

April 27, 1965

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PROCESS FOR SEPARATING SUBSTANTIALLY PURE ALKALI METAL  
GOLD CYANIDES FROM IMPURE SOLUTIONS THEREOF

Filed July 2, 1963

2 Sheets-Sheet 1

FIG. 1

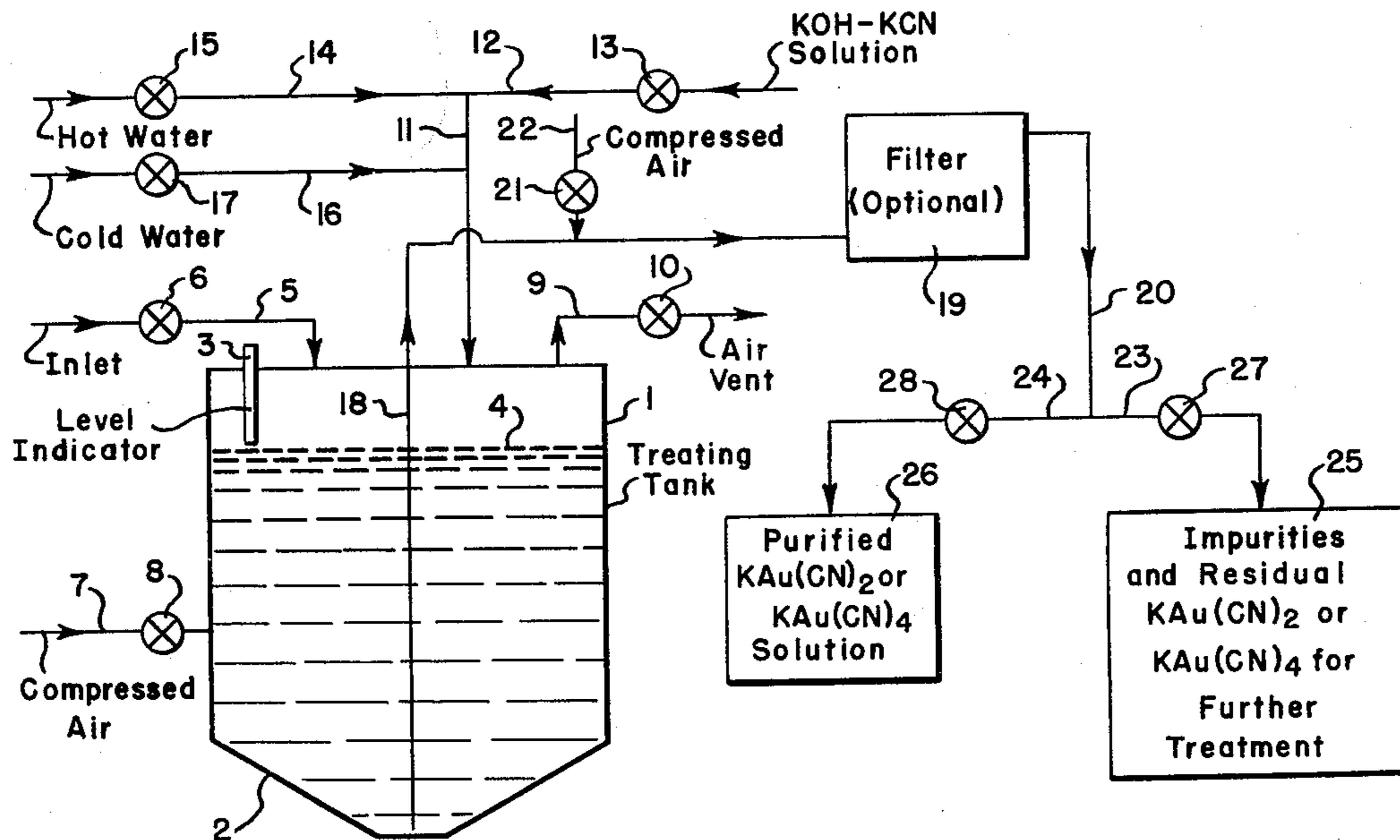
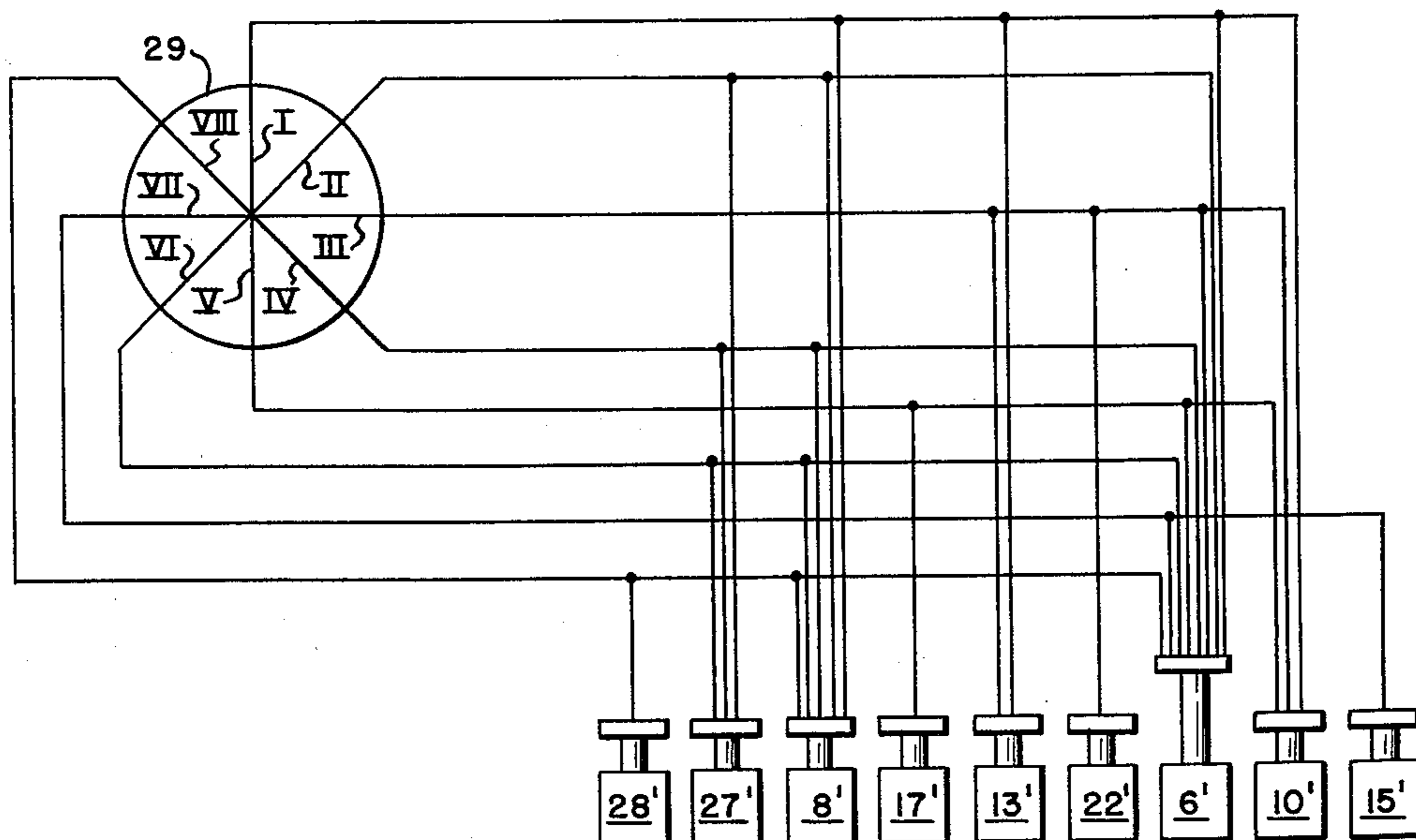


