COMPOSITIONS FOR AND METHODS OF REMOVING GOLD DEPOSITS BY CHEMICAL ACTION

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This application is a continuation-in-part of application Ser. No. 189,979, filed April 25, 1962, now abandoned.

The invention herein relates to stripping of gold from articles on which it has been deposited as a thin plate, usually by an electroplating process. The invention is directed to compositions for and methods of removing these gold deposits by chemical action solely, without significant concomitant attack on the substrate or basis metal of the articles.

In recent years, especially as a result of new developments in electronics, gold plating of various metal components has increased at an unprecedented rate. The excellent electrical conductivity of gold coupled with its high corrosion and oxidation resistance under adverse conditions makes for greater reliability of electrical devices plated with this metal. As a result, gold plating has been found to have an indispensable application in the manufacture of printed circuits and various contacting devices in the computer and communications industries. Such uses are in addition, of course, to decorative gold plating which is one of the oldest applications in the art.

As in any practical industrial operation, a certain percentage of rejects or defective articles is unavoidable. This is especially true in gold plating where finishing parts undergo very stringent inspection for appearance, adhesion, thickness and uniformity of the deposit, as well as checks for dimensional accuracy and operability also. The salvaging, if possible, of rejected articles is therefore of prime economic importance, both as a means of reclaiming the gold as well as recovering the article itself for reprocessing. If replateing with gold is all that is necessary to correct the defect, this can only be done, of course, provided the substrate metal is not itself appreciably etched during the striping operation. As in some instances, where there may be a plurality of substrate metal layers on the articles, reprocessing of these may still be economically desirable even if a metal layer directly below the gold is removed with the gold, provided again of course that the basic article itself is not adversely affected either dimensionally or otherwise.

Prior methods of stripping gold have utilized electrolytic procedures for the most part, wherein the object to be stripped is made the anode in a suitable electrolyte and current passed through it to a cathode. A typical electrolyte used successfully in this way for removing gold from ferrous alloys or nickel electroplate is a soluble cyanide, usually sodium cyanide because of its low cost. An obvious shortcomings of such electrolytic striping is that it requires individual racking of the pieces and consequently is laborious and time-consuming. Another disadvantage is that it cannot be successfully applied to alloys having high electrical resistivity, nor does the process lend itself to stripping of gold from articles which are composed primarily of non-conducting material such as plastics, ceramics or semi-conductors.

Furthermore, if composite assemblies are involved, for example copper-steel assemblies, such prior methods result in severe corrosion of the copper base.

A similar procedure commonly employed heretofore comprises electrolytic striping in an aqueous solution of sulfuric acid. This method permits gold to be stripped from copper-base components. The copper will not be appreciably etched in this process if the acid concentration is carefully maintained within critical limits, and provided also that the electrical potential is closely controlled. Both of these requirements make this method somewhat difficult to handle, especially in practical commercial installations. This method also requires that electrical contact be made between each piece to be stripped and the plating rack, and in many cases this is impractical because of the small size and large number of the parts. Again, this method cannot be used on composite assemblies of copper and steel, for example, because of the corrosive attack of the acid in this instance on the ferrous component.

Still other methods have been tried which involve the use of a soluble cyanide, such as sodium or potassium cyanide, with an oxidizing agent. Striping here is achieved solely by chemical action and the oxidizing electric current is thus obviated. Hydrogen peroxide has commonly been used as the oxidizing agent in this process, however cyanide-peroxide mixtures are inherently unstable and represent a safety hazard to personnel. Furthermore, such mixtures have an extremely short useful life, usually not over one hour, and therefore cannot be reliably counted on for industrial striping operations. A further disadvantage of the cyanide-peroxide solutions is their severely corrosive effect on copper alloys and silver, resulting in the destruction of articles fabricated of these metals. In place of hydrogen peroxide, attempt has also been made to use nitro-substituted aromatic compounds in combination with sodium or potassium cyanide. While such compositions are useful for dissolving many metals more reactively than gold, the rate of reaction on gold is far too slow to be of any practical use in commercial application. Furthermore, since the alkaline cyanide plus oxidizing agent compositions do attack other metals as well as gold, it is not possible to strip gold from basis metal components without also adversely affecting the basis metal.

