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DEPOSITION OF LEAD WITH HEXANOL-3 TAILS

Lead and tin are similar in many chemical and electrochemical properties, including the tendency to form crystalline or spongy cathode deposits from acid electrolytes. Therefore, both the qualitative and quantitative effects of hexanol-3 tails as an addition agent in the deposition of lead were determined. The Betts' fluosilicate electrolyte was used in these tests, except that hexanol-3 tails replaced glue as the addition agent. The electrolyte contained 80 g./L (10.75 oz./gal.) lead as $PbSiF_6$ and 150 g./L (20 oz./gal.) fluosilicic acid. The tests were made in hard rubber cells with a current density of 2.16 amp./dm.² (20 amp./sq. ft.). Cast lead anodes and sheet iron cathodes, both 4 x 5 cm. (1.6 x 2.0 in.), were used. A uniform composition of electrolyte during electrolysis was maintained by stirring. Hexanol-3 tails gave a cathode deposit similar in appearance to that obtained using glue as the addition agent. The presence of 1 to 2 g./L of the addition agent were required to obtain a cathode deposit suitable for refining purposes. Data obtained on a continued electrolysis showed that 0.8 lb (0.36 kg.) of hexanol-3 tails was required per ton of lead refined.

¹ A. G. Betts, "Refining Lead by Electrolysis," John Wiley and Sons, New York (1908).

Resumen del artículo: "Una Sustancia Aditiva Nueva para la Refinación de Estaño y de Plomo."

Se ha descubierto que cierta mezcla comercial de compuestos aromáticos de la serie de fenol sirve bien para eliminar depósitos esponjosos o aciculares en la refinación electrolítica de estaño en baño de sulfato y de plomo en baño de fluosilicato. Esta mezcla impura da mejores resultados que los compuestos puros solos o mezclados (Tabla I).

A paper presented at the Ninetieth General Meeting held at Toronto, Canada, October 16, 1946, F. A. Lowenheim presiding.

**MILITARY APPLICATIONS OF ELECTROPLATING
IN WORLD WAR II †**

By WILLIAM BLUM ‡

ABSTRACT

A brief review. Many thousand dies, gages, molds, forming and cutting tools were plated with hard chromium. Very little bright chromium was employed. Of special interest is the chromium plating of caliber-50 gun barrels. Porous chromium plate was applied to cylinders of aircraft and of Diesel engines. Important applications of nickel plating were made for the Manhattan Project (atomic bomb). Copper plating was used extensively to protect steel surfaces during case hardening. An important application of zinc plating was on steel cartridge cases. Lead took the place of zinc in many applications. Tin plating strip steel saved many tons of tin over and against hot-dipped tin plate. Bearings for aircraft engines were silver plated. Notable are the thin coatings of silver on radar equipment. Large searchlight reflectors were rhodium plated. Anodizing aluminum was carried out on a very extensive scale. Of special interest was the use of indium alloys for corrosion resistant bearings.

INTRODUCTION

In 1918 I had the privilege of presenting to this Society a paper with a similar title, in which the uses of electroplating on military supplies in World War I were summarized.¹ The far more extensive applications of electroplating in World War II are the joint result of such factors as: (1) advances in electroplating, especially in its technical control and specification; (2) increased intricacy and precision of military weapons; and (3) shortage of strategic metals as a result of the unprecedented scale of military operations. As a consequence of the large military applications, the total volume of plating conducted up to VJ day* was probably greater than in a corresponding peace time, though the types and applications were different.

¹ Manuscript (revised) received August 21, 1946.

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³ Trans. Electrochem. Soc., **34**, 169 (1918).

* Victory over Japan Day, August 15, 1945.

The applications of electroplating to military supplies were far too many to enumerate, much less to discuss fully in any brief report. They included large quantities of supplies for "military housekeeping," which did not differ essentially from normal civilian products, except in so far as substitutions were made for strategic metals. Only minor reference will be made to these applications of plating.

The uses of plating on specialized equipment for ordnance, aviation and communications involved in many cases the selection of metal coatings to meet unusual or severe conditions. Even though these particular conditions may not exist in domestic or industrial operations, the experience gained in the war may point the way to significant industrial developments. Details of many of the military uses have not been released, so that only brief references may be made to them at this time.

At best, any such summary will be incomplete, but it is hoped to make it sufficiently comprehensive to indicate the scope of these uses of electroplating. No effort will be made to give specific credit for each development, but pertinent specifications and publications will be referred to. The important applications will be classified in accordance with the principal metals deposited.