FIG. 1A



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2 Sheets-Sheet 2

FIG. 2

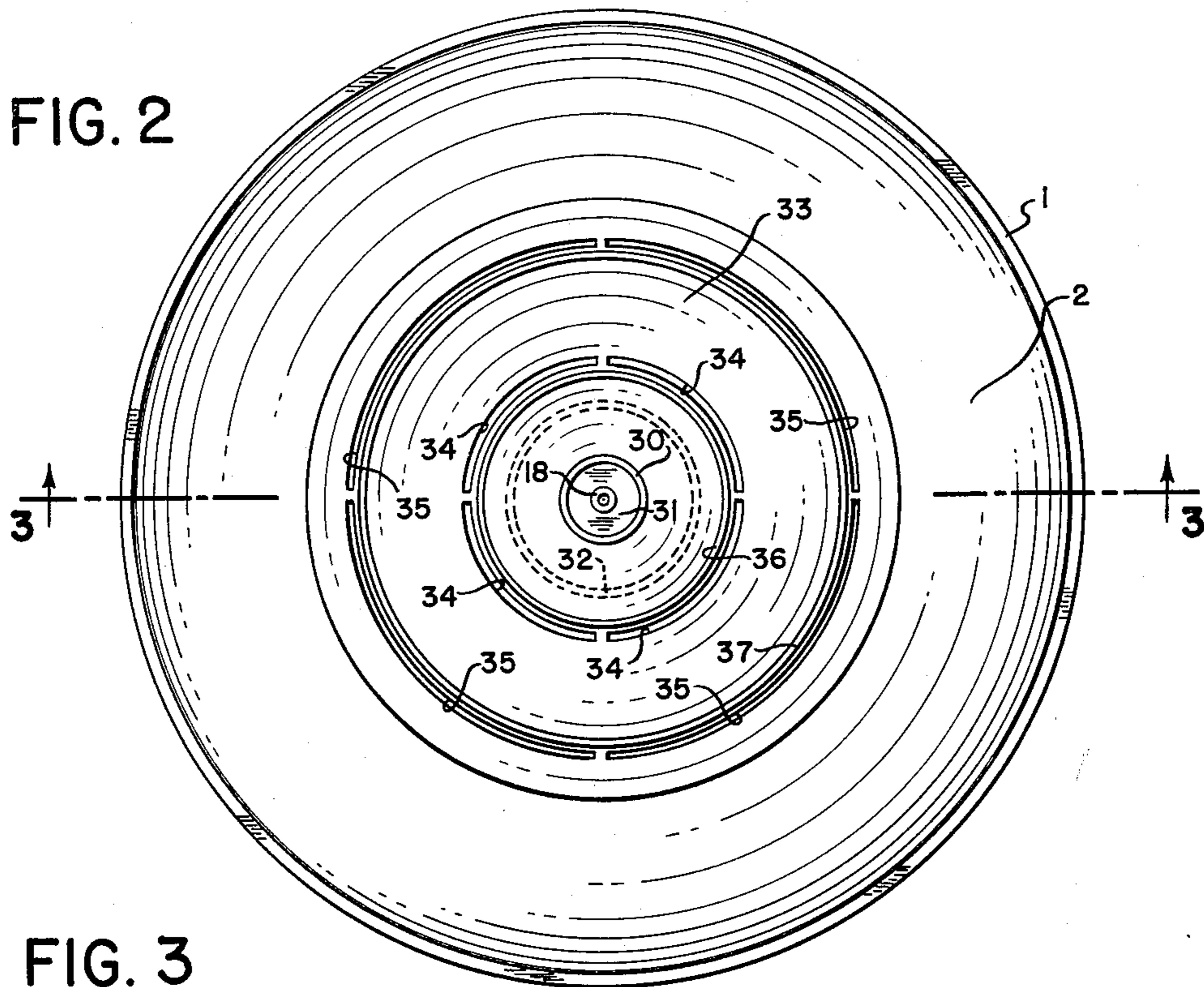
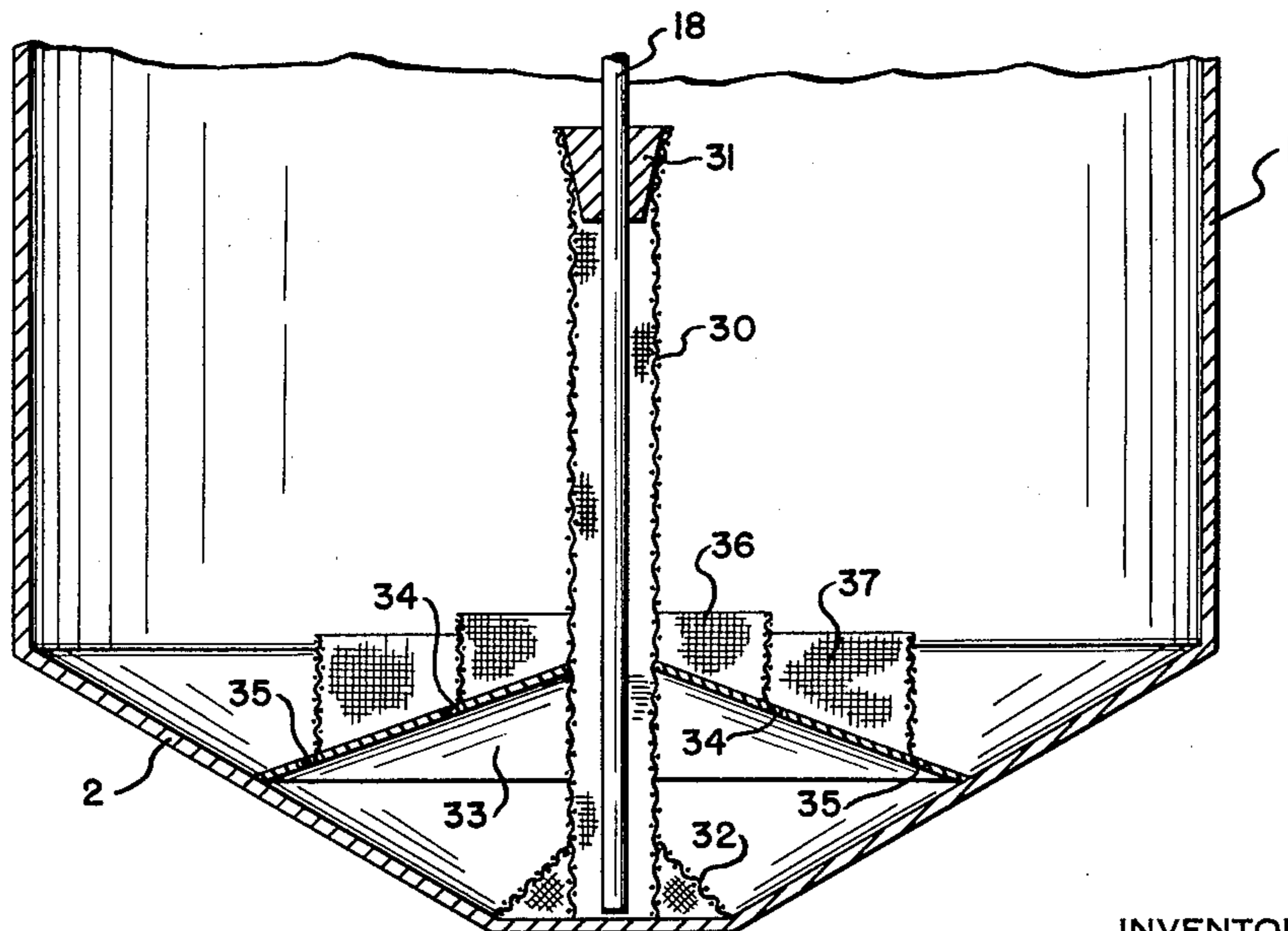


