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METHOD OF ELECTROPOLISHING STERLING SILVER

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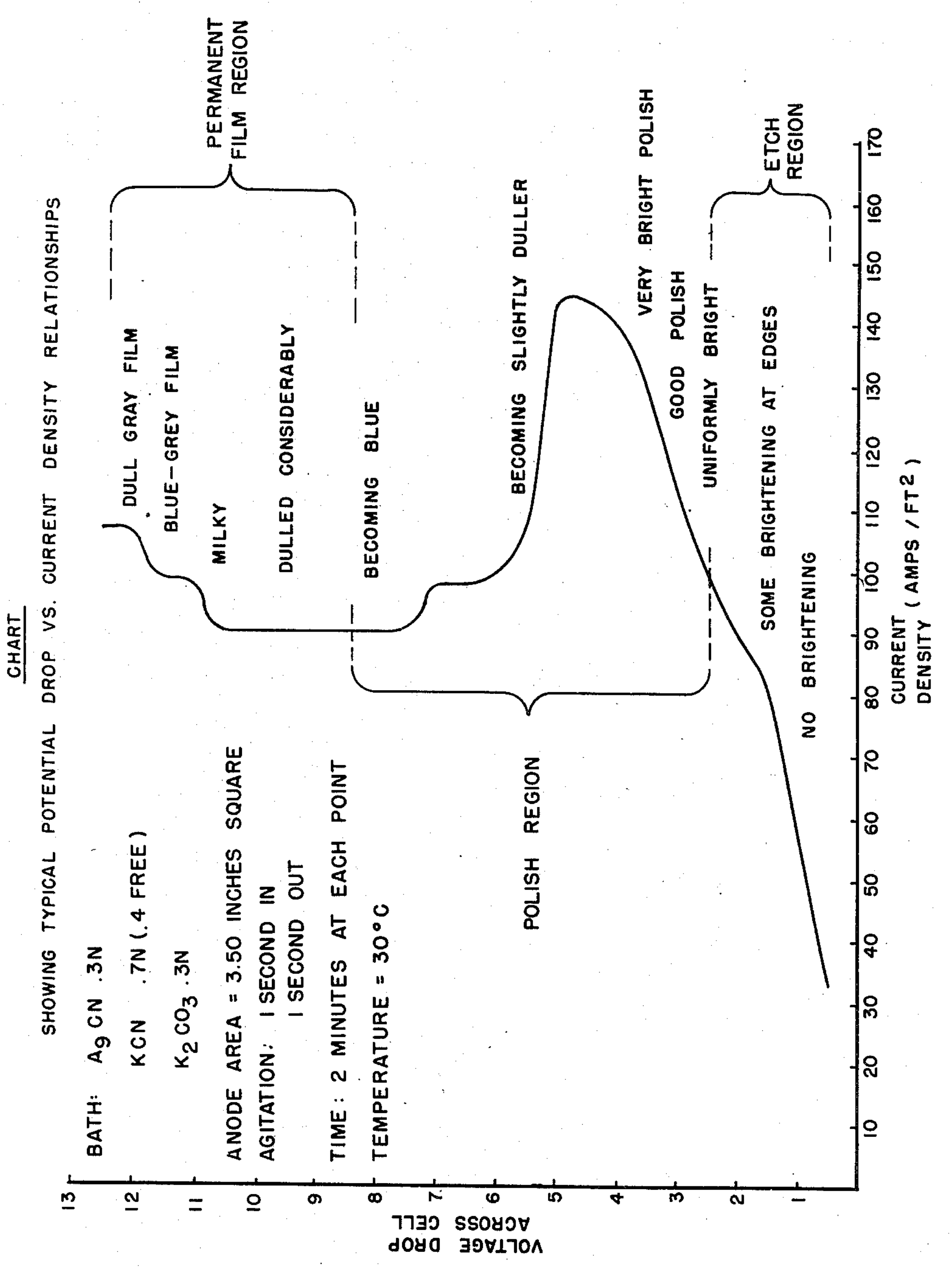

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## METHOD OF ELECTROPOLISHING STERLING SILVER

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This invention relates to the electropolishing of silver and copper alloys and more particularly to the electropolishing of sterling silver in cyanide baths.

