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“BLACK NICKEL” PLATING SOLUTIONS

BY

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*Bureau of Standards*

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# "BLACK NICKEL" PLATING SOLUTIONS

By George B. Hogaboom, T. F. Slattery, and L. B. Ham

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## ABSTRACT

To produce the so-called "Government bronze" finish on military hardware, "black nickel" plating was frequently applied. Investigation showed that for this purpose very complicated solutions were frequently employed, and at times great difficulty was encountered in producing uniform results. This paper describes the results of a few experiments on such solutions and contains recommendations regarding the composition and conditions of operation which will yield satisfactory deposits.

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## CONTENTS

	Page
1. Introduction.....	3
2. General principles.....	3
3. Alkaline cyanide solutions.....	4
4. Sulphocyanate solutions.....	6
5. Applications of black nickel.....	8
6. Conclusion.....	9

### 1. INTRODUCTION<sup>1</sup>

During the war a very considerable demand arose for a black finish, the so-called "Government bronze," on military hardware and equipment. Owing to the difficulty of specifying definitely the color or other desired properties of the deposit, or the composition of solutions or methods of deposition, there was frequent uncertainty and even confusion in the various specifications and methods of inspection. In consequence numerous inquiries for information and assistance were received by the Bureau of Standards, directly and through military channels. The present paper is simply a summary of experiments and observations made and conclusions reached in the effort to answer such inquiries.

### 2. GENERAL PRINCIPLES

The principal formulas proposed for "black nickel" solutions<sup>2</sup> fall roughly into two classes—the alkaline cyanide baths and the neutral or slightly acid baths. Arsenic is usually an essential

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<sup>1</sup> These notes were first published in the Monthly Review of the American Electroplaters' Society, July, 1919.

<sup>2</sup> For a summary of such formulas, see O. P. Watts, *Metal Industry*, 12, p. 24; 1914.

constituent of the alkaline baths; in fact, as has been shown and is confirmed by this work, the deposits from such baths may consist principally of arsenic, thus approaching in composition and properties the deposits obtained from "arsenic black" baths (prepared by the solution of arsenic trioxide in sodium hydroxide and sodium cyanide). Such deposits, therefore, hardly justify the term "black nickel," except as an indication that the solutions contain (or originally contained) nickel salts and are operated with nickel anodes. The neutral baths contain nickel sulphate or nickel ammonium sulphate, together with salts of zinc, copper, etc., and usually some sulphur compound, such as a sulphite, thiosulphate (hypo), or sulphocyanate. Of these, the sulphocyanate solutions have been most frequently used. The experiments and observations of the Bureau were confined chiefly to the alkaline cyanide baths and the sulphocyanate baths, which will be considered separately.

### 3. ALKALINE CYANIDE SOLUTIONS

It is probable that these baths were originally prepared (as they still are in some cases) by adding to a portion of the regular nickel-plating bath a solution of sodium arsenite—that is, arsenic trioxide dissolved in sodium hydroxide—forming a precipitate (essentially nickel arsenite) which was then dissolved by the addition of sufficient sodium cyanide. It is, therefore, not surprising that difficulty was experienced when efforts were made to state a definite formula for preparing such solutions from the original chemicals. In order to obtain clear solutions, or to produce the particular shade of deposit desired, other additions were made to the solutions, which resulted in very complicated and even irrational formulas. Perhaps the best illustration of such a formula is the so-called Rock Island formula (which, however, probably did not originate at the Rock Island Arsenal).

#### SOLUTION No. 1

1. Dissolve 6 pounds of double nickel salts in 6 gallons of water.
2. Add 4 ounces of sulphuric acid.
3. Add 1 pound of "phosphoric zinc" (prepared by dissolving zinc in sirupy phosphoric acid diluted with an equal volume of water).
4. Add 5 pounds of carbonate of ammonia (a small amount at a time).
5. Add 4 pounds of sodium cyanide.

SOLUTION No. 2

1. Dissolve 10 pounds of arsenious acid and 10 pounds of caustic soda in 5 gallons of warm water.

Mix solutions No. 1 and No. 2 and dilute to 12 gallons.