FIG. 3



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3,180,705  
**PROCESS FOR SEPARATING SUBSTANTIALLY  
PURE ALKALI METAL GOLD CYANIDES FROM  
IMPURE SOLUTIONS THEREOF**

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8 Claims. (Cl. 23—77)

The present invention relates to the treatment of gold-bearing solutions or solids and relates, more particularly, to an improved method for separating objectionable impurities therefrom, and also to apparatus especially adapted to the carrying out of the process.

Though not restricted thereto, the invention is especially useful in the production, recovery or regeneration of aqueous gold-bearing solutions suitable for use in the electroplating of gold on metal objects, for instance so-called costume jewelry or the like.

In the electroplating of gold on costume jewelry, for instance, one may use as the electroplating bath a solution of gold cyanide or gold chloride. In order to give the resultant gold plating the proper color and sheen, and also for economy reasons, one may include in the electroplating bath the salts of other metals, for instance copper, iron, nickel or silver, so that the resultant plating is of the nature of gold alloyed with one or more of the other metals. But the rates at which the respective metals are plated out from the solution are usually such that the relative concentrations of the respective metals remaining in the electroplating bath do not remain at the desired level. The plating bath must be renewed periodically and, for economic reasons, the gold in the discarded bath must be recovered.

Also, the pieces of jewelry, or the like, which have been gold-plated are customarily removed from the electrolytic bath and water-washed to remove the adhering plating solution and the gold must be recovered from the wash water.

In the plating bath, the gold is usually present in the form of potassium gold cyanide,  $\text{KAu}(\text{CN})_2$  or  $\text{KAu}(\text{CN})_4$  or other alkali metal gold cyanides. The bath will also usually contain potassium cyanide and may contain other alkali metal cyanides. In addition, as indicated above, the plating bath will usually contain carbonates or phosphates to increase conductivity and to serve as pH buffers, and frequently will contain other anions, in addition to metals such as the copper, iron, nickel and silver mentioned above. The wash water, or the discarded electrolytic bath, will usually also contain some precipitated metallic gold.

I have discovered that I can effect a substantially complete separation of the alkali metal gold cyanide, e.g., potassium gold cyanide, from such impure plating baths or from the wash water, or other solution, by adding to the impure solution, under the conditions hereinafter more fully described, a substantial excess of the hydroxide or of a salt of the alkali metal and an excess of the alkali metal cyanide and cooling the solution to room temperature or below.

At an elevated temperature, all, or substantially all, of the salts present in the solution, augmented as just described, will go into solution. But by lowering the temperature of the mixture to room temperature or lower, say about 60–70° F., I have found that the alkali metal gold cyanide is substantially completely precipitated out from the solution while the carbonates, phosphates, cyanides and other salts of other metals present as impurities will be retained in the solution and that the precipitate may be filtered from the solution and washed, as hereinafter more fully described, and a substantially pure alkali

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metal gold cyanide recovered from the filter in solid form or recovered in aqueous solution by dissolving in hot water.

In a further aspect of the invention, impure gold dust or impure precipitated gold or other impure gold-bearing materials may be dissolved in aqua regia or in an alkali metal cyanide and treated in accordance with my process. Where aqua regia is used, as just indicated, acidity of the resultant solution should be neutralized by the addition of ammonia or caustic and all oxidizing agents present in the solution may be destroyed.

Though it will be understood that the present invention is applicable to all of the alkali metal gold cyanides, potassium gold cyanide is the one most frequently used in electroplating and, for simplicity, I shall hereinafter describe and illustrate the invention as applied to the recovery or purification of the potassium gold cyanides. When applied to the gold cyanides of the other alkali metals, corresponding reagents of that particular alkali metal will, of course, be used. Reference herein to alkali metals will be understood to include ammonia.

The potassium gold cyanide to be purified in accordance with the present invention may be either in the form of gold I, i.e.,  $\text{KAu}(\text{CN})_2$  or in the form of gold III,  $\text{KAu}(\text{CN})_4$ . Where it is desired to obtain purified potassium auro cyanide, gold III may be converted to gold I, as described and claimed in my copending application Ser. No. 139,060, filed September 19, 1961, now Patent No. 3,112,174, issued November 26, 1963. This reduction of the gold may be accomplished either prior to or following the purification of the potassium gold cyanide.

