Jan. 27, 1959 E. D. BOELTER, JR 2,870,709

ELECTROFORMED ARTICLES AND PROCESS FOR THEIR MANUFACTURE

Filed Oct. 28, 1955

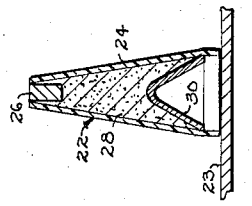


FIG. 2

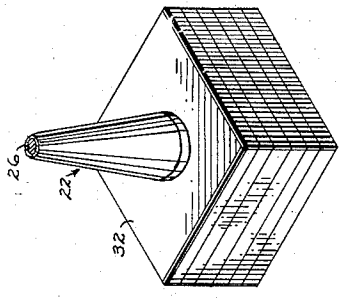


FIG. 3

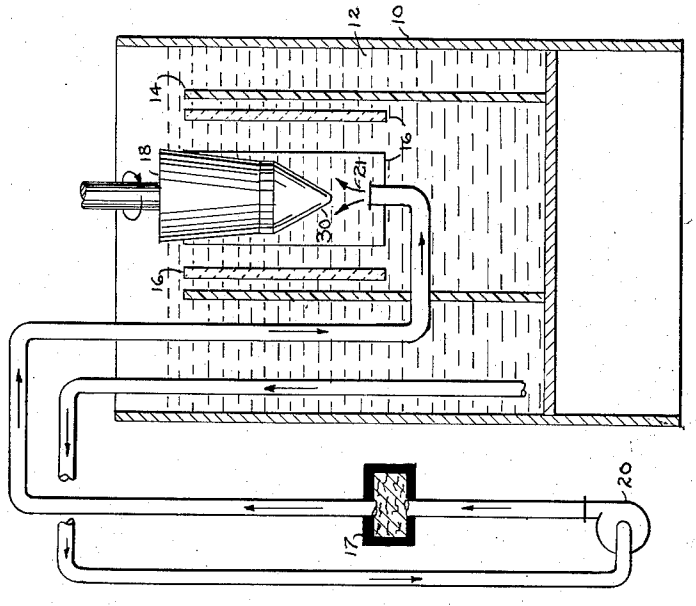


FIG. 1

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United States Patent Office 2,870,709 Patented Jan. 27, 1959

2,870,709

ELECTROFORMED ARTICLES AND PROCESS FOR THEIR MANUFACTURE

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Application October 28, 1955, Serial No. 543,496
2 Claims. (Cl. 102—24)

This application, a continuation-in-part of my copending application Serial Number 426,950, filed May 3, 1954, and now abandoned, relates to electroformed copper articles and to a process for preparing the same.

In the above-mentioned application there is claimed a process for electrodepositing copper at unusually high current densities from a substantially conventional aqueous copper cyanide bath modified by the inclusion therein of an inorganic selenide such as sodium or copper selenide. The quantity of additive used is not sharply critical but should comprise between about 50 and 1000 p. p. m. of the bath.

It has now been found that copper will deposit from the selenide bath at very high rates of speed, i. e., one mil per minute or greater, in an extremely ductile form. This copper is free of internal strain and can readily be deposited to any predetermined thickness on surfaces having a low radius of curvature. If the surface is one to which copper will adhere, such as carbon steel, the electrodeposit will be held tenaciously. If, on the other hand, the surface is one to which copper will not adhere, such as polished chromium or stainless steel, the copper can easily be stripped therefrom retaining the shape of the base.

Copper can thus be plated at high speeds from the novel baths onto a mandrel and easily removed from the latter. Articles terminating in a point or other closed base can, in particular, be formed as described. Such articles, which may be termed concave, include cones, cups, bowls, fountain-pen caps and the like.

The cones of this invention have an entirely unexpected property which makes them of great value: they are extremely effective as liners for small shaped charges. When so adapted, they surprisingly increase the penetrating power of the charges to a value about 12–15% greater than that obtained with liners made by conventional methods such as deep-drawing or forming the copper.