DEPOSITS OF SPECIFIC METALS

1. *Chromium.* The extensive prewar use of bright chromium, *e.g.*, on automobiles, was almost completely abandoned with the curtailment of civilian products, and very little bright chromium was employed on military supplies. However, the use of "hard chromium" on dies, gages, molds, and many forming and cutting tools increased and contributed directly to the war effort by prolonging the useful life of manufacturing equipment under very drastic service conditions. The use of chromium plating to salvage worn parts also increased. Most of these applications were extensions or modifications of prewar practice.

Chromium plating of large naval guns had been practiced for many years at the Washington Naval Gun Factory, but no detailed studies of the plating and performance of different types of guns had been conducted. During the war extensive researches on the cause and prevention of gun erosion were conducted by Division One of NDRC. In this connection studies on chromium-plated gun bores were made by the National Bureau of Standards in cooperation with the General Physical Laboratory, the Franklin Institute, and the War and Navy Departments. Similar work was conducted by Battelle Institute and also by the Armament Research Department in England. The detailed results of these studies have not been released. They led to the adoption in caliber-50 barrels of chromium plating over nitrided steel or in conjunction with stellite liners. These barrels were plated commercially by Doehler-Jarvis Co., and before VJ day several other plants were being equipped for this plating.

One significant result of these investigations is a realization of the wide variation in properties of chromium deposits. The ordinary chromium used for both hard and bright coatings, deposited *e.g.*,

45° to 55° C and 10 to 30 amp./dm.², has a hardness of about 900 Brinell. It is brittle and contains cracks that increase in size and number when heated, as a result of its contracting by as much as 1%. This type of chromium may contain over 1% of Cr₂O₃. In contrast, chromium deposited at about 85° C and at 40 to 120 amp./dm.² is relatively soft, *i.e.*, about 450 Brinell, and does not contract or crack appreciably when heated. It contains only about 0.2% of Cr₂O₃. The regular deposits were designated as "high-contraction" and the softer as "low-contraction" chromium. Studies on the applications of these types of chromium to various weapons are being continued at the Bureau of Standards in cooperation with the War and Navy Departments.

Other applications of chromium plating included steel mess trays and tableware. In spite of the fact that deposits of "hard" chromium about 0.0003 in. (7.6 microns) thick are very porous and permit corrosion of the steel, *e.g.*, in a salt spray, they proved very serviceable because they withstood the severe handling of camp service. For this purpose, chromium was generally applied over case-hardened steel, which increased the resistance to scratching and to impact.

The largest war-time development of chromium deposition was the use of "porous chromium" or "oil-absorbent chromium," on cylinders of aircraft and Diesel engines and piston rings. This process depends upon the fact that ordinary hard chromium deposits usually contain fine cracks. If the surface is etched, *e.g.* anodically, these cracks are enlarged, to produce a surface which retains lubricating oil and thereby reduces wear. As these methods have been fully described in the literature² only a brief outline of the process and applications will be given.

Two types of porosity may be distinguished, viz: Type I or "channel" porosity, in which the depressions are connected to form a fine net work of channels; and Type II or "pin-point" porosity, in which the pores are distinct and not connected by channels. The specifications³ for porous chromium for a particular purpose usually define the final thickness, type of porosity, and the "percent porosity," *i.e.*, the proportion of the surface represented by the pores or channels.

Porous chromium was successfully applied for the salvage of aircraft cylinders, which in many cases had a much longer life than the new, unplated cylinders. It was extensively applied to Diesel engine cylinders and to piston rings. It will no doubt have many postwar uses.

2. *Nickel.* During the early part of the war the greatly increased demand for nickel in steels used for tanks, guns and armor plates prohibited the use of nickel plating not only on civilian goods but also on most military supplies. For example, it was only by great effort that small quantities of nickel were released for plating of steel surgical instruments. Serious but not very successful efforts were made to salvage the nickel present in the then unused nickel plating baths in large plants.

²H. Van der Horst, *Metal Finishing* (N. Y.), **40**, 69 (1942); T. G. Coyle, *Am. Electroplaters Soc. Convention Proc.*, p. 20 (1944); R. Pyles, *Am. Electroplaters Soc. Convention Proc.*, p. 136 (1944); T. C. Jarrett and R. D. Guerke, *Metal Finishing* (N. Y.), **42**, 732 (1944).

³Bureau of Ships, Navy Department, *Ad Interim Specification 43P3* (Nov. 1, 1945); Army Air Force Specification 20031A (Dec. 19, 1944).

