



\*159159\*



\*G00002\*

## MAINTENANCE OF AN ELECTROLYTE

The invention pertains to a method for the care and maintenance of an electrolyte.

The control and maintenance of electrolytes is necessary in order to guarantee problem-free operation of the electrolyte. In particular, threshold values, the predetermined density, the composition, the pH value, and the temperature are to be observed. Here, the ion composition, in particular, is a determinative factor. Also, the electrolyte must be kept free from contaminants in order to guarantee problem-free operation. Thus, the task is to prevent deposits and other essentially insoluble contaminants.

The care and maintenance of electrolytes is also a determinative factor in gold plating. For the most part, cyanide systems are used as the electrolyte in gold plating, wherein the gold is separated from anionic complexes. The stability of cyanide gold complexes is high, so that plating is also possible and advantageous in the acidic pH range.

For the use of acidic gold electrolytes, insoluble anodes are predominantly used. The supplementation of the electrolyte with a gold salt is thus necessary. Such gold salts predominantly contain potassium as cations. In addition, it is typical for the flushing water to be fed back into the plating bath for the purpose of cost reduction. Thus, in the course of the bath operation, the concentration of potassium ions increases and the counterions belonging to the bath remain constant. This leads to a strong increase in the density of the bath, which results in a reduction of the bath operating time.

Further, the use of insoluble anodes results in the problem that large shifts in pH value occur during operation. This also means that the cathode efficiency for the gold reduction is below 100%, which leads to the condition that hydrogen ions are also reduced. This leads to an increase in the pH value. The pH value may only change within certain limits for such metal-depositing electrolytes, because the deposition behavior is strongly influenced by the pH

value. In order to compensate for the increase in the pH value, an acid is typically added to the electrolyte. This can be, e.g., sulfuric acid or also an organic acid.

The addition of acids for the purpose of pH value correction can lead to the formation of deposits because the potassium ions can form deposits with corresponding ions of the acids, resulting in the precipitation of, e.g., potassium sulfate. Such deposits are undesired and disadvantageous because the electrolyte is to be kept clean and, in particular, free from possible floating particles.

Therefore, the control and maintenance of the electrolyte has special significance, particularly for gold baths and, until now, has been very expensive. In addition to the control of the gold content, the concentration of a few alloy metals must be monitored, the concentration of free potassium cyanide and potassium carbonate must be controlled, the density and the pH value must be monitored, and drag-out losses must be supplemented. In spite of these expensive controls, the known baths only have a limited lifetime due to the circumstances mentioned above.

Thus, the object of the invention is based on providing a simple method for maintaining an electrolyte, which can lengthen the lifetime of the electrolyte by maintaining a constant ion concentration and ion composition in the electrolyte.

This object is realized by using at least one ion exchanger that can adjust the ion concentration and the ion composition of the electrolyte.

The present invention proposes to adjust the ion composition and the ion concentration in the electrolyte by means of an ion exchanger. The electrolyte is guided through the ion exchanger and, during the exchange process, the counterions in the matrix of the ion exchanger are exchanged with ions from the electrolyte. Thus, the method according to the invention allows the ion composition of the electrolyte and the corresponding ion concentration to be regulated in an

advantageous way. The method according to the invention is particularly advantageous in that through the use of the ion exchanger according to the invention, ions that negatively affect the bath quality can be exchanged with ions that are necessary to maintain a constant bath quality. Thus, the composition of the electrolyte and the corresponding ion concentration can be adjusted in an advantageous way. The ion exchanger preferably contains counterions that are included in the electrolyte and that are relevant for the bath quality. In this way, the ion exchanger can be advantageously regenerated after use.

The method according to the invention provides an unexpected solution to the problem in the state of the art that the bath composition must be adjusted with an expensive process using additives, which, e.g., for gold baths, holds the risk of forming deposits as described above. The present invention discloses a method for the care and maintenance of electrolytes that is extremely advantageous because conventional means that negatively influence the lifetime of an electrolyte bath become superfluous and, further, because chemicals can be spared. This leads to minimal strain on the environment. Further, the method according to the invention is less expensive because processes that otherwise had to be regulated separately are now regulated by a single processing step, i.e., by guiding the electrolyte fluid through the ion exchanger. Also, with the method according to the invention, measurement and control steps can be eliminated because the bath composition no longer must to be monitored with expensive processes. Therefore, processing steps and costs can be eliminated. Further, by means of the method according to the invention, the lifetime of an electrolyte is no longer limited because its composition can be kept essentially constant. The constant composition and thus constant quality of the electrolyte results in fewer quality defects for the deposited films. Furthermore, the feature according to the invention of using an ion exchanger for care and maintenance of an electrolyte is also advantageous due to the regenerability of the ion exchanger, so that the method has a low material expense and thus is also cost effective.