The reducing of the gold III to gold I is accomplished in accordance with my said copending application by heating the gold III solution with a small amount of cuprous cyanide and, where desired, that step may be readily combined with my purification process, as hereinafter illustrated.

Where the gold to be purified is in metallic form, such as impure gold dust or precipitated gold tailings in finely-divided form, it should first be dissolved either in KCN in the presence of an oxidizing agent or in aqua regia.

Where dissolved in aqua regia, the solution should be boiled to remove excess  $\text{NO}_2$  and  $\text{Cl}_2$ , then diluted with water and the acidity neutralized by the addition of potassium hydroxide and sufficient KCN added to dissolve all of the metal impurities present as the corresponding metal cyanide. Any particles of gold in the solution should be dissolved, as by adding a small amount of peroxide. Interfering oxidizing agents present in the solution may be eliminated, for instance by heating with an organic salt such as Rochelle salt or other tartrate.

Where the gold is present as gold III and it is desired to convert it to gold I, in accordance with my above-noted copending application, the solution may be treated with from 5% to 10% by weight of cuprous cyanide, based on the amount of gold present in the solution, and the solution heated for several hours. The cuprous cyanide will be oxidized to cupric cyanide in reducing the gold III to gold I and the cupric cyanide automatically reconverts to cuprous cyanide and is available for the reduction of further amounts of gold III. The copper salts will be removed, along with other impurities, by the process of my present invention.

Where the gold to be purified is in solution, or substantially so, the above described use of aqua regia will be unnecessary. But care must be taken to insure a complete solution of the gold and all impurities present. This may usually be accomplished, as indicated above, by the adding of potassium hydroxide and potassium cyanide and a suitable oxidizing agent, for instance hydrogen peroxide, the latter to insure the dissolving of any metallic gold which may be present. This solution is then heated

to effect complete solution and, where gold III is present, to reduce the gold to gold I, if the cuprous cyanide has been added.

As a second step of my process, the solution prepared by either of the methods noted above is cooled to about room temperature or below, advantageously about 60° F., at which the  $\text{KAu}(\text{CN})_2$  or  $\text{KAu}(\text{CN})_4$  will precipitate and is filtered off. The filtrate containing the impurities, and which may contain some residual gold, is retained for further treatment. The precipitated potassium gold cyanide will contain some entrapped soluble metal salts and may also contain some insoluble impurities such as silicates. For removing these impurities, the precipitate is, with advantage, redissolved in concentrated hot caustic solution containing potassium cyanide to maintain any contaminating cyanides in solution. The resultant solution is then cooled as described above to reprecipitate the potassium gold cyanide.

After separation, the precipitate is washed with a small amount of cool water to remove residual hydroxides and contaminating cyanides. The purified alkali metal gold cyanide may then be dissolved in a small amount of hot water, in which the potassium gold cyanide is readily soluble, and any residual insolubles present may be removed by filtration.

Though the process has been carried out very successfully as just described, I have found that by substituting sodium hydroxide and sodium cyanide for the corresponding potassium salts in preparing the initial solution, preceding the first precipitation and filtration steps, the amount of gold remaining in the filtrate may be materially reduced. I have found, for instance, that the solubility of sodium gold cyanide in sodium hydroxide can be lowered to about 0.5 gram per liter, as compared with two grams per liter for potassium gold cyanide in potassium hydroxide. Thus the recovery of gold from the solution in the initial precipitation effected by cooling the solution may be materially increased. However, in the subsequent purification steps, I prefer to use potassium hydroxide in forming the solutions so as to convert the gold into the more soluble potassium gold cyanide.

Where cadmium, silver or copper is present as an impurity in the gold-containing material, I have found that a substantial excess of hydroxide in the solution tends toward the formation of hydroxide-cyanide complexes of the silver, gold, cadmium and copper, and that these complexes tend to interfere with the purification and recovery of the gold. These complexes have solubility characteristics somewhat resembling those of the alkali gold cyanide and therefore tend to precipitate with the gold cyanide upon cooling the solution. To minimize this problem, when cadmium, silver or copper is present, I have found it advantageous to adjust the gold solution, such as results from aqua regia treatment, to a pH of about 8 before adding the alkali metal cyanide.

Where calcium or magnesium is present as an impurity, I have found it advantageous to add to the solution a small amount of ammonium sulfate prior to the initial cooling step. This appears to result in the forming of calcium or magnesium sulfate which are more stable than the corresponding cyanides and therefore remain in solution in the final filtrate or decant. The amount of ammonium sulfate required for this purpose will, of course, depend upon the amount of calcium and magnesium present.

Where the initial gold-bearing solution contains metals such as chromium, iron, indium, or other metals which yield insoluble hydroxides, it is sometimes desirable to filter the hot alkali metal hydroxide solution to separate therefrom undissolved hydroxides prior to cooling the solution for precipitation of the gold salts.

An outstanding advantage of my present process is its ready adaptability to automatic operation and control by readily available apparatus for timing and controlling the

sequence of the various process steps with a minimum of attention by operating personnel.