These shaped charges are particularly valuable in devices such as jet perforators. Jet perforators are described in many publications as, for example, the Muskat et al. U. S. Patent 2,494,256. Used for piercing oil well casings, they consist primarily of a small shaped charge of high explosives held within a container, a means for detonating the charge from one end and an internal metallic liner in the end opposite the point of detonation. When the charge is set off the conical liner collapses from apex to base and ejects a metallic stream of such high velocity and small cross section that it readily penetrates anything before it. The initiating means is usually a detonating fuse, but a detonator may be employed if desired.

A specific object of the invention is, therefore, provision of a method for making copper cones adapted for use in producing jet perforators.

Other objects will be apparent from the remainder of the specification and from the drawings, in which:

Figure 1 shows an electroplating bath and apparatus for producing the cones of the invention;

Figure 2 is a section of a jet perforator, positioned for use, showing the electrodeposited conical liner; and

Figure 3 is an elevation of a jet perforator mounted on a pile of steel plates for testing perforation.

Figure 1 discloses tank **10** containing bath **12**, shield

14, and anode **16**. Rotating mandrel **18**, partly insulated, serves as the cathode. Pump **20** is provided to remove part of the bath from the lower portion of the tank, pass it through filter **17**, and impinge a spray **21** onto the tip of the mandrel and the cone **30** being formed. Use of such a spray is almost essential to insure strength and uniformity of the deposit at the closure when articles terminating in a point or rounded apex, as the preferred cones of the invention, are made.

The composition of and conditions for operating the bath of Figure 1 are essentially those of the copending application except for use of the liquid spray. The spray is maintained by the pump operated at a rate proportional to the desired plating speed. A spray velocity of about 500–1000 ft./minute is satisfactory for a plating speed of 1 mil/minute.

Usable bath compositions and conditions include:

CuCN—oz./gal.	4–30
Free KCN—oz./gal.	0–4
KOH—oz./gal.	0.5–6
Na_2Se—p. p. m.	50–1000
Temperature—° C.	25–95
Current density—amperes sq. ft.	100–850

Preferred conditions permitting use of current densities of about 850 amperes per square foot or a plating speed of up to about one mil/minute are:

CuCN	About 10 oz./gal.
Free KCN	About 1 oz./gal.
KOH	About 1 oz./gal.
Na_2Se	About 200 p. p. m.
Temperature	About 85°–90° C.

Since the selenium is deposited with the copper to the extent of about 2–300 p. p. m. the desired concentrations must be maintained by occasional additions to the bath. These additions may be made, as may the original, in the form of Cu_2Se if it is so desired. An organic anti-pitting agent such as methylene-bis(naphthalene sulfonic acid) in the α- or β- form, C-decyl betaine or the like should also be used to improve the copper deposits. The concentration of this agent may vary in the bath from about 100 to 500 p. p. m., about 200 p. p. m. being preferred.

Other plating techniques may be used in operating the process of the invention including current reversal and current interruption. Neither of these current manipulations appreciably affects the properties of the preferred cones of the invention.

As noted above, when cones prepared from a copper cyanide bath containing a selenide are utilized as the liner for the small shaped charge of a jet perforator, they increase the penetrating power of the latter about 12–15%. This increase in penetrating power renders the perforators especially valuable for use in oil wells. Figure 2 shows a jet perforator **22** positioned for use against oil well casing **23**. The perforator consists of container **24**, initiating means **26**, and shaped charge **28**. In the broad end of the shaped charge is inserted liner **30**, preferably formed on the apparatus of Figure 1.

Electrodeposited cones are of primary value at small sizes, i. e., up to two inches in both diameter and height, and with small charges of 10–25 g. of explosive. Both larger cones and larger charges can be used although in such cases the improvement due to electrodeposition from the selenium-containing bath becomes more difficult to assess.

The reason for the enhanced penetrating power of shaped charges lined with electroformed copper cones is not precisely known but is believed due to the exact uniformity of the cone structure. The uniformity of the cone in thickness and around the center axis prevents collapse from a number of centers and thus yields a reproducible jet. The structure of the cone is due to the

method by which it is prepared. It is well known that copper deposited from cyanide baths possesses very small grains. Copper deposited from the selenium-containing cyanide baths actually possesses such fine metallographic structure that separate grains cannot be detected with an ultramicroscope. The metal is also strain-free.