The method according to the invention can also maintain, in particular, acidic gold electrolytes. As described at the beginning of the document, the disadvantage for this gold

electrolyte is that the potassium ions become enriched and the pH value of the electrolyte increases. The precise maintenance of the pH value, and thus the hydrogen ion concentration, is a determinative factor, particularly for gold electrolytes. In an advantageous way, the present invention can eliminate the excessive addition of inorganic or organic acids for the purpose of pH value correction through the use of an ion exchanger since the pH value can be corrected by means of the ion exchanger. Because these additives can be predominantly eliminated, they cannot lead to undesired deposits that negatively influence the bath quality. In this way, the principle of the ion exchanger is used with the present invention in an extremely advantageous way, wherein one type of ion can be easily exchanged with another, so that the ions negatively influencing the bath quality of the electrolyte, such as potassium ions for acidic gold baths, can be exchanged with counterions positively influencing the bath quality, such as hydrogen ions for acidic gold baths.

A cation exchanger can be used for control. In this way, the use of an acidic cation exchanger is a feature of the care and maintenance of an acidic gold electrolyte. The cations contained in the electrolyte can be exchanged with hydrogen ions of the cation exchanger. For the care of gold baths, preferably, the potassium ions that are disadvantageous for the operation of the bath are exchanged with hydrogen ions that are necessary in order to prevent an increase in the pH value. Therefore, the essential problems in the operation of an electrolyte bath, particularly those of an acidic gold electrolyte, are solved in an uncomplicated way by means of the method according to the invention. By means of the ion exchanger, excess potassium ions that lead to an increase in density of the bath and thus produce a shortened lifetime for the bath are removed from the electrolyte. They can be exchanged with hydrogen ions that advantageously replace the hydrogen ions reduced by the electrolysis. This process acts against an undesired increase in pH. In this way, the addition of greater amounts of inorganic or organic acids can be largely eliminated. This further prevents the otherwise occurring precipitation of potassium salt, e.g., potassium sulfate, according to the acids that are used.

Advantageously, the ion exchanger can be regenerated. After loading or exchange of the ions localized at the anchor groups of the ion exchanger matrix, such as hydrogen ions in the case of the maintenance of an acidic electrolyte, with the appropriate cations from the electrolyte, the places of the ion exchanger are loaded with the appropriate cations. Because ion exchange is a reversible process, treatment with acid and water can transform the ion exchanger back to its original state loaded with hydrogen ions, in which the cations are eluted out of the electrolyte from the matrix of the ion exchanger. Through this extremely advantageous property, the ion exchanger has a long service life and enjoys essentially unlimited use. This leads to a valuable cost reduction, e.g., for the operation of a gold bath.

The decomposition of the basic chemicals results in an unavoidable increase in electrolyte density. The density of an electrolyte is given by the salt, alkali, or acid concentration. In an advantageous way, the ion exchanger can also adjust the electrolyte density within certain limits, which leads to an advantageous lengthening of the operating time of the electrolyte. The method according to the invention can prevent a disadvantageous increase in density, because, e.g., in the case of acidic gold electrolyte, excess potassium ions are exchanged with hydrogen ions and, in addition, by means of the method according to the invention, the addition of organic or inorganic acids, which contributes to increasing the density of the bath, can be largely eliminated.

Through the method according to the invention, the composition of the electrolyte bath can be held constant, whereby the lifetime of the electrolyte bath is not limited. In this way, continuously determined amounts can be removed from the electrolyte bath by means of transport devices and guided through the appropriate ion exchanger. The electrolyte fluid that is freed from potassium ions in the case of the maintenance of an acidic gold bath and that is enriched with an essentially equivalent amount of hydrogen ions can be fed back to the electrolyte bath. Flushing steps must be added in order to regenerate the ion exchanger matrix loaded with potassium ions, wherein the captured ions of the electrolyte are eluted and, in turn, the matrix is loaded with hydrogen ions. In an advantageous way, the column for the purpose of elution of the captured ions from the electrolyte is alternately washed with diluted acid and

water. After this process, the column is again ready for use. The means and steps are to be adapted to the ion exchanger that is used.

Due to the high cost of metals, gold is generally recovered from flushings that have settled out, rejected electrolytes, and defective tools. Because gold ions can be captured in the matrix of the ion exchanger during the cleaning process by means of the ion exchanger, the eluate that possibly has gold ions can be fed into other flushing solutions, or the like, which perform a gold recovery. The gold recovery can be performed, e.g., by means of highly basic anionic exchanger resin or electrolysis cells. Feeding the eluate into the other gold recovery processes guarantees that no gold is lost with the method according to the invention.