After the close of the war it was disclosed in the public press that two important applications of nickel plating were made for the Manhattan Project, upon which details have not yet been released. The Chrysler Corporation developed and perfected methods of applying thick impervious coatings of nickel on the inside of pipes and other equipment used in the Project. At present nickel-lined steel pipe, with 0.005 to 0.010 in. (0.125 to 0.25 mm.) of nickel, is being sold commercially. The Houdaille-Hersey Corporation is reported to have produced "nickel screens" by electrodeposition, but no details of their manufacture or use have been published. These two examples illustrate the fact that almost every branch of science and industry contributed directly to the studies on nuclear energy.

3. *Copper.* While copper was not so relatively scarce as nickel, its use in plating was restricted. Some of its applications rested on the fact that thinner coatings of copper could be applied by plating than otherwise. Much copper-clad steel with fairly thick copper coatings was used for such purposes as bullet jackets. On caliber-45 ammunition, however, the bullet jackets consisted of steel electroplated with about 0.0005 in. (13 microns) of copper.

Another extensive use of copper coatings, usually produced by chemical immersion, was on steel to lubricate it during drawing operations, *e.g.*, in making steel cartridge cases. Copper was plated on certain areas of aluminum radio and radar equipment, to facilitate soldering. Certain applications of copper electroforming proved valuable, such as the production of Pitot tubes and airplane models. Copper plating was extensively used to protect steel surfaces during case-hardening.

4. *Zinc and Cadmium.* These two metals may well be considered together because they both give sacrificial protection to exposed steel, and to some extent are interchangeable. In fact, the scarcity of cadmium during the war led to the substitution of zinc for cadmium wherever feasible. Extensive exposure tests have shown that, under practically all atmospheric conditions, a given thickness of zinc yields at least as much protection against the corrosion of steel as the same thickness of cadmium. Cadmium, however, preserves a better appearance and is less likely than zinc to form bulky white corrosion products. The latter objection to zinc was overcome for many purposes by the application of a supplemental chromate film.

Owing to the scarcity and greater cost of the cadmium, its coatings were usually thinner than those of zinc. For example, Army-Navy Aeronautical Specification *AN-P-32a* (Aug. 1, 1944) required for most purposes 0.0005 in. (13 microns) of zinc, while the corresponding *AN-P-61* (Aug. 1, 1944) required only 0.0003 in. (7.6 microns) of cadmium. In further efforts to conserve cadmium, its use on aircraft was confined by Conservation Directive *5B* (Oct. 28, 1943), to bolts, nuts, screws and washers; carburetor and magneto parts; external parts of engines in combat aircraft; parts subjected to 260° C (500° F) or higher; parachute and similar safety hardware; and to electric contacts.

In order to prevent brittleness caused by plating, both zinc-plated and cadmium-plated steel springs were heated to expel hydrogen. No conclusive data are available regarding the relative embrittlement produced by zinc and cadmium plating. Many of the cadmium-plated parts were dipped in chromic acid solutions to improve their appearance or the adhesion of paint; while zinc-plated parts often received chromate or phosphate treatments.

One important application of zinc plating was on steel cartridge cases. Extensive corrosion and firing tests showed that good performance could be secured with steel cases that were either zinc-plated and given a chromate finish, or were coated with a baked phenolic varnish.

Early in the war large quantities of fuse parts were cadmium plated, but subsequently zinc plating was largely substituted. Cadmium plating was preferred to zinc on radio chassis and other parts, though on condensers, as previously reported, cadmium coatings sometimes developed fine "whiskers" that caused short circuits.⁴ Many applications of zinc plating arose from the substitution of plain-carbon steel for stainless steel, brass, aluminum and zinc die castings. Zinc-plated steel mess kits were used for a short time, but were objectionable because the zinc is readily attacked by acid foods, to form emetic though not seriously toxic compounds. The coinage of zinc-plated steel pennies for one year saved over 5,000,000 lb. (2,300 metric tons) of copper.

At various times demands arose for steel sheets preplated with zinc for fabrication of numerous articles such as caps for ammunition containers. Only a few large plants for heavily zinc plating steel sheet or strip were installed, but considerable steel strip was plated with thin zinc coatings and bonderized for subsequent painting.

5. *Lead.* The relatively greater availability of lead than of zinc resulted in considerable substitution of lead coatings on steel. "Terne plate" (steel coated with a hot-dipped layer of lead containing 10% to 25% tin) had been extensively used for years for roofing, which was generally painted. Scarcity of tin necessitated a reduction in the tin content of terne plate to 2.5%. It was then found that for many purposes lead-plated steel sheet was equally satisfactory, though results recently reported⁵ indicate that some tin in the electrodeposits increases their protective value. All of these uses of lead-coated steel depend upon the fact, not fully appreciated in earlier years, that even though lead coatings permit initial corrosion of steel exposed through any pores, they tend to be "self-healing," *i.e.*, to seal the pores and to prevent continued corrosion of the steel. The relative value of zinc and lead coatings on steel for long-time exposure is now being investigated by Committee *B-8* of the American Society for Testing Materials.