It is therefore a principal objective of the present invention to provide compositions for and methods of selectively removing gold from various basis metal components including copper and copper alloys, steel and other ferrous alloys, silver, aluminum, magnesium, zinc, nickel and nickel alloys, as well as from plastic or ceramic base components. It is the purpose of this invention to accomplish this objective without the use of electric current and also to avoid the use of hazardous or unstable chemicals.

Concurrently with the foregoing it is an important object to provide a method for chemically dissolving gold from the aforementioned basis materials without producing appreciable attack on those materials, whereby the latter may be recovered in condition for replateing or reprocessing. In accomplishing these objectives it is also important that the method employed not be critical in operation in order that reasonable deviation from optimum conditions can be tolerated in practice without adverse effect.

Still a further object of the invention is to provide an easy method for reclaiming gold from scrap whereby the gold is converted to a soluble form from which it may be readily recovered.

I have discovered that the use of certain complex cyanides, and especially complex tetrahydroquinolines of the group hereinafter defined, in combination with suitable oxidizing agents, makes possible the dissolution of gold deposits from practically all metals and alloys commonly used in electroplating, without appreciable attack on the basis metal. The use of the complex metal cyanide ion, rather than the normal cyanide, is the key to my invention and results in unexpected improve-
ment both in increased dissolution rates and in selectivity of attack. As will be illustrated hereinafter, the replacement of the heretofore conventionally used alkali cyanides (which are essentially completely dissociated in aqueous solution to give alkali metal ions and free cyanide ions) by complex cyanides of the above-mentioned type to provide the corresponding complex metal cyanide anions (in which the cyanide radical is virtually undissociated in solution), permits preferential dissolution of gold deposits without appreciable attack on all basis metals used practically in electrodeposition.

As just mentioned, normal alkali cyanides such as sodium cyanide are essentially completely dissociated in aqueous solution to give the alkali metal ions and free cyanide ions. A very different result is obtained, however, in the case of the complex metal cyanide ions, such as the zinc cyanide complex for example. In aqueous solution, the complex zinc cyanide ion is dissociated as follows:

$$[Zn(CN)_4]^- \rightarrow Zn^{++} + 4CN^-$$

The equilibrium constant of the above dissociation process can be written as follows:

$$K = \frac{[Zn^{++}][CN^-]^4}{[Zn(CN)_4]^2}$$

The value of K is given as $1.3 \times 10^{-27}$ in Oxidation Potentials,” page 170, by W. M. Latimer, (Prentiss Hall, 2d edition). From this it will be apparent that the concentration of free cyanide ions in an aqueous solution of complex zinc cyanide is extremely small, and that the complex $[Zn(CN)_4]^2-$ is the predominant ionic species.

The preferred metal cyanide complex is the zinc complex noted above. However, several other complexes appear useful. These are $[Cu(CN)_4]^2-$ and $(CD(CN)_4)$.

In all cases the tetra form is the lowest complex which provides satisfactory results but there may be higher complexes produced by the presence of excess cyanide which show improvement over the free cyanide. The soluble metal salts, and hence usually the alkali metal salts, of the metal cyanide complexes are used, being formed in solution by mixing the appropriate complexing metal and alkali cyanide salts.

