

COMPARISON OF RUST PROTECTION OF IRON BY ZINC, BY CADMIUM, AND BY ZINC-COPPER ALLOYS AND THE ELECTRODEPOSITION OF SUCH ALLOYS.¹

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ABSTRACT.

Deposits of cadmium upon iron have recently become very extensively used especially in the automobile industry. Such deposits render the iron rust proof and are much more ornamental or decorative than are deposits of zinc. This paper reports attempts to measure the relative protection against rust given by zinc, by cadmium, and by zinc-copper alloys.

Zinc gives fine protection to iron as long as any considerable amount of the zinc coating remains on the iron. Zinc itself is so strongly anodic to iron and most other commercial metals that it reacts faster than is needed for the purposes of protection. Cadmium is nearer to iron than is zinc in the electrochemical series but it is still anodic to the iron. Therefore cadmium gives longer protection than does an equal thickness of the zinc, because the cadmium, being less active or less anodic, does not dissolve or corrode so rapidly. A zinc-copper alloy of about 15 per cent copper has nearly the same single potential or solution pressure as cadmium; hence it was thought that such an alloy might give as durable protection as does the cadmium. A survey of the literature indicates that such a thing might be possible. However, only actual salt spray tests could determine this point. Such an alloy might not dissolve or corrode homogeneously. If a coating rich in copper was finally left on the iron, the single potential might reverse. If this happened, the iron might become anodeic and its rate of corrosion would be increased.

Descriptions of experiments to determine the relative rustproofing power of zinc-copper alloys were not found. However, statements that zinc-copper alloys might be used for rustproofing were found. Cowper Coles (Brit. Pat. No. 154,108, Feb. 24, 1920) used a 50 per cent zinc-copper alloy. This alloy was electrodeposited from a potassium copper cyanide bath to which zinc compounds were constantly added. The patent also states that small zinc anodes might be used. Law⁴ describes an alloy of 25 per cent copper and 75 per cent zinc that was used to protect iron and steel.

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⁴ "Alloys," G. Griffin & Co., (1919).

"Proc. Ind. Acad. Sci., vol. 38, 1928 (1929)."



Zinc⁵ containing from 0 to 13 per cent of copper has about the same solution tension as pure zinc. With 15 per cent of copper there is a sudden drop in potential.

The E. M. F. of the cell zinc-copper alloy/zinc sulphate/potassium chloride/mercury drops 0.07v. by increasing the copper from 0 to 32 per cent.⁶

Zinc containing 0.19 per cent of copper dissolves as rapidly in acids as when the impurity is arsenic or antimony.⁷

However, the corrosion of the zinc alloy in 5 per cent sodium chloride was uniform for varying amounts of lead, iron, cadmium, arsenic, antimony, tin and copper. This uniformity of action was probably due to a protective coating of hydrated zinc oxide.

Electrodeposition of Zinc-Copper Alloys. No formula was found for a bath from which to deposit electrolytically an alloy of zinc containing small amounts of copper. The use of zinc-copper anodes of the desired composition in the ordinary brass baths did not give satisfactory results.

A pair of anodes, one of pure zinc and one of yellow brass, was hung in each side of the plating bath. By suitable electrical connections operated by an eccentric, the current was automatically changed every minute or two from the two zinc anodes to the two brass anodes and then, after an interval, back to the zinc anodes again. By careful regulation of the relative periods during which the current was on the brass anodes and on the pure zinc anodes, it was possible to control the composition of the bath and thereby obtain deposits of any desired composition up to 15 or 20 per cent copper. The composition of the bath used was 6 grams of sodium cyanide, 4 grams of zinc cyanide, 1 gram of copper cyanide and 4 grams of sodium hydroxide per 100 ml. (8 oz. sodium cyanide, 5.1 oz. zinc cyanide, 1.3 oz. copper cyanide and 5.1 oz. of sodium hydroxide per gal.). The current density at the cathode was 0.3 amp./sq. dm. (2.8 amp./sq. ft.). The bath was run at room temperature. One third of an ounce of metal per square foot (1.1 grams/sq. dm.) was deposited. This is the thickness recommended⁸ for best commercial work.

The length of time in the salt spray before any rust appeared on the pure zinc coated pieces was taken as 100. The hours of protection afforded by the other coatings under the same conditions in the salt spray were compared to this value.

The time of resistance to rusting in the salt spray varies with the conditions of operation of the salt spray. However all these results are strictly comparable, as they were all obtained under the same conditions. Several methods of operating the salt spray were tried. A convenient form was a wheel revolving in the 5 per cent salt solution. This wheel splashed the solution upon the pieces to be tested. This spray acted more slowly than a spray blown by air. The same relative results were obtained for the three types of coatings regardless of the conditions of the operation of the spray.

⁵ Pushin, J. Russ, Phys. Chem. Soc., 39, 353.

⁶ Gambi, Rend. r. ist Lombardo (2) 48, 826.

⁷ Prost, Bull. Soc. Chim. Belg., 28, 94.

⁸ Proctor, Metal, Ind., 21, 326 (1923).

The deposits of cadmium and of pure zinc were made electrolytically from well known cyanide baths. The thickness of the deposits on the various test pieces were determined by calculation from the ampere hours used and the surface being covered and the density of the metal being deposited. Careful experiments with a coulometer were made with each bath to determine its electrochemical efficiency for use in the above calculations.

The single potential values were made with the ordinary potassium chloride calomel cell.

The results of the test are summarized in Table I.

TABLE I. Relative Protection against Rust of Various Metals and Alloys.

Composition of the coating or deposit	Single potential of test piece		Protection (in per cent, with pure zinc as 100)
	Before salt spray	After rusting	
21.32% copper.....	-0.36	+0.26	
14.88% copper.....	-0.51	+0.21	85.52
9.49% copper.....	-0.49	+0.11	85.72
Pure zinc.....	-0.57	+0.08	100.
Pure cadmium.....	-0.30	+0.19	176.
Red brass.....			37.5

CONCLUSIONS.

These experiments show that the presence of copper in the zinc deposit on iron lessens the time of protection in the salt spray.

Cadmium gives almost twice as long protection as does an equal weight of zinc.

If only the cost of the actual metal for the coating is considered, the protection by the cadmium at 75 cents per pound costs about seven times as much as the protection from the zinc at 8 cents per pound.

This paper gives a method of controlling the composition of electrodeposited alloys by using anodes of two different compositions. The current is automatically shifted back and forth between the anodes of the different compositions. A proper regulation of the period during which each kind of anode is in the circuit will give the desired composition to the bath and to the deposit.