Sterling silver is an alloy consisting usually of 92.5 per cent of silver and 7.5 per cent of copper, but variations in the amount of copper are occasionally employed commercially in similar alloys containing up to about 10 per cent copper.

In the preparation of silver articles it is essential that they have a polished surface. Polishing of sterling silver has been accomplished for many years by means of buffing the surface with various types of fine abrasives. While this technique yields a surface which is very satisfactory, the process requires expensive handwork. It has also been known that silver articles and copper articles, as well as articles fashioned from alloys of copper and silver, may be polished electrolytically in cyanide baths. While silver surfaces and copper surfaces when composed of the pure metals may be readily polished electrolytically in cyanide baths under certain conditions to a specular finish, difficulty has been encountered in readily attaining the same brightness on sterling silver articles. It is believed that the difficulty is due to a variation in the rate of dissolution of silver and copper in the alloy.

It is an object of this invention to polish electrolytically in a cyanide bath sterling silver to a specular brightness.

These, and other objects which will become apparent, may be attained by employing the process hereinafter described.

The process of this invention is carried out in an electrolytic cell containing free cyanide; the article to be polished is made the anode under the proper voltage-amperage conditions and by repeated immersions and withdrawals from solution is rapidly and completely polished in a short time. For the sake of simplicity the cycle of anode movement may be termed a stroke.

As the amount of free cyanide is increased while keeping the molar concentration of metal cyanide constant, the efficiency of the bath falls, i. e. an increasing amount of current is required to plate out (or remove) a given amount of silver. The decrease in efficiency is evidenced by the gassing which occurs to an increasing extent with increasing amounts of cyanide. It is nevertheless necessary in my process that more than the usual amount of free cyanide be present. At least 0.35 mol of free cyanide is required to secure specular brightness, while free cyanide in an amount of at least 0.4 mol to 0.5 mol is preferred, although higher amounts also give

polished surfaces. The free cyanide may be any of the soluble alkali metal cyanides. Potassium cyanide and potassium carbonate are customarily employed in plating baths in preference to the corresponding sodium salts. The reason for this is that carbonate is formed during operation and since potassium carbonate is more soluble than sodium carbonate the bath life is longer using potassium salts. The presence of sodium does, however, reduce the amount of current required to produce a given polish, and since corresponding sodium salts are also considerably cheaper in cost, it has been found advantageous to replace at least some of the potassium cyanide required with sodium cyanide.

It is preferred that silver cyanide be added to the bath to aid in maintaining the stability of the bath and to lower the current density required for polishing. While polishing is possible at very high current densities in a bath containing initially no silver cyanide, it is evident that as silver begins to deplate, the silver ions will combine with the free cyanide present until sufficient alkali metal silver cyanide has been built up to allow plating out of the silver on the cathode. The reaction of silver ions with the cyanide reduces the amount of free cyanide so that it must be adjusted and otherwise interferes with starting operations. If the molar quantity of free cyanide is maintained at a constant figure, and increasing amounts of silver cyanide are added, the current density required for polishing gradually falls. A point is reached where no polishing may be accomplished. By adjusting the free cyanide upward, the high metal-high cyanide bath will again polish, but the current density in such cases is very high. An amount of silver cyanide equal to about 0.3 mol has been found to be adequate. As in all cyanide baths, it is also desirable to add a salt such as potassium carbonate or sodium sulfate to increase the conductivity of the bath; it also appears to be particularly beneficial during operations at relatively high current densities.

Addition agents such as wetting agents, and brighteners appear to be of no value in my process.

The above discussion refers only to the addition of silver cyanide even though copper is present in the alloy. The addition of copper cyanide has no observable value, though a small amount may be added without appreciable harm.

Electrodes employed consist of the anode the sterling silver article, and a cathode which may be of any metal on which silver will plate. Such metals as copper, stainless steel, brass and silver are satisfactory. The power supplied may be from any suitable source such as a rectifier, motor generator, or battery.