The oxidizing agents used in conjunction with the complex metal cyanide may, in general, be the same as those previously used in connection with the normal cyanide anion. The oxidizer must be one possessing sufficient potential when in solution to enable it to convert gold from a valence of zero to plus one, and from the kinetic standpoint must itself be sufficiently reducible to dissolve copper in a normal alkali cyanide solution. Nitro-substituted aromatics such as the nitrobenzene sulfonic acids, nitrobenzoic acids, nitroanilines, nitrochlorobenzenes, nitrophenols, nitrobenzaldehydes, and the soluble sodium, potassium and ammonium salts thereof, are especially suitable. The salts must be reasonably soluble, of course, to obtain effective rates of reaction and accordingly the selection of the cation should be made to avoid low solubility compounds. The potassium salt of nitrobenzene sulfonic acid is an example, as this is of very poor solubility and precipitation will occur. However the potassium salt of nitrobenzoic acid does not present this disadvantage. In general, the meta and para isomers of the oxidizers are best because of their greater activity; the ortho compounds are also operative but usually at substantially reduced rates of reaction. As disclosed in U.S. Patent 2,649,361, these nitroaromatic compounds are those which in aqueous solution produce an electromotive force of —0.9 volt, or higher, as measured between a sheet nickel electrode and a saturated potassium chloride calomel electrode under specified conditions. These conditions are given as follows: The concentration of the nitro-compound is at its saturation value or 0.25 gram-mol per liter of solution, whichever is smaller; there is present in the solution 2 gram-mols of sodium cyanide per liter of solution; if the nitro-compound is an acid or otherwise tends to cause an evolution of hydrocyanic gas, there is also added sufficient sodium hydroxide to neutralize or to render the solution sufficiently alkaline to substantially prevent the evolution of hydrocyanic gas; and finally, the temperature is 80° C. ± 1° C.

If the oxidizing agent selected is acidic, as for example one of the nitrobenzeno sulfonic acids, the stripping solution containing this agent together with the cyanide complex should be made sufficiently alkaline by the addition of a suitable hydroxide to prevent the release of free hydrocyanic gas. Sodium, potassium and ammonium hydroxides are the practical bases useful here, and may be used interchangeably providing the cation of the selected base is not one that produces insolubility and resulting precipitation of the oxidizer upon reaction in solution, as mentioned above.

It is believed that the reaction involved in stripping gold in accordance with the teaching of the invention, as exemplified by the reaction in an alkaline solution of sodium zinc cyanide complex and sodium meta-nitrobenzene sulfonate, proceeds according to the following equation:

$$2Au^++Na_2Zn(CN)_4+ + SO_4Na + 2NaOH \rightarrow Zn_2S_2O_7^2- + 3Au + H_2O$$

Where the gold deposit is present on a copper basis metal, a gray coating, presumably a metallic layer of zinc, forms on the basis metal in the stripping solution as the action proceeds. It is this immersion zinc layer which appears to inhibit copper dissolution after the gold is removed. This is a salient feature of this invention and serves to distinguish it sharply from the normal sodium cyanide stripping process in which concomitant copper dissolution is so rapid as to cause excessive etching of the piece. The formation of the immersion zinc layer on a copper surface exposed to the metal stripping solution is presently visualized as resulting according to the following equation:

$$6CuCN + 3[Zn(CN)_4]^2- = 6[Cu(CN)_3]_2 + 3Zn^2+$$

In order to show the basic difference between the action of normal alkali cyanides and the complex metal cyanide of this invention, comparative tests have been run with gold and copper. Copper has been selected for this comparison because of its great similarity in chemical behavior to gold, which makes chemical stripping of gold from copper a difficult task.

For comparison purposes two aqueous solutions, one containing the complex metal cyanide in accordance with the invention, the other containing the normal alkali cyanide, were prepared to provide the following bath compositions:

**SOLUTION A (INVENTION)**

<table>
<thead>
<tr>
<th>Mol/liter</th>
<th>Sodium zinc cyanide complex (Na_2Zn(CN)_4)</th>
<th>0.122</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sodium m-nitrobenzene sulfonate</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>Sodium hydroxide</td>
<td>0.12</td>
</tr>
</tbody>
</table>

1 Total cyanide=0.488 equiv./L

**SOLUTION B (PRIOR ART)**

<table>
<thead>
<tr>
<th>Mol/liter</th>
<th>Sodium cyanide</th>
<th>0.49</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sodium m-nitrobenzene sulfonate</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>Sodium hydroxide</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Thus it will be observed that the total cyanide radical content of both solutions is equivalent, while the oxidizer and hydroxide contents are identical. However, while Solution A contains cyanide in the complex form, in which the complex cyanide ion is only very slightly dissociated, Solution B contains the normal alkaline cyanide which is substantially completely dissociated to the free cyanide and sodium ions.