In any event, equivalent cones cannot be prepared from the prior art sulfate or cyanide baths. Copper is deposited from sulfate baths onto a curved mandrel in a state of tension. Strains are thus set up which can be eliminated only by polishing the workpiece during interruption in the deposition. The mandrel employed must be adherent to the copper to retain the latter during polishing operations but also fusible so that it can eventually be separated from the article produced. Copper prepared in this manner is non-uniform and possessed of no unusual properties in regard to lining shaped charges. Conventional cyanide baths heretofore utilized employ current densities which are too low for electroforming.

There follow some examples serving to illustrate the practice of the invention:

EXAMPLE 1

This example shows the penetrating power of jet perforators lined with copper cones prepared on the apparatus of Figure 1.

Copper cones were electrodeposited from an aqueous cyanide bath upon a polished chromium mandrel under the following conditions:

CuCN ---------- oz./gal--	15
Free KCN ---------- oz./gal--	1–2
KOH ---------- oz./gal--	2
Na_2Se ---------- p. p. m--	50–200
Temperature ---------- ° C--	86
Rate of revolution of the mandrel--R. P. M--	600–2000
Spray velocity ---------- ft./min--	850–1000
Distance between jet outlet and tip of mandrel ---------- inch--	¼
Current (D. C.) ---------- A./S. F--	200–340

The cones were subsequently directly stripped from the mandrel in a single operation. Each cone was 1 inch high externally, 1.31 inches in diameter at its base and possessed an angle of 60°. The copper was electrodeposited to a thickness of about 17–20 mils.

Into each cone was forced, at a pressure of 20,000 p. s. i., an 18 gram charge of cyclonite and wax having a weight ratio of 95:5. The resultant assembly was tested as shown in Figure 3, which displays the jet perforator **22** positioned on a stack of steel plates **32** each one inch in thickness. The perforator was detonated and the depth of penetration into the plates and the diameter of the hole formed were measured. Results are given in Table I.

Table I.—Penetration with electroformed cones

Cone	Depth of Penetration, inches	Diameter of Hole in 1st Plate, inches
1	4.5	0.4
2	4.5	0.5
3	4.4	0.4
4	4.4	0.5
5	4.4	0.5
Average	4.44	0.46

The tests recorded in Table I were repeated with cones made utilizing both current reversal and current interruption. Results were the same with this second group of cones.

EXAMPLE 2

This example shows the results of penetration tests with cones made from sheet copper and is included solely as a control.

The tests of Example 1 were substantially repeated except that the lining utilized were prepared by deep-drawing sheet copper. The dimensions of the cones and the weights of the charges were substantially the same as in that example. Results are given in Table II.

Table II.—Penetration with drawn cones

Cone	Depth of Penetration, inches	Diameter of Hole in 1st Plate, inches
1	4.0	0.5
2	3.7	0.5
3	3.8	0.5
4	3.9	0.5
5	4.0	0.5
6	3.9	0.5
7	4.0	0.5
8	4.0	0.5
9	4.0	0.5
10	3.8	0.5
Average	3.91	0.5

EXAMPLE 3

This example, also included as a control, shows the results of penetration tests with electroformed cones prepared by prior art electroforming processes.

The tests of Example 1 were substantially repeated except that the linings utilized were prepared by electroforming copper from a conventional bath containing no selenium. The dimensions of the cones and the weights of the charges were substantially the same as in that example. Results are given in Table III.

Table III.—Penetration with electroformed cones

Cone	Depth of Penetration, inches	Diameter of Hole in 1st Plate, inches
1	3.4	0.5
2	3.0	0.5
3	4.2	0.5
4	3.9	0.5
5	4.4	0.5
6	4.2	0.5
7	4.2	0.5
8	4.0	0.5
9	3.4	0.5
10	3.9	0.5
Average	3.86	0.5

Having described my invention, I claim:

1. In a jet perforator comprising a shaped charge, means for detonating said shaped charge, a container substantially surrounding the shaped charge and a cavity in the base of the same, a lining in said cavity comprising a substantially strain-free copper cone produced by electrodepositing copper from an alkaline copper cyanide bath ing 50–1000 p. p. m. of an inorganic shelenide.

2. A liner for a shaped charge comprising a substantially strain-free copper cone produced by electrodepositing copper from an alkaline copper cyanide bath containing 50–1000 p. p. m. of an inorganic selenide.

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