As stated before, the anode is repeatedly inserted in and withdrawn from solution. The number of strokes per minute for best results is dependent upon the voltage employed. The voltage must, however, be sufficient to be above that which will cause etching of the anode, and below that of permanent film.

The relationship of voltage to current density may be understood most clearly by reference to the accompanying drawing called a chart. The chart is a graph showing the effect on the anode in various stages during increasing voltage from zero to 12.5 volts while repeatedly immersing the anode for 1 second and withdrawing it for 1 second at a regular rate in a uniform manner. Tables I to VI below show that as the strokes per minute are increased, the optimum voltage is increased, as is the current density. An examination of the chart, a plot of voltage across the cell during the time of immersion against the current density, will show that three regions are apparent. The first, or lowest region, is one where etching takes place; the second or middle region, is the polishing region; the third, or highest region, is the region where permanent discoloration occurs.

The preferred rate of strokes per minute will depend upon the particular conditions met in the plant, the article to be polished, etc. As stated above, increasing the strokes per minute increases the current density; it follows that the more rapid the strokes the more metal is removed and the more rapidly the sterling article is polished. This is borne out experimentally. But at least 10 strokes per minute are required to obtain brightness, and at least 20 strokes per minute to obtain the specular brightness desired by this invention; fewer strokes per minute than 10 do not permit the production of a polish. While not essential, regularity of motion is of value in securing reproducible results and splashing is to be avoided. To polish spoons, for instance, the spoons are racked so that they will slide in and out of solution with the minimum of agitation of the bath.

The reason for the marked improvement in the polishing of sterling silver when repeatedly removed from solution is not known. It is known that plated or pure silver, when subjected to the same treatment, does not attain a polish equal to that obtainable on sterling silver. It is also known that sterling silver may not be polished to a specular finish if polishing is accomplished without repeated immersion in the bath. Thus the advantage of this procedure appears to be unique as applied to sterling silver.

The following examples are given as specific embodiments of the invention described above.

## EXAMPLE I

A bath having the following composition was prepared:

.3 mol AgCN
.3 mol $K_2CO_3$
.78 mol KCN (.48 mol KCN free)

A sterling silver bracelet having a surface area of 5 square inches was made the anode. The bracelet was frosted with a white etch. A 25 ampere, 10 volt rectifier was set at 5 volts with no current flowing and the bracelet immersed and withdrawn at a rate of 60 strokes per minute. The bracelet became mirror bright in about three minutes. The temperature of the bath was at room temperature.

## EXAMPLE II

A bath having the following composition was prepared:

0.3 mol AgCN
0.7 mol KCN (.4 mol KCN free)
0.3 mol $K_2CO_3$

At 5 volts and 144 amperes per square foot seven sterling silver soup spoons were suspended from a rack and repeatedly immersed and withdrawn from the bath at a rate of 30 times a minute. The original weight of the spoons was 304.3 grams and the final weight 278.3 grams after several minutes of operation. The spoons were all of specular brightness and required no mechanical buffing whatsoever to attain further brilliance.

In the following tables the data was accumulated using the bath and rectifier described in Example I and a bath having the following composition:

| | |
|---|---|
| AgCN | 0.3 mol |
| KCN | 0.7 mol (0.4 free) |
| $K_2CO_3$ | 0.3 mol |

A sterling silver spoon having a surface area 3.50 square inches was employed as the anode.

*Table I*

| Volts | Amperes | Strokes per Minute | Comments |
|---|---|---|---|
| 2 | .9 | 10 | dull gray. |
| 2 | 1.2 | 20 | slight cloudiness. |
| 2 | 2.0 | 40 | center dull. |
| 2 | 2.0 | 60 | Do. |
| 2 | 2.0 | 80 | all dull. |

*Table II*

| Volts | Amperes | Strokes per Minute | Comments |
|---|---|---|---|
| 4 | 1.4 | 10 | fairly bright. |
| 4 | 1.4 | 20 | good polish. |
| 4 | 2.8 | 40 | center dull. |
| 4 | 3.2 | 60 | Do. |
| 4 | 3.2 | 80 | Do. |
| 4 | 3.2 | 100 | poor polish. |