Test panels of copper, brass and gold were immersed in Solutions A and B under identical conditions for periods of five minutes each. Each of the brass and copper panels measured 1" x 1" square; the gold panels measured 1.25" x 2". The weight losses of the several panels were then determined and the results are tabulated below, corrected in the case of the copper and brass panels for the difference in size to give directly comparable results:

## TABLE I

<table>
<thead>
<tr>
<th>Panel</th>
<th>Temp. (°F)</th>
<th>Immersion Time (min)</th>
<th>Weight Loss in Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sol. A (Invention)</td>
</tr>
<tr>
<td>Copper</td>
<td>140</td>
<td>5</td>
<td>0.0192</td>
</tr>
<tr>
<td>Brass</td>
<td>140</td>
<td>5</td>
<td>0.0131</td>
</tr>
<tr>
<td>Gold</td>
<td>140</td>
<td>5</td>
<td>0.1127</td>
</tr>
</tbody>
</table>

The corrosion rate of both the copper and brass panels in Solution A, the invention solution, is only about one tenth of that in Solution B. Yet surprisingly the dissolution rate of gold in Solution A is about 30% higher than that in Solution B, under identical conditions. This is contrary to expectations in view of the complexed form of the cyanide present in Na₂[Zn(CN)₄].

A copper panel with a total area of 2 square inches immersed for a period of one hour in Solution A produced a corrosion rate of 0.18 mils per hour. An identical panel in Solution B produced a corrosion rate of 1.8 mils per hour under the same conditions. Thus it appears that the 1-to-10 ratio of corrosion rate for copper in Solutions A and B, respectively, obtained in short periods of immersion shown in Table I, holds also for much longer periods.

Further examples of practical, commercial applications involving the stripping of gold from various components in accordance with the invention are enumerated below:

### Example 1

Small brass pins used in the electronic industry and plated with 0.0003" of gold were immersed in Solution A, using a stainless steel basket. The parts were kept in solution for a period of 30 minutes at 140 °F, while the basket containing the parts was periodically agitated. At the end of 30 minutes, the gold was completely stripped, leaving a dark gray film on the brass pins which was easily removed by a 1 to 2 second dip in a chromic-sulfuric acid mixture. The pins, upon being examined after stripping, showed no appreciable dimensional losses and were suitable for immediate replating after normal, pre-plating cleaning.

### Example 2

A copper part plated with 0.0002" of bright nickel and an overlay of 0.000006" of gold was immersed in Solution A for approximately one minute at 150–160 °F. All of the gold plate was removed, while the nickel plate substrate showed no noticeable corrosion and was immediately suitable for replating with gold after normal cleaning.

### Example 3

A part which was an assembly of copper-lead-nickel plated with 0.0002" of gold was immersed in Solution A for a period of 10 to 15 minutes at 150 °F. This resulted in the complete removal of its gold, while the underlying basis metals showed no appreciable attack. The part could thus be salvaged and replated after adequate cleaning.

### Example 4

An aluminum part plated with copper, nickel and an overlay of gold, was immersed in Solution A at 160 °F for a sufficient period of time to completely strip the gold coating. Subsequent inspection of the part showed no appreciable dimensional losses, even in deep recesses where the substrate aluminum was completely bare.

### Example 5

A zinc die casting plated with copper, nickel and an overlay of 0.000008" of gold, was dipped in Solution A at 150 °F for approximately one minute. Complete dissolution of the gold was effected without attacking the part, even in those areas of deep recesses where the zinc die casting was unplated.

### Example 6

A small brass piece plated with silver and 0.0001" of gold was immersed in an aqueous solution containing 0.25m./l. of Zn(CN)₂, 0.69 m./l. of NaCN and 0.26 m./l. of sodium m-nitrobenzenesulfonate. The gold plate was completely removed in approximately five minutes at a solution temperature of 160 °F and the part was satisfactory for replating. The system is somewhat less selective in the case of silver, due to the very closely similar reaction rates of gold and silver, and the use of somewhat less alkaline (lower pH) solution, as in this example, gives better control.

