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PROCESS FOR PRODUCING GOLD CYANIDE SOLUTIONS OF HIGH GOLD CONTENT

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This invention relates to the production of substantially pure alkali metal gold cyanides having exceptionally high water solubility and which in aqueous solution exhibit exceptionally high tolerance for alkali metal hydroxides and other salts. The invention also provides stable aqueous solutions of the resultant alkali metal gold cyanides in high concentration.

Alkali metal gold cyanides, for instance potassium and sodium gold cyanides, are extensively used as the source of gold in the electroplating art. These salts are customarily supplied to the electroplater in the form of dilute aqueous solutions which also contain substantial amounts of other alkali metal salts, e.g., KCN or KOH.

The shipping and storing of these dilute commercial gold cyanide solutions, as well as container costs, have long been recognized to be unduly costly, and it has been recognized that considerable economic advantage could be derived through marketing the gold solutions in a more concentrated form. However, this has not heretofore been feasible because of the low solubility of the alkali metal gold cyanides in their customary commercial form and purity.

More particularly, the concentration of these salts in commercial aqueous solutions has customarily not exceeded about 1 or 2 troy ounces of gold per gallon of solution. Higher concentrations have been found to be unstable and have resulted in crystallization and precipitation of the gold salts, so that the solution is no longer uniform.

In accordance with my present invention, I can produce stable aqueous solutions of sodium, or potassium, or other alkali metal gold cyanides containing as high as 165 grams of gold per liter of the solution or, in other words, in excess of 20 troy ounces of gold per gallon of solution.

Potassium gold cyanide has been more extensively used in the electroplating industry and, for brevity, my invention will hereinafter be more particularly described and illustrated with reference to potassium salts. However, it will be understood that the invention is also applicable to the complex gold cyanides of the other alkali metals, corresponding reagents of the particular alkali metal being used. Reference herein to alkali metals will also be understood to include ammonia.

As indicated above, it is customary in the electroplating art to obtain the gold from the refiner in aqueous solution ready for use in the electroplating bath after suitable further dilution or blending where desired. It is well-recognized that, in the plating of gold or other precious metals, a considerable amount of the precious metal salt in aqueous solution is carried from the plating bath adhering to the articles plated, generally referred to in the art as "drag-out." The drag-out is washed from the plated articles and must be recovered from the wash-water in order to avoid excessive economic loss. The drag-out is usually recovered from the wash-water, concentrated in some manner and the concentrate returned to the refiner for reclaiming and restoration to the commercial solution for return to the plater. Further, the electroplating bath must be replaced from time to time, and the used bath is likewise returned to the refiner for purification and reclaiming of the precious metal.

The gold present in the drag-out concentrate and used bath may be either in the form of potassium auric cyanide, $KAu(CN)_4$, or in the form of potassium auro cyanide, $KAu(CN)_2$, sometimes written $Au(CN)_3.KCN$ and $Au(CN).KCN$ respectively. It will be observed that, in the former, the gold is present as gold III, i.e., in the 3-valence state, and in the latter as gold I, i.e., in the 1-valence state. In the solution supplied to the plater by the refiner the gold is customarily present in the gold III form.

The gold in solutions produced through the use of aqua regia or by electrolysis is in the gold III form. There has, heretofore, been no practical method, of which I am aware, for converting the $KAu(CN)_4$ to $KAu(CN)_2$. The only practical method, of which I am aware, for producing $KAu(CN)_2$ has been by dissolving finely-divided gold powder with potassium cyanide in the presence of an oxidizing agent, such as air or a peroxide. This procedure is slow and difficult to control on a small scale, though it has been used in gold mining operations.

I have discovered that the solubility of these alkali metal gold cyanides, e.g., potassium gold cyanide and their tolerance of potassium hydroxide and other potassium salts without precipitating from solution at normal temperatures, can be markedly increased by reducing the gold of the solution to the gold I form. I have further discovered that this may be accomplished without danger of reduction to metallic gold, by reacting the auric salt in solution with cuprous cyanide, as hereinafter more fully described.