*Table III*

| Volts | Amperes | Strokes per Minute | Comments |
|---|---|---|---|
| 6 | 1.2 | 10 | dull. |
| 6 | 1.4 | 20 | milky. |
| 6 | 2.4 | 40 | very bright. |
| 6 | 3.3 | 60 | very bright (best). |
| 6 | 3.8 | 80 | very bright. |
| 6 | 4.2 | 100 | Do. |

*Table IV*

| Volts | Amperes | Strokes per Minute | Comments |
|---|---|---|---|
| 8 | .8 | 10 | dull. |
| 8 | 1.4 | 20 | Do. |
| 8 | 2.4 | 40 | fairly bright. |
| 8 | 3.3 | 60 | brighter. |
| 8 | 4.0 | 80 | very bright. |
| 8 | 4.2 | 100 | Do. |

*Table V*

| Volts | Amperes | Strokes per Minute | Comments |
|---|---|---|---|
| 10 | 1.4 | 10 | dull. |
| 10 | 1.6 | 20 | Do. |
| 10 | 3.4 | 40 | milky. |
| 10 | 4.2 | 60 | fairly bright. |
| 10 | 4.4 | 80 | very bright. |
| 10 | 4.8 | 100 | Do. |

*Table VI*

| Volts | Amperes | Strokes per Minute | Comments |
|---|---|---|---|
| 12 | 2.0 | 10 | dull. |
| 12 | 2.6 | 20 | milky. |
| 12 | 4.0 | 40 | Do. |
| 12 | 5.2 | 60 | fairly bright. |
| 12 | 6.4 | 80 | very bright. |
| 12 | 6.5 | 100 | Do. |

The process of this invention is readily applicable to automatic machinery since once the conditions of best polish have been determined, i. e. bath, voltage and number of strokes, handwork is reduced to a minimum.

The conditions of operation in a plant for polishing a given number of pieces of any configuration may be readily determined in the following manner. Whether the pieces be flatware, such as knives, spoons, or forks; hollowware such as bowls, costume jewelry, or any other of the many commercially produced sterling articles, such as cigarette cases, candlesticks, etc., the position of the article producing the least turbulence should be first selected together with the desired number of strokes per minute equal to at least 20 strokes per minute. Having established these conditions, the three regions (etch, polish, and permanent discoloration) should be established experimentally. It is then only necessary to operate at the best voltage established for the particular bath and the strokes per minute previously determined. Thus if the bath and strokes per minute were the same as that used for arriving at the curve shown in the chart, the voltage can be set at from 3 to 5 volts, and a brilliant, specular finish will result in two minutes.

I claim:

1. A method for the anodic polishing of silver-copper alloys containing at least 90% silver in an electrolytic cell containing a cyanide bath, which comprises the steps of applying electric current and potential difference between such silver-copper alloy as the anode surface, and the cathode of the cell, and of imposing a cycle of movement of the anode in and out of the cyanide bath at a rate equal to at least 10 cycles per minute, said potential difference between such alloy as the anode surface, and the cathode of the cell during the period of immersion being below that which will form permanent discoloration and above that which will form etching, until the silver alloy acquires a polish thereon, said cyanide bath containing at least 0.35 mol of free cyanide.

2. A method for the anodic polishing of sterling silver in an electrolytic cell containing a cyanide bath having at least 0.35 mol of free cyanide which comprises the steps of applying a continuously unidirectional electric current and potential difference between such sterling silver as the anode surface, and the cathode of the cell, and of imposing a cycle of movement of the anode in and out of the cyanide bath at a rate equal to at least 20 cycles per minute, said potential difference between such sterling silver as the anode surface, and the cathode of the cell during the period of immersion being below that which will form permanent discoloration and above that which will form etching, until the sterling silver acquires a polish thereon.

3. The method in accordance with claim 2 wherein the cyanide bath contains from 0.4 to 0.5 mol of free cyanide.

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