One difficulty frequently experienced in attempting to adapt to an automatic time-sequence system processes involving precipitation and washing has been clogging of the filter. My present invention provides a novel precipitation, decanting and washing system whereby such difficulties are avoided.

The invention will be further described and illustrated with reference to the accompanying drawings of which

FIG. 1 represents, diagrammatically, apparatus especially adapted to the carrying out of my process as an automatically-controlled sequence of operations,

FIG. 1A represents conventionally and diagrammatically a sequence timing device adapted to control automatically the sequence and timing of operations in the apparatus of FIG. 1,

FIG. 2 is a somewhat enlarged horizontal sectional view of the treating tank shown in FIG. 1, and

FIG. 3 is a sectional view along the lines 3—3 of FIG. 2.

A treating tank is represented at 1 having a downwardly concave bottom 2, shown in the drawing as frusto-conical, and adapted to maintain a body of liquid. At 3, there is shown a level indicator or sensor, e.g., electrodes, adapted to put in action other mechanisms, hereinafter described, when the level of the liquid within the tank has reached a predetermined point, for instance as indicated at 4.

The solution to be treated is charged to the tank through conduit 5 which is controlled by a solenoid-actuated valve indicated at 6. A conduit 7, which enters the tank below the normal liquid level, is provided for charging compressed air, or the like, either for agitating the liquid within the tank or for forcing the liquid from the tank, or both, and is controlled by a solenoid-actuated valve 8. An air vent conduit 9 leads from the upper end of the tank and is controlled by solenoid-actuated valve 10. The tank is also provided with an inlet conduit 11 to which there is connected a branch line 12, controlled by solenoid-actuated valve 13 and leading from a source of KOH-KCN solution; a branch line 14, controlled by solenoid-actuated valve 15, leading from a source of hot water; and branch line 16 controlled by solenoid-actuated valve 17 leading from a source of cold water.

Leading from the lowermost point in the tank, so as to permit complete discharge of liquid therefrom, is a discharge line 18 leading to filter 19 or may be connected directly to line 20, where filter 19 is omitted.

A second compressed air line 21 is, with advantage, provided leading into discharge line 18 by which the air may be blown through line 18 into the bottom of the solution in the tank to agitate the solution or blown through filter 19 to free any precipitate therein from residual filtrate, line 21 being controlled by solenoid-actuated valve 22.

Branch lines 23 and 24 lead from line 20 to receivers 25 and 26, respectively, for collecting filtrate and wash water and purified solution as indicated. Lines 23 and 24 are controlled, respectively, by solenoid-actuated valves 27 and 28.

The normal position of valve 6, i.e., when the solenoid is not activated, is open so as to permit charging to the tank of the solution to be treated as it becomes available. The normal positions of each of the other valves is closed.

A sequence timer system, such as diagrammatically represented in FIG. 1A is provided for actuating the valve-controlling solenoids 6', 8', 10', 13', 15', 17', 22', 27', and 28', respectively, in predetermined order, these solenoid reference numerals corresponding to those of the respective valves shown in FIG. 1 with which the solenoid is associated.

The sequence timer mechanism is diagrammatically represented at 29 of FIG. 1A and may be of any known type provided with the desired number of stations. The particular timer indicated is electrically operated and is

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provided with 8 stations. However, fewer stations may be provided should it be desired to omit or combine one or more operations of the process. For instance, only one inlet for water need be provided, if separate means for heating or cooling the water is provided.

As schematically shown in FIG. 1A, one or more of the valve-actuating solenoids is electrically connected to selected stations of the sequence timer, depending upon the particular operation desired. At the termination of the time period at any station, the respective valves will return to their normal position.

Previous attempts to adapt processes involving a series of precipitations and washings to automatic sequence control have encountered serious separation difficulties due to unreliable or faulty functioning of filters or the like. My present invention provides improved means whereby such previously experienced difficulties may be entirely avoided.

In accordance with this aspect of my invention, I effect each of the operations, including precipitation, separation and washing, in a single tank such as shown at 1, provided with a series of decanting baffle screens, as hereinafter more fully described and illustrated by FIGS. 2 and 3 of the drawings. By this means, all or practically all of the precipitate may be retained in the treating tank during the entire operation so that the use of a filter, such as indicated at 19 is frequently unnecessary. Where a separate filter is used, the amount of solids separated thereon is so small that no filter difficulty is experienced.

By reason of the fact that the process of my invention may be carried out in a single treating tank, it is especially adapted to automatic control, such as just described, though the sequence of operation can, if desired, be manually controlled.

Referring more particularly to FIGS. 2 and 3, the means for retaining the precipitate in the treating tank during the various states of the operation comprise a cylindrical screen 30 coaxially positioned with respect to the exit conduit 18 and supported at its upper end by said conduit through fitting 31. The screen 30 extends to the bottom of the tank and, extending therefrom near its lower end, is a conical screen 32 also extending to the bottom of the tank. A slotted metal cone, its sides extending outwardly and downwardly from cylinder 30, is shown at 33, the lower portion of said cone extending to the sloping bottom of the tank.