6. *Tin.* Cutting off the supplies of tin from the Orient necessitated drastic conservation of tin for both military and civilian purposes. Before the war, most of the hot-dipped tin plate used in the canning industry carried about 2 lb. of tin per base box, equivalent to about

⁴H. L. Cobb, *Monthly Rev. Am. Electroplaters Soc.*, **33**, 28 (1946).

⁵A. H. DuRose, *Trans. Electrochem. Soc.*, **89**, Preprint 7 (1946).

0.00012 in. (3 microns) of tin. It was not found practicable to reduce this thickness much below 1.25 lb. per base box (1.9 microns) by the hot-dipping process.

Studies and experience before the war showed that by plating it was possible to produce tin coatings down to 0.5 lb. per base box (0.00003 in.) and thereby to extend the supply of tin that was available. Several large strip-plating plants were installed, in some of which acid baths were used, and in others alkaline stannate solutions. In plating flat sheets or strips, the difference in throwing power of these baths is not significant. One important difference in the two types of bath is that the acid baths require tanks with rubber or other acid-proof coatings, while the alkaline baths can be used in unlined steel tanks.

Even relatively thick hot-dipped tin coatings are notably porous. The thin electrolytic tin coatings were more porous than the ordinary hot-dipped tin though usually less so than an equal thickness of hot-dipped tin. To improve the appearance and solderability of the electrolytic tin and to reduce its porosity somewhat, the electrolytic coatings were melted, either by a flame, hot oil, resistance heating, or induction heating.

For some purposes, especially "dry packs," thin electrolytic tin was satisfactory. For other uses it was inferior, even when lacquered, and for some purposes it was quite unsuitable.⁶ It is probable that electrolytic tin, especially with intermediate weights, *e.g.*, 0.75 to 1 lb. per base box, will find a permanent place in industry but will not entirely displace hot-dipped tin.

7. *Silver.* The most extensive use of silver plating was for lining bearings for aircraft engines. This process was applied in several large plants, including the Oneida Community⁷ and the Chrysler Corporation.⁸ The principal new problems to be overcome were to increase the speed and uniformity of deposition and to secure the most perfect adhesion. Success in achieving these goals on a very large scale is a tribute to "electroplating engineering." Ingenious methods of testing the adhesion of the silver coatings were developed, including a high-speed centrifugal test employed by the Pratt & Whitney Co.

These silver bearings were usually coated with a lead-indium alloy, which is resistant to corrosion by the lubricants. A coating of lead was first applied to the finished silver surface, followed by a thin layer of indium, after which the combination was heated to a low temperature to alloy the lead and indium. This application of indium illustrates the fact that rare or unusual metals may find specific uses.

One new, important application of silver plating was on parts of radar equipment. This use depends on the fact that most of the conduction of very high-frequency current is a "skin effect" and that hence the maximum conductivity of the surface layer is desirable. A coating of about 0.0002 in. (5 microns) of silver was generally employed. Silver is the best conducting of the metals, but is subject

⁶K. W. Brighton, *Trans. Electrochem. Soc.*, **84**, 227 (1943).

⁷F. C. Mesle, *Monthly Rev. Am. Electroplaters Soc.*, **33**, 937 (1946).

⁸J. S. Hart and C. E. Heussner, *Monthly Rev. Am. Electroplaters Soc.*, **33**, 143 (1946).

to tarnish, especially by sulfides. Silver sulfide is a conductor, but not nearly equal to silver. Application of a thin film of palladium over the silver surface to prevent tarnish was proposed but not extensively used. Gold plating was also applied over silver, or as a substitute for silver. Because of the high intrinsic costs of silver and gold, and of the high manufacturing costs of many of the parts, non-destructive methods for measuring the thickness of coating would be very desirable. No such methods have yet been fully developed.

There was some consumption of silver on plated steel tableware, but for severe camp service the hard chromium coatings were superior.

8. *Platinum Group Metals.* Rhodium plating was applied in several plants to large electroformed search light reflectors made by processes described in 1898 by Sherard Cowper-Cowles, and developed by the Bart Reflector Co. Rhodium has a reflectivity of only about 75% as compared with 95% for clean silver. However, silver readily tarnishes and is softer and more easily scratched than rhodium. Some success was obtained with lacquered silver coatings, which yielded higher initial reflectivity than rhodium.

