline cleaner mixture purchased from the MacDermid Company.

**This electropolishing process is disclosed in United States Patent No. 2,334,699, assigned to Battelle Development Corporation.

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Plating Procedure

After pumping the filtered solution through the tube for one to two minutes, chromium-iron alloy was deposited at 100 amp/sq ft (16.5 amperes per tube) for 2 to 3 hours, depending upon the thickness of deposit desired. The temperature of the plating bath was maintained in the range of 115 to 118 F. The pumping rate was between 0.25 and 0.4 gal/minute. The solution was filtered through a porous carbon tube, coated with a filter aid and with activated carbon.

The plating bath was prepared with the following:

2.5 lb/gal (300 g/l) chromium ammonium sulfate,
 $\text{Cr}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

0.85 lb/gal (100 g/l) ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$

0.038 lb/gal (4.5 g/l) ferrous ammonium sulfate,
 $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

Approximately 50 ml/gal ammonia solution, 29%
 NH_3 , to raise the pH to 2.0

WHS:JEB:GMS:CAS:CLF/mpk
December 1, 1952