All of the foregoing examples employ a solution of the preferred sodium salt of the zinc tetracyanide but it should be noted that the ammonium salt as well as the sodium is equally operative in this system. Potassium, because it forms a relatively insoluble compound with nitrobenzenesulfonic acid, is not particularly suitable in the sulfonic acid system, but the potassium salt is entirely satisfactory in a system otherwise identical except that nitrobenzoic acid is used in place of nitrobenzenesulfonic acid as the oxidizer. For example, potassium m-nitrobenzoate in combination with potassium zinc tetracyanide strips gold from copper at a rate that is about 20% faster than obtained in Solution A. In this case, attack on the copper substrate is also increased, but not to the same extent as the increase in the gold stripping rate, with the result that the potassium salt in the nitrobenzoic acid system gives entirely practical and useful results. Similar conditions obtain in the use of other oxidizers specifically mentioned above, and where one cation causes precipitation or results in an unstable composition, another cation will of course be preferred. For most practical applications, nitrobenzenesulfonic acid and the sodium and ammonium salts thereof, and nitrobenzenoic acid and the sodium, potassium and ammonium salts thereof, give the best results in commercial operations.

All of the foregoing examples are also characterized in that they employ a solution of the preferred complex zinc cyanide ion. In order to test the usefulness of cyanide complexes, other than the zinc, the following series of examples is given.

### Example 7

An aqueous solution was prepared containing 0.25 m./l. of mercuric chloride (HgCl₂), 1.0 m./l. of sodium cyanide, and 0.12 m./l. of sodium m-nitrobenzenesulfonate. The sodium cyanide content here is just sufficient to form the complex mercuric cyanide anion (Hg(CN)₃⁻). A gold panel having dimensions of 1.25" x 2" was immersed for five minutes in the foregoing solution at a temperature of 140 °F. At the conclusion of this period, the weight loss of the sample was 0.0044 gram, as compared to 0.1127 gram in Solution A, the preferred composition. (See Table I.) In addition to the fact that this weight loss was very low, it was further observed that the gold
panel was coated with a uniform white immersion layer of metallic mercury or perhaps a gold alloy thereof. From this it would appear that the complex mercureic cyanide compounds are not very satisfactory for gold stripping.

**Example 8**

An aqueous solution was prepared containing 0.12 m./l. of cuprous cyanide \( \text{Cu}_2(\text{CN})_2 \), 0.24 m./l. of sodium cyanide, 0.12 m./l. of sodium m-nitrobenzene sulfonate. The sodium cyanide added in this solution is just sufficient to form the complex copper cyanide anion \( [\text{Cu(CN)}_3^-] \). Panels of copper and gold, as in Table I, were immersed in this solution at a temperature of 140° F. for five minutes. The copper panel showed a weight loss of 0.0144 gram, while the gold panel showed a weight loss of only 0.0015 gram, from which it appears that the cuprous tricyanide complex \( [\text{Cu(CN)}_3^-] \) is not practical for gold stripping.

**Example 9**

The following aqueous solution was prepared: 0.12 m./l. of cuprous cyanide, 0.36 m./l. of sodium cyanide, 0.12 m./l. of sodium m-nitrobenzene sulfonate. The amount of sodium cyanide present in this instance is just sufficient to combine with copper to form the cuprous tetracyanide complex ion \( [\text{Cu(CN)}_4^-] \). Copper and copper panels, identical to those described above were immersed in this solution at 140° F. for periods of five minutes. The copper panel showed a weight loss of 0.0312 gram while the gold panel showed a weight loss of 0.0330 gram. It is apparent from this that the cuprous tetracyanide complex \( [\text{Cu(CN)}_4^-] \) is a fair solvent for gold and although the corrosion rate of copper is nearly the same in this solution, it is not so excessive as to rule out its possible use under some circumstances even for copper components. Obviously its practicality increases with base metals less reactive than copper.