Cone 33 is provided with circumferential slots, more clearly shown in FIG. 2, at 34 and 35. Extending upwardly from the cone, just in from slot 34, is a cylindrical screen 36. A similar screen of larger diameter, extending upwardly from the cone, just in from slot 35, is shown at 37.

These baffle screens 30, 32, 36 and 37 are, with advantage, fabricated of 60 mesh screen wire cloth, though the coarseness of the screen may be varied from about 20 mesh to about 200 mesh depending upon the coarseness of the precipitate.

It will be understood that, instead of air pressure, a pump may be provided for removing the liquid from the treating tank.

In carrying out the process in the illustrated apparatus, at station I of the sequence timer, the inlet valve 6 is closed and valve 13 is opened to admit KOH-KCN solution in a predetermined amount and of a predetermined concentration, air valve vent 10 is opened and compressed air valve 8 is opened to admit air for agitating the solution. The mixture is then heated to a temperature of about 150°-180° F. for several hours to insure complete solution. The heating may be effected by any convenient means, for instance heating coils in heat-exchange relation with the solution. Following the heating period, the solution is cooled to about room temperature or below, for instance by means of cooling coils, and the mixture allowed to stand unagitated to permit precipitation and settling of the potassium gold cyanide which is caught

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and retained on the decanting screen baffles, previously described.

After this operation has been effected, the sequence timer moves to station II at which valve 6 remains closed, and valves 8 and 27 are opened and the solution within the treating tank is forced through line 18 and filter 19, where used, and line 20 into the receiving tank 25, the precipitate being retained in the treating tank, as just described.

At station III, valves 10, 13 and 22 are opened, admitting a predetermined amount of KOH-KCN solution for redissolving the precipitate and agitating the solution by compressed air introduced through lines 21 and 18. The solution is again cooled, as indicated above, to precipitate the potassium gold cyanide.

At station IV, valves 8 and 27 are open and the solution forced by the compressed air into the receiver tank 25, the precipitate being retained in the treating tank.

At station V, valves 10 and 17 are opened to admit a predetermined amount of cold water for rinsing excess KOH and KCN from the precipitate. At station VI, valves 8 and 27 are open and the wash water thereby forced into the receiving tank 25.

At station VII, valves 10 and 15 are opened to permit the charging of a predetermined amount of hot water to the treating tank for redissolving the precipitate, and at station VIII, valves 8 and 28 are opened and the purified solution thereby discharged into the receiving tank 26. During each of the sequence of operations, valves 6 will be closed.

My present process, in its broader aspect, is based primarily on a recognition of the fact that the alkali metal gold cyanides, whether the gold is present as gold I or as gold III, becomes relatively insoluble in an aqueous solution of the type described as the temperature of the solution is decreased to room temperature or below and will precipitate from the solution while the carbonates, phosphates and alkali cyanides of copper, nickel, iron, silver and the like remain in solution.

The process of my invention will be illustrated by the following specific examples. It will be understood, however, that these examples are for illustrative purposes and are not limitative.

#### Example I

A gold-bearing material in impure, finely-divided form is dissolved in aqua regia and the resultant acidic solution is made alkaline by the addition of ammonia or caustic and sufficient alkali metal cyanide is added to insure complete solution of all the materials present. Where any undissolved gold is present, it should be brought into solution by the addition of a small amount of hydrogen peroxide or other oxidizing agent. About 10 grams of KCN and about 500 grams of potassium hydroxide or potassium salt in aqueous solution, per gallon of the solution being treated, is then added and the resultant mixture heated to about 150° F. to insure solution of all salts present. The solution is then cooled to about 60° F. and the potassium gold cyanide thereby precipitated and the solution is removed by decanting. The precipitate may then be redissolved in a KOH-KCN solution, reprecipitated, separated and washed with cold water as previously described.

#### Example II

The following procedure may be followed where the gold to be purified is in the gold III form, such as results from dissolving the gold-bearing material in aqua regia and it is desired to obtain  $\text{KAu}(\text{CN})_2$  of high purity. The solution resulting from the dissolving of the impure gold in aqua regia is boiled down to remove excess  $\text{NO}_2$  and  $\text{Cl}_2$  and then diluted with water and made alkaline by the addition of potassium hydroxide and sufficient potassium cyanide added to insure complete solution. Interfering oxidizing agents are then destroyed by heating with Rochelle salt and 5 to 10% by weight of cuprous cyanide, based on the amount of gold III present, is

added and the mixture heated to a temperature of about 150°-170° F. for about 2 hours. The solution was then cooled to about 60° F., thereby precipitating potassium auro cyanide. The precipitate is separated from the solution, redissolved in KOH-KCN solution, reprecipitated by cooling and decanted from the solution. The resultant  $\text{KAu}(\text{CN})_2$  is then washed with cold water and may then be redissolved to form a substantially pure solution of  $\text{KAu}(\text{CN})_2$ . Where optimum purity is not required, the step of redissolving of the precipitate in KOH-KCN solution may be omitted.