Whatever the origin of this or equally complicated solutions suggested for military supplies, it is obvious that their use could not lead to satisfactory results. One of the difficulties experienced in attempting to follow some of the suggested formulas was that most of the metal in the salts was precipitated to the bottom, forming a sludge of cyanides, carbonates, or arsenites of nickel, zinc, etc. In one case after thorough mixing of the ingredients, only 7 per cent of the nickel added was found in the solution. Such solutions are, therefore, very wasteful, as well as unsatisfactory in operation.

In the effort to obtain a simple, satisfactory, alkaline "black nickel" solution, a large number of experiments were conducted, with frequent analyses of the solutions and the deposits. Assuming that the nickel is present as the double cyanide, and the arsenic as sodium arsenite, the simplest solution would consist of nickel sulphate treated with sufficient cyanide to dissolve the precipitate first formed, and arsenic trioxide with sufficient sodium hydroxide to dissolve it. Such solutions yielded, however, only unsatisfactory grayish deposits, which consisted principally of arsenic. When zinc sulphate was present in the solution more satisfactory deposits were obtained.

The exact function of the zinc is difficult to determine, since very little enters into the deposit. In the effort to employ certain of the commercial formulas, it was found that a very considerable excess of cyanide was necessary to obtain a clear solution. From such solutions, containing, for example, the ingredients here listed, good gray-black deposits were obtained.

Ingredients	Ounces per gallon	Grams per liter
Nickel ammonium sulphate (double salt).....	6	45
Zinc sulphate.....	.5	3.8
Ammonium carbonate.....	5	37.5
Arsenic trioxide.....	.7	5
Sodium hydroxide.....	.7	5
Sodium cyanide.....	6	45

On continued operation, however, the deposits became lighter in color, a large amount of sludge formed in the solution, and the latter changed very materially in composition, losing both arsenic and zinc. This is to be expected, since in these solutions nickel anodes are used and there is no opportunity for the deposited arsenic and zinc to be replaced. The nickel content decreases less rapidly, although nickel anodes are not readily corroded in cyanide solutions.

The net result of a large number of experiments and analyses upon alkaline "black nickel" baths was the conclusion that no bath of this type can produce uniformly satisfactory results unless it is controlled by very frequent and decidedly difficult chemical analyses, such as are not usually available in commercial plating plants. We do not feel justified, therefore, in recommending any formula for such solutions.

#### 4. SULPHOCYANATE SOLUTIONS

A typical formula of this type, which has been used for many years and is given in numerous texts on plating, is as follows:

Ingredients	Ounces per gallon	Grams per liter
Nickel ammonium sulphate (double salt).....	8	60
Zinc sulphate.....	1	7.5
Sodium <sup>a</sup> sulphocyanate.....	2	15

<sup>a</sup> Originally potassium or ammonium sulphocyanate was used commercially, but recently the sodium salt has almost entirely replaced it with equal satisfaction. (See C. H. Proctor, *Metal Industry*, 16, p. 26: 1918.)

Since it has been found in practice that such solutions give entirely satisfactory black deposits, the experiments conducted were directed to securing simple means of control of these solutions rather than to securing new or possibly better formulas.

Analyses of deposits produced from such solutions when freshly prepared showed a considerable variation in composition, due no doubt to slight differences in the original neutrality of the solutions and to slight fluctuations in the voltage.

In this, as well as in the alkaline "black-nickel" solutions, even slight changes in voltage produce marked differences in the proportion of the metals precipitated and hence in the color and physical properties of the deposits. Thus in the above sulphocyanate solution a good black deposit is produced with 0.5 to 0.7 volt (between anode and cathode); while if the voltage be in-

creased to 1.5 to 2 volts, a light-colored, bright nickel deposit is secured. In the operation of such solutions, therefore, control of the voltage is more important than is the control of the current density. The latter probably will not, under good conditions, exceed 1 ampere per square foot (0.11 amp./dm<sup>2</sup>).

Good "black-nickel" deposits were found to contain from 40 to 60 per cent of nickel, 20 to 30 per cent of zinc, 10 to 14 per cent of sulphur, and 10 per cent or more of organic matter of undetermined composition. (The organic matter was formed by the decomposition of the sulphocyanate upon electrolysis.) The ratio of sulphur to nickel was always less than that required for nickel sulphide, which contains about 65 per cent of nickel and 35 per cent of sulphur. It therefore appears reasonably certain that the black deposit consists essentially of a mixture of nickel sulphide, nickel, zinc, and organic matter.