**Example 10**

An aqueous solution of 0.12 m./l. of hydrated cadmium sulfate \( \text{CdSO}_4 \cdot 8/3 \text{H}_2\text{O} \), 0.5 m./l. of sodium cyanide and 0.12 m./l. of sodium m-nitrobenzene sulfonate was prepared. The cadmium sulfate in this solution combines with the sodium cyanide in the proportion stated to form the cadmium tetracyanide complex \( [\text{Cd(CN)}_4^-] \). Again copper and gold panels were immersed in this solution for five minutes at a temperature of 140° F. The copper panel showed a weight loss of 0.0024 gram, while the gold panel lost 0.0145 gram. The cadmium tetracyanide complex \( [\text{Cd(CN)}_4^-] \) therefore does not dissolve gold preferentially over copper but its low rate of dissolution of gold renders it less effective than the preferred zinc cyanide complex.

The concentration of the metal cyanide complex in solution may vary appreciably without serious effect on the preferential dissolution of gold to other metals, although the rate of dissolution will change. The upper limit of concentration should not exceed saturation of the solution, and more specifically should not exceed the limit of solubility of the complex metal cyanide in solution at a temperature of about 180° F. A practical upper limit for most purposes is about one mol. In general, the lower limit at which effective dissolution can be obtained is on the order of about 0.02 mol per liter of complex cyanide (or 0.08 mol per liter computed as total cyanide radical). In the case of sodium zinc cyanide complex this lower limit is on the order of about 0.4 gram per liter of the total complex. Concentrations of the complex anion as low as about .002 mol per liter are still operative, although the dissolution rate of the gold is so low that for most purposes it would not be practical. Nevertheless, because such solution would not corrode basis metals which would be badly corroded by the normal cyanide solution, use of such dilute complex anion concentrations is not completely out of the question in special situations.

The concentration of the oxidizing agent may likewise be varied from around 0.001 mol per liter to saturation, but approximately 0.1 to 0.5 mols per liter is most satisfactory. In the case of the preferred sodium m-nitrobenzene sulfonate, the lower limit is equivalent to 0.23 gram per liter, with the preferred range being 20 to 120 grams per liter.

As already mentioned, the solution should be kept alkaline to prevent evolution of hydrocyanic gas and if necessary, a suitable hydroxide should be added to the solution. Optimum results obtain at solution pH of 11.5 to 13.0.

The following examples give dissolution rates at various different concentrations of the components:

**Example 11**

A gold panel 1.2" x 2" was immersed in a solution containing 0.012 m./l. of sodium zinc tetracyanide complex, 0.445 m./l. of sodium m-nitrobenzene sulfonate and 0.012 m./l. of sodium hydroxide. The temperature of the solution was 170° F. and the weight loss after five minutes was 0.0180 gram.

**Example 12**

A panel of the same size as in Example 11 was immersed for the same length of time at the same temperature in a solution containing 0.0024 m./l. of the complex sodium zinc tetracyanide, 0.455 m./l. of the same oxidizer and 0.0024 m./l. of sodium hydroxide. The weight loss in this instance was 0.0085 gram.

**Example 13**

The same test was made in a solution containing the preferred content of the complex cyanide and the hydroxide (i.e., 0.12 m./l. each), but wherein concentration of the oxidizer (sodium m-nitrobenzene sulfonate) was only 0.0022 m./l. The weight loss in the gold panel in this instance was 0.075 gram in five minutes.

Temperatures of from about 140° to 160° F. are found to be optimum, but anything from about 100° F. up to boiling is operative.

The preferred composition of the zinc tetracyanide complex and nitrobenzene sulfonate or nitrobenzoate can be prepared initially in dry admixed powder form. Thus a dry composition from which the preferred bath can be readily prepared simply by dissolution in water consists of roughly equal parts by weight of the oxidizer and the total of the combined zinc and sodium cyanide salts. The ratio of sodium cyanide to zinc cyanide here must of course be adjusted stoichiometrically to produce the desired tetracyanide complex in solution. An amount of sodium or potassium hydroxide, to equal approximately one-twelfth of the combined weights of the other two components, is added to provide the desired alkalinity.