The invention makes practical the marketing, shipping and storing of stable gold solutions of much higher gold content.

Where the gold solution to be treated is acidic and contains oxidizing agents, e.g., NO_2 or Cl_2, such as solutions prepared with aqua regia, the solution should be neutralized or made alkaline by the addition of KOH, and where the solution is not clear, it should be clarified as by adding KCN and a small amount of H_2O_2. Also, objectionable oxidizing agents should be removed or destroyed, for instance by adding an organic salt, such as Rochelle salt or other tartrate, and heating the mixture for several hours.

The proportion of cuprous cyanide required is surprisingly small. An amount of cuprous cyanide as low as 1% by weight of the gold III present in the solution is surprisingly effective, through proportions of about 5%, on the indicated basis, are usually more advantageous. Proportions as high as 10%, or even larger proportions, even as high as 50%, may be used, since the copper salt may be readily removed from the resultant $KAu(CN)_2$ along with other impurities, as hereinafter described. Proportions of cuprous cyanide in excess of 10% are usually unnecessary.

Though I do not intend to be bound as to any theory expressed, it presently appears that the cuprous cyanide is oxidized to cupric cyanide, reducing the gold III to gold I. The cupric cyanide is unstable and automatically reverts to cuprous cyanide and is thus available for reducing further gold III. Accordingly, a relatively small amount of cuprous cyanide, such as indicated above, is effective for reducing far in exces of its equivalent of gold III and this is accomplished, in accordance with my present invention, without danger of reducing the gold to its metallic form.

In effecting the reduction of the gold III to gold I, a solution of the gold III salt, such as described above, and to which the cuprous cyanide has been added, is heated for several hours. The temperature and time of heating appear to be somewhat interdependent and accordingly subject to variation. But highly advantageous

results have been obtained, for instance, by heating the mixture for about 2 hours at a temperature of 150°–180° F.

The resultant $KAu(CN)_2$ may, with advantage, be separated from the solution by adding a substantial excess of an aqueous solution of KOH or potassium salt and cooling the resultant solution to room temperature or lower, e.g., about 60° to 70° F. At this temperature, in the presence of excess potassium ion, the $KAu(CN)_2$ is substantially completely precipitated from the solution and may be separated therefrom by filtration. The precipitate may then be washed with cold water to remove residual KOH and salts and the washed precipitate redissolved in hot water and, where necessary, refiltered at a temperature of about 160°–200° F. to remove any solid particles present. Thorough washing is recommended in order to obtain maximum solubility of the $KAu(CN)_2$.

Where the $KAu(CN)_4$ solution treated contains substantial amounts of impurities such as compounds of copper, iron, nickel or silver, they may, with advantage, be separated from the alkali metal gold cyanide by the procedure described and claimed in my copending application Ser. No. 139,228, filed concurrently herewith.

The invention will be further illustrated by the following specific examples but is not intended to be limited thereto:

Example I

5 troy ounces of pure gold leaf was dissolved in 600 cc. of concentrated aqua regia and the solution boiled down to a volume of about 100 cc. to remove excessive chlorine and NO_2. The resultant solution is then diluted in water to a volume of 2000 cc. and carefully neutralized with KOH and 500 cc. of 50% aqueous solution of KCN was added to dissolve auric hydroxide. 50 grams of Rochelle salt and 30 grams of cuprous cyanide were then added to the solution and the solution heated at a temperature of 150°–180° F. for about 2 hours. 500 grams of KOH was then added with constant stirring and the solution was then cooled to room temperature, resulting in the precipitation of $KAu(CN)_2$ which was filtered off, washed with cold water and then redissolved in 1500 cc. of hot water to form a solution of $KAu(CN)_2$ stable at normal temperature. Thorough washing is recommended for obtaining maximum solubility of the potassium auro cyanide.