If the zinc content of the solution is increased very much above that indicated by the above formula, grayish deposits, with high zinc content, are produced. If, on the other hand, the zinc content of the solution is greatly reduced or actually eliminated, the deposit is nearly pure nickel, with a light or bright nickel color. It is, therefore, important to maintain a fairly constant composition of solution, although good results can be obtained over a moderate range. In the normal operation of such a solution, the changes that are likely to occur are (a) a decrease in sulphocyanate, which must, therefore, be replenished at intervals; (b) a decrease in zinc content; and (c) an increase in nickel content. The latter arises from the fact that with nickel anodes, nickel is going into solution more rapidly than it is deposited, since part of the current is used in depositing zinc. At first it might appear possible to replenish the zinc and prevent an increase in nickel content by the substitution of zinc anodes for part of the nickel anodes. Attempts to do this, however, resulted in too high a zinc content, owing to the fact that zinc anodes are so much more readily corroded than nickel. The most practical way, therefore, to reduce the nickel content is to use nickel anodes which do not corrode very readily—for example, those with 96 per cent or more of nickel—and, if necessary, to restrict the anode surface.

In general, and especially when using high percentage nickel anodes, there is a tendency for the solution to become acid. Among the various additions which have been proposed to maintain neutrality are ammonia and nickel carbonate. Neither is

entirely satisfactory, since addition of ammonia tends to precipitate the zinc from the solution unless great care is used, and, on the other hand, the use of nickel carbonate tends to still further increase the nickel content. For this purpose zinc carbonate should, therefore, be more satisfactory, since to the extent that it neutralizes the solution the zinc content will be maintained. Experiments have shown that by having an excess of zinc carbonate always present, good deposits may be secured over a considerable period. Whether in any case its use is sufficient to maintain the zinc content will depend upon the conditions of operation, and can be determined only by occasional analyses. Nickel, zinc, ammonia, and sulphocyanate may be determined in such solutions by the usual methods, which are not especially difficult where laboratory facilities and experience are available. Wherever possible, it is desirable to have such analyses made at intervals, although by observance of the above suggestions it is believed that the solutions will change in composition less rapidly than under the usual conditions.

#### 5. APPLICATIONS OF "BLACK NICKEL"

In the application of "black nickel" plating to brass, a preliminary copper plating is frequently recommended or specified. It has not been found that deposits produced under such conditions are intrinsically more adherent or serviceable than those produced directly on brass. Where, however, the "Government bronze" effect is desired, the copper plating is an advantage in that whenever the black coating is removed—for example, by abrasion—an underlying copper coating produces a more pleasing effect than does brass. If the copper plating is so produced as to have a dull surface, it also tends to produce a matte effect in the "black nickel." This is frequently desired, especially when the sulphocyanate solution is used, which, on a polished surface, tends to produce a bright black finish. The actual wearing properties of the "black nickel" surface are largely determined by the quality of the lacquer subsequently applied.

Although "black nickel" may be deposited directly upon steel, it is more difficult to secure good results than if the steel is first plated with some other metal. For this preliminary coating, copper and nickel are most frequently used. Since, however, neither the copper nor the nickel, nor the "black nickel" deposits afford any appreciable protection against corrosion, finishes so



produced are not desirable for outdoor exposure. For this purpose the steel should be first zinc plated, either in the sulphate or cyanide bath. Experiments have shown that steel plated with zinc and then with "black nickel" possesses about the same resistance to the salt spray test as does steel plated with the same thickness of zinc. In other words, the "black nickel" does not appreciably add to or detract from the protective value of the zinc coating.

6. CONCLUSION

A bath prepared from the ingredients here listed, kept neutral with an excess of suspended zinc carbonate, and operated with nickel anodes will give satisfactory black deposits upon brass, copper, and zinc; upon brass plated with copper; and upon steel plated with copper, nickel, or zinc. The deposit is probably a mixture of nickel, nickel sulphide, zinc, and organic matter of undetermined composition.

Ingredients	Ounces per gallon	Grams per liter
Nickel ammonium sulphate.....	8	60
Zinc sulphate.....	1	7.5
Sodium sulphocyanate.....	2	15

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