9. *Miscellaneous Applications.* The use of iron deposition as a substitute for at least part of the copper and nickel normally used in electrotypes proved to be feasible,⁹ but was not widely adopted. Instead, measures were taken to salvage most of the copper used in electrotyping. This was done largely by electrorefining methods adapted to these particular materials.

Most of the war-time plating was applied to steel, partly because of shortages of non-ferrous metals. Efforts were made to substitute plated plastics for the plated brass in buttons and insignia. These appeared to be satisfactory, but were not extensively adopted. Some of the well-known discharge buttons were made of plated plastic.

Some developments were made in alloy deposition. "White brass" deposits, and also white deposits consisting of copper, zinc, and tin were announced. While these were applied successfully to some articles, few large military uses were made of them, partly because of the scarcity of tin.

There was considerable increase in the use of colored coatings on metals, some produced by immersion and some by electrolysis. Among the former were several methods of producing black oxide films on steel in hot nitrate and nitrite baths. These coatings furnished little protection against rust unless they were supplemented by suitable films of oil or wax.

The anodizing of aluminum and electrolytic methods of protecting magnesium alloys represent processes allied to electrodeposition that were very extensively applied, especially on airplane parts.

⁹V. A. Lamb and W. Blum, *Tech. Bull. No. 7, Internat. Assoc. Electrotypers & Stereotypers* (April 15, 1942).

CONCLUSIONS

The foregoing examples, which by no means cover all the military applications of electroplating, illustrate the ability of this industry to adapt its methods and products to meet new and unusual conditions. The interest thereby aroused in plating, by both producers and consumers, augurs still further progress in meeting peace-time requirements.

Resumen del artículo: "Aplicaciones Militares de Electrodeposición en la Segunda Guerra Mundial."

Durante esta guerra se empleó electrodeposición mucho más que en la anterior, pues es hoy día más precisa que antes, las armas son más complicadas, y faltaban ciertos metales debido a la gran escala geográfica de la guerra.

El cromado de gramiles, moldes, etc., aumentó considerablemente, como también el recobro de objetos desgastados. Se estudió detenidamente el cromado del interior de cañones, descubriéndose que el cromo duro depositado a 50° C. es quebradizo y se contrae y agrieta al calentarse, mientras que el cromo blando depositado a 85° no se contrae. La principal aplicación nueva es el cromo poroso, que retiene aceite. Se deposita cromo duro sobre cilindros y segmentos de émbolo, ensanchándose las grietas luego por disolución anódica.

Se electrodepositaron tamices de níquel y cañería de acero revestido de níquel para la bomba atómica. Se depositó cobre sobre balas de acero, sobre acero para lubricarlo al estirarlo en moldes, sobre aluminio para facilitar la soldadura, y sobre modelos de aeroplanos para reproducirlos. Faltaba cadmio, empleándose el cinc más que antes, y reemplazándose éste a veces por plomo, aún más abundante. Se depositó plata sobre cojinetes en motores de aeroplano, y sobre conductores para aparatos de "radar."

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A MECHANICAL RECTIFIER

The Contact Converter as Developed by Siemens-Schuckert in Berlin, Germany¹By OTTO JENSEN²

ABSTRACT

The contact converter was developed by Siemens-Schuckert of Berlin. It comprises a contact mechanism synchronously driven and adjusted to make metallic contact between the a.c. source and the d.c. load at proper time intervals. To prevent arcing at the contact, a contact making choke coil is introduced in such a way as to oppose the build-up of the load current. The contact *making* choke coil is considerably smaller than the contact *breaking* choke coil. The moving contacts are approximately 32 mm. x 32 mm. and are silver inlaid. All moving parts are enclosed.

INTRODUCTION

In 1940 a new electric machine known as the contact converter made its appearance in Germany. It caused quite a sensation as development of new electric machines seemed to have come to a standstill and nothing fundamentally new was expected.

The contact converter found a ready market waiting for it in the electrochemical industry, but when large scale production was started a number of difficulties were encountered and for a while it looked as though the new development would have to be abandoned. But by thoroughly investigating the various difficulties experienced and by paying close attention to details, performance of the converter was improved and in 1943 the size of the converter had grown to such an extent that it was possible to build a successful machine delivering 10,000 amperes at 400 v. d.c. and 5,000 amp. at 800 v. d.c.

A number of plant installations have been made, the largest one consisting of four 8,000 amp. units, 400 v. machines installed at the I. G. Farben plant at Heydebreck. Conversion equipment totalling 111,000 amperes had been installed up to the time of the close of the War. At this time a number of converters were being built by the

¹ Manuscript received June 4, 1946.² I. T. E. Circuit Breaker Co., Philadelphia, Pa.