It will be noted that the cuprous cyanide may be added with the Rochelle salt and the destruction of the oxidizing agents and reduction of the gold accomplished by a single heating operation.

Example II

5 troy ounces of gold was dissolved by anodically electrolyzing it in KCN solution separated from the cathode by a porous cup. The resultant gold cyanide was in the gold III form. Since no oxidizing agents were present, treatment to remove the oxidizing agents, as by use of Rochelle salt described in Example I, was unnecessary. 30 grams of cuprous cyanide was added to the solution and the solution otherwise treated as described in Example I.

The proportion of potassium hydroxide used in the final addition thereof, described in Example I, is subject to considerable variation and may, with advantage, range from about 200 to about 1000 grams per liter of the gold solution. Its purpose is to promote precipitation of the $KAu(CN)_2$ at the lower temperatures to which the solution is cooled to effect precipitation.

Where the gold III solution to be treated contains minor proportions of metallic gold, a small amount of hydrogen peroxide may be added with the KCN to promote dissolving of such gold particles. For this purpose, proportions of hydrogen peroxide ranging from about 10 cc. to about 100 cc. of 10 volume H_2O_2 may be added along with the KCN solution of Example I.

I claim:

1. Method for reducing an alkali metal auric cyanide to the corresponding alkali metal auro cyanide in aqueous solution, without reduction of gold to metallic form, which comprises reacting cuprous cyanide with the alkali metal auric cyanide, while the latter is in clear, alkaline, aqueous solution which is substantially free from oxidizing agents and which contains an excess of the corresponding alkali metal cyanide, by mixing the cuprous cyanide with the aqueous solution of the alkali metal auric cyanide in a proportion not less than about 1% and not exceeding about 50% by weight of the gold in the 3-valence state present in the solution, and heating the resultant mixture for several hours, thereby reducing the gold in the 3-valence state substantially completely to gold in the 1-valence state.

2. Method for reducing potassium auric cyanide to potassium auro cyanide in aqueous solution, without reduction of gold to metallic form, which comprises reacting cuprous cyanide with potassium auric cyanide while the latter is in clear, alkaline, aqueous solution which is substantially free from oxidizing agents and which contains an excess of KCN, by mixing the cuprous cyanide with an aqueous solution of the potassium auric cyanide in a proportion of not less than about 1% and not exceeding about 50% by weight of the gold in the 3-valence state present in the solution and heating the resultant mixture, thereby reducing the gold in the 3-valence state substantially completely to gold in the 1-valence state.

3. The method of increasing the water solubility of an alkali metal gold cyanide in which the gold is present, at least in part, in the 3-valence state, which comprises reacting cuprous cyanide with the alkali metal auric cyanide, while the latter is in clear, alkaline, aqueous solution which is substantially free from oxidizing agents and which contains an excess of the corresponding alkali metal cyanide, by mixing the cuprous cyanide with an aqueous solution of the alkali metal auric cyanide in a proportion not less than about 1% and not exceeding about 50% by weight of the gold in the 3-valence state present in the solution and heating the resultant mixture to a temperature within the range from about 150° F. to about 180° F. for several hours, thereby converting the gold in the 3-valence state substantially completely to gold in the 1-valence state and separating the resultant alkali metal auro cyanide from the solution.

4. The process of claim 3 in which the alkali metal is potassium.

5. The process of claim 3 in which the alkali metal auro cyanide is precipitated from the solution by cooling the solution to a temperature not exceeding room temperature and the precipitate is washed with cold water to remove residual alkali metal compounds.

6. The process of claim 5 in which, prior to washing the precipitate with cold water, it is redissolved in a hot aqueous solution of the alkali metal hydroxide and reprecipitated by cooling.

7. The process of claim 5 in which, prior to washing the precipitate with cold water, it is redissolved in a hot aqueous solution of the alkali metal salt and reprecipitated by cooling.

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