In a typically preferred formulation a dry composition comprises, by weight, about 24% zinc cyanide, 20% sodium cyanide, 48% sodium m-nitrobenzene sulfonate and 8% sodium hydroxide, or the equivalent sodium or potassium nitrobenzoate and hydroxide which may be either sodium or potassium in this case. Storage and shipping thus are facilitated and there is presented no unusual or dangerous problems as the components are inherently stable in admixture, unlike the normal cyanide-oxidizer mixtures. Alternatively the components may be prepared in concentrated liquid form and subsequently diluted to the want of use.

The bath composition and process herein described afford a simple and effective means of chemically stripping gold from basis metals which is highly selective in respect to most metals more reactive than gold, thus permitting recovery of basis metal objects in reusable condition for repeat use. The inconvenience and economic disadvantages of electrolytic depleting or stripping methods are avoided, as are the hazards of the conventional normal cyanide baths. Finally, the recovery of the gold
from the spent solution by precipitation is facilitated due to the low concentration of free cyanide. What is claimed is:

1. A composition for selectively stripping plated gold deposits by chemical action in aqueous solution, which consists essentially of:
   (a) a water soluble complex metal tetracyanide salt, the cation portion of which is selected from a group consisting of sodium, potassium and ammonium, and the complexing metal of the anion portion of which is selected from a group consisting of zinc, cadmium and copper, said salt being present in proportion to provide the equivalent of from 0.002 mol to saturation of the complex metal cyanide anion per liter of solution; and
   (b) a nitro-substituted aromatic compound selected from the group consisting of nitrobenzene sulfonic acid, nitrobenzoic acid and the water soluble sodium, potassium, and ammonium salts thereof, nitroaniline, nitrochlorobenzene, nitrophenol and nitrobenzaldehyde, wherein the nitro-substituted aromatic compound selected does not produce an insoluble compound in solution with the selected complex metal tetracyanide, said nitro-substituted aromatic compound being present in proportion to provide the equivalent of from 0.001 mol to saturation per liter of solution.

2. A composition as defined in claim 1, wherein said complex anion is zinc tetracyanide in amount sufficient to provide from 4 grams per liter to saturation in solution.

3. A composition as defined in claim 2, wherein the nitro-substituted aromatic compound is sodium m-nitrobenzene sulfonate in proportion to provide from 0.1 to 0.5 mol per liter of solution.

4. A composition as defined in claim 1, which further contains a base selected from a group consisting of sodium, potassium and ammonium hydroxide in sufficient proportion to produce a solution pH of from about 11.5 to 13.0.

5. An aqueous alkaline solution for selectively stripping plated gold deposits by chemical action, which solution consists essentially, in addition to water, of the following:
   (a) a water soluble complex metal tetracyanide salt, the cation portion of which is selected from the group consisting of sodium, potassium and ammonium, and the complexing metal of the cyanide anion portion of which is selected from the group consisting of zinc, cadmium and copper, said salt being present in amount sufficient to provide from 0.02 to 1.0 mol per liter of complex metal cyanide anions; and
   (b) a nitro-substituted aromatic compound selected from the group consisting of nitrobenzene sulfonic acid, nitrobenzoic acid and the water soluble sodium, potassium and ammonium salts thereof, nitroaniline, nitrochlorobenzene, nitrophenol and nitrobenzaldehyde in amount sufficient to provide in solution from 0.1 to 0.5 mol per liter of said compound, wherein said nitro-substituted aromatic compound selected does not produce an insoluble compound in solution with the selected complex metal tetracyanide.

6. An aqueous solution as defined in claim 5, wherein a base selected from a group consisting of sodium, potassium and ammonium hydroxide is included to maintain the pH of the solution at from 11.5 to 13.0.

7. An aqueous alkaline solution for selectively stripping plated gold deposits by chemical action, which consists essentially, in addition to water, of from 0.02 to 1.0 mol per liter of a complex zinc tetracyanide salt, the cation portion of which is selected from the group consisting of sodium and ammonium, in combination with from 0.1 to 0.5 mol per liter of a member selected from a group consisting of nitrobenzene sulfonic acid and the sodium and ammonium salts thereof.

8. An aqueous alkaline solution for selectively stripping plated gold by chemical action, which consists essentially, in addition to water, of from 0.02 to 1.0 mol per liter of a complex zinc tetracyanide salt, the cation portion of which is selected from the group consisting of sodium, potassium and ammonium, in combination with from 0.1 to 0.5 mol per liter of a member of the group consisting of nitrobenzoic acid and the sodium, potassium and ammonium salts thereof.