### Example III

Gold drag-out, depleted baths or other gold solutions are first concentrated as by evaporation. Three gallons of this concentrate is heated for about 2 hours at about 150°-180° F. together with about 1500 grams of potassium hydroxide, about 30 grams of cuprous cyanide, about 50 grams of Rochelle salt and about 50 cc. of 20 volume hydrogen peroxide. The solution is then cooled to about 60° F. which results in a precipitation of the potassium auro cyanide which is then separated from the solution. The precipitate is then dissolved in 1-2 liters of hot water containing about 200-1000 grams of KOH and about 25-100 grams of KCN per liter, and the solution again cooled to precipitate the  $\text{KAu}(\text{CN})_2$  which is separated from the solution and washed with about 100 cc. of cold water. After separating the wash water therefrom, the substantially pure  $\text{KAu}(\text{CN})_2$  is dissolved in a minimum of hot water, refiltered, if necessary, and is ready for reuse.

### Example IV

A gold sludge containing 5 to 10 ounces of gold and also containing silver, copper, calcium and other impurities, which has been precipitated from the filtrate of my process by means of zinc or aluminum, is washed free of cyanide and about 1000 cc. of concentrated hydrochloric acid added to an equal volume of the sludge and the mixture heated to dissolve out calcium salts and some metals, including copper, cadmium and zinc. The remaining gold, after filtering and washing is then dissolved in about 1000 cc. of concentrated aqua regia and boiled down to a low acid content. By this procedure, silver was precipitated from the solution as silver chloride and is filtered off. The solution is then boiled to a volume of about 100 to 200 cc. and then diluted with about 2000 cc. of water. The resultant solution is then neutralized with potassium hydroxide and sufficient potassium cyanide added to dissolve the precipitate. There may also be added 50 grams of Rochelle salt and 30 grams of cuprous cyanide where it is desired to reduce gold III to gold I. The resultant solution is then treated as described in the foregoing examples to separate the potassium gold cyanide from the remaining impurity.

This application is in part a continuation of my co-pending application Ser. No. 139,228, filed September 19, 1961.

I claim:

1. Process for separating substantially pure alkali metal gold cyanides from impure gold-bearing materials which comprises adding to a clarified, aqueous cyanide solution of the gold-bearing material an excess of a compound of the alkali metal selected from the group consisting of the hydroxide and salts and heating the mixture to effect complete solution, cooling the solution to a temperature of about 60°-70° F. and thereby precipitating the alkali metal gold cyanide, redissolving the precipitate in a hot, aqueous caustic solution containing the alkali metal cyanide and again precipitating the alkali metal gold cyanide by cooling and washing the precipitate with cold water to remove residual caustic and contaminating cyanides.

2. The process of separating substantially pure alkali metal gold cyanides from solutions thereof containing salts of other metals which comprises adding to the solution excess alkali metal cyanide in an amount sufficient to effect complete solution of all material present and rendering the solution alkaline by the addition of an excess of the hydroxide of the alkali metal, heating the resultant mixture to a temperature of about 150°-180° F. for several hours to insure complete solution of all of the materials present and thereafter cooling the solution to a temperature of about 60°-70° F., thereby effecting precipitation of the alkali metal gold cyanide, separating the precipitate from the solution and redissolving the precipitate in a hot, aqueous solution of alkali metal hydroxide and alkali metal cyanide, again precipitating the alkali metal gold cyanides by cooling the solution to about 60°-70° F. and separating the precipitate from the solution and washing the precipitate with cold water to remove residual caustic and contaminating cyanides.

3. The process of claim 2 in which the alkali metal gold cyanide is potassium gold cyanide.

4. The process of claim 2 in which gold is present in the solution to be purified as gold III and is reduced to gold I prior to the initial precipitation of the alkali metal gold cyanide.

5. The process of claim 1 in which the aqueous cyanide solution is a sodium cyanide solution and the alkali metal compound, of which an excess is added to the aqueous cyanide solution, is sodium hydroxide.

6. The process of claim 2 in which the gold-bearing cyanide solution contains as an impurity a metal of the group consisting of cadmium, silver and copper and the pH of the solution is adjusted to about 8 prior to the adding of the alkali metal cyanide.

7. The process of claim 1 in which the alkali metal cyanide solution contains as an impurity a metal of the group consisting of calcium and magnesium and a small amount of ammonium sulfate, effective to convert the metal of the said group to the sulfate thereof, is added to the solution.

8. The process of claim 1 in which the gold-bearing aqueous cyanide solution, following addition of the alkali metal hydroxide and while hot, is subjected to an initial filtration to separate any undissolved hydroxides.

### References Cited by the Examiner

#### UNITED STATES PATENTS

1,283,365	10/18	Trent et al.	23-285
2,366,915	1/45	Lento et al.	23-77
2,419,027	4/47	Nerlinger	23-77
2,764,476	9/56	Etter	23-285
3,112,174	11/63	Freedman	23-77

MAURICE A. BRINDISI, *Primary Examiner.*