9. The method of selectively stripping plated gold deposits by chemical action from substrates of copper, nickel and silver, which method comprises immersing the deposited gold in aqueous alkaline solution consisting essentially, in addition to water, of the following:
   (a) a complex metal tetracyanide salt, the cation portion of which is selected from the group consisting of sodium, potassium and ammonium, and the complexing metal of the anion portion of which is selected from the group consisting of zinc, cadmium and copper, said salt being present in amount to provide per liter of solution from 0.002 mol to saturation; and
   (b) a nitro-substituted aromatic compound selected from the group consisting of nitrobenzene sulfonic acid, nitrobenzoic acid, and the water soluble sodium, potassium and ammonium salts thereof, nitroaniline, nitrochlorobenzene, nitrophenol and nitrobenzaldehyde in proportion to provide from 0.001 mol per liter to saturation of said nitro-substituted aromatic compound in solution, wherein said nitro-substituted aromatic compound selected does not produce an insoluble compound in solution with the selected complex metal tetracyanide; while maintaining said solution at a temperature of from 100° F. to boiling.

10. The method of selectively stripping plated gold deposits by chemical action from substrates of copper, nickel and silver, which comprises immersing the deposited gold in an aqueous solution consisting essentially, in addition to water, of from 0.02 to 1.0 mol per liter of a complex zinc tetracyanide salt, the cation portion of which is selected from the group consisting of sodium and ammonium, in combination with from 0.1 to 0.5 mol per liter of a member selected from the group consisting of nitrobenzene sulfonic acid and the sodium and ammonium salts thereof; maintaining the pH of said solution at from 11.5 to 13.0 by the addition of a base selected from the group consisting of sodium and ammonium hydroxide; and maintaining the temperature of the solution at from 100° F. to boiling.

11. The method of selectively stripping plated gold deposits by chemical action from substrates of copper, nickel and silver, which comprises immersing the deposited gold in aqueous solution consisting essentially, in addition to water, of from 0.02 to 1.0 mol per liter of a complex zinc tetracyanide salt, wherein the cation portion is selected from the group consisting of sodium, potassium and ammonium, in combination with from 0.1 to 0.5 mol per liter of a member selected from a group consisting of nitrobenzoic acid and the sodium, potassium and ammonium salts thereof; maintaining the pH of said solution between 11.5 and 13.0 by the addition thereto of a base selected from a group consisting of sodium, potassium and ammonium hydroxides; and maintaining the temperature of the solution between 100° F. and boiling.

12. A dry composition for use in preparing an aqueous solution for selectively dissolving plated gold deposits by chemical action, which composition consists essentially of approximately equal parts by weight of sodium m-nitrobenzene sulfonate and combined weight of zinc and sodium cyanides, there being present in the combined cyanide salts sufficient sodium cyanide to ensure the formation of the tetracyanide complex metal anion when the composition is in solution.
13. A dry composition as defined in claim 12, which also contains sodium hydroxide in the amount of approximately one-twelfth part by weight of the oxidizer and cyanide salts.

14. A dry composition for use in preparing an aqueous solution for selectively dissolving plated gold deposits by chemical action, which composition consists essentially of approximately equal parts by weight of sodium m-nitrobenzoate and combined weights of zinc and sodium cyanides, there being present in the combined cyanide salts sufficient sodium cyanide to ensure the formation of the tetracyanide complex metal anion when the composition is in solution.

15. A dry composition as defined in claim 14, which also contains a base selected from a group consisting of sodium and potassium hydroxide in the amount of approximately one-twelfth part by weight of the oxidizer and cyanide salts.

References Cited by the Examiner

UNITED STATES PATENTS

2,088,844 8/1937 Alzugaray 75—105
2,093,958 9/1937 Edquist 75—105
2,649,361 8/1953 Springer et al. 252—79.1 XR

FOREIGN PATENTS

482,095 3/1938 Great Britain.

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