In an advantageous way, the method can be adapted to a wide range of different electrolytes and thus enjoys a broad field of application. Its use is not restricted to the care and maintenance of acidic gold baths described here. The method according to the invention can be used for the maintenance of any arbitrary electrolyte, because the core concept of the invention states that the ion composition of an electrolyte can be adjusted by means of an ion exchanger, and that undesired ions that negatively influence the quality of the electrolyte are exchanged with ions that are used in the electrolyte but must be kept constant for maintaining the bath quality. Here, attention should be brought particularly to the adjustment of the pH value, but the concept of the invention is not expressly restricted to this process. Due to the fact that the electrolyte composition, and particularly the pH value of an electrolyte, can be adjusted with the method simply, efficiently, and in an uncomplicated way, the method according to the invention is also well-suited to maintaining a constant composition and ion concentration of, e.g., alkali electrolytes. Only the corresponding parameters, e.g., of the ion exchanger, which, e.g., can be a basic anionic exchanger, the flushing steps, and the regeneration, etc., must be adapted.

These parameters can be adapted in an uncomplicated way and are obvious for someone skilled in the art from the combination of the appropriate ions to be removed from the electrolyte, the desired ions, and the ion exchanger with the corresponding counterions to be used depending

on the ions to be exchanged. Further, the corresponding matrices are subject to different requirements for the regeneration and the operation, which are indicated by the corresponding manufacturer of the ion exchanger to be used.

In an advantageous way, the method according to the invention also allows the setting of additional fine adjustments. Thus, small pH value deviations that cannot be regulated by means of the ion exchanger are regulated by means that supplement the ion exchanger. According to one configuration of the method according to the invention, the relevant parameters of the electrolyte are measured by means of measurement devices, compared with the desired values, and appropriate means are automatically started. Thus, depending on the measurement values, the flow rate of the electrolyte fluid through the ion exchanger can be increased, a fine adjustment of the pH value, which cannot be done by the ion exchanger, can be performed by means of an inorganic or organic acid, and further, possible drag-out losses are supplemented. Further, measurement devices can determine the amount of floating particles, and, if necessary, filtration can be done by means of filter systems. In this way, other parameters can also be considered.

Further, the invention proposes a device for the care and maintenance of an electrolyte, particularly an acidic gold electrolyte, which has measurement devices that measure the relevant parameters of the electrolyte to be maintained in the form of actual values, as well as storage devices that store the desired values of the relevant parameters of the electrolyte to be maintained, as well as at least one calculation unit that compares the measured actual value with the stored desired value and a control unit that controls the means in order to adjust the actual value of the electrolyte to the desired value. Furthermore, the device has an ion exchanger that exchanges the ions negatively influencing the bath quality from the electrolyte with its own counterions that are also contained in the electrolyte and that are required for good electrolyte quality, transport devices that guide the electrolyte fluid to the ion exchanger as well as back into the electrolyte bath, and flushing devices that regenerate the ion exchanger loaded with the electrolyte ions. However, less complex devices that exhibit constant operating parameters and

that can function without measurement, storage, and calculation units are also included within the scope of the invention.

The effectiveness of the method according to the invention can be proven with reference to laboratory tests. Here, the results for the maintenance of an acidic gold electrolyte are cited as an example. This test description serves just as a more detailed explanation and is not restrictive. In this process, an aqueous electrolyte solution was used that contained as essential components citric acid/potassium citrate, a cobalt (II) citrate complex, formic acid/potassium formate, as well as a gold complex (potassium gold cyanide). The electrolyte exhibited a pH value of 5.0, as well as potassium in a concentration of 75 g/L. For the test, 500 mL of electrolyte solution was led through a column with 75 g exchanger resin, wherein the resin was chosen such that it could exchange hydrogen ions with potassium ions. The electrolyte solution was led through the column and captured. The test showed that the electrolyte flowing through the matrix of the ion exchanger reduced the potassium concentration from 75 g/L to 59 g/L and a pH value of 4.7 was measured. These results verify the effectiveness of the method for one example. The stability of the gold cyanide complex was not negatively influenced. Further, subsequent studies showed that no other significant ions were retained in the matrix of the ion exchanger. This shows the selectivity of the method according to the invention, which is particularly advantageous from the background that no ions are removed from the electrolyte that must be replaced at great cost, such as gold ions, whereby the method is also suitable for industrial use.

The ion exchanger resin is then regenerated with 5% sulfuric acid. Multiple repetitions of the test gave the same results, which shows that the method functions consistently with good results and also that the ion exchanger is subjected to essentially no aging effects due to its regenerability.

### Claims

1. Method for maintenance of an electrolyte, characterized in that the ion concentration and the ion composition of the electrolyte are adjusted by means of at least one ion exchanger.
2. Method according to Claim 1, characterized in that the ion exchanger has ions that are a component of the electrolyte as counterions.
3. Method according to Claim 1 or 2, characterized in that the pH value is held constant by means of the ion exchanger.
4. Method according to Claims 1-3, characterized in that a cation exchanger is used for controlling the ion concentration and the ion composition of an electrolyte.
5. Method according to Claims 1-4, characterized in that an acidic cation exchanger is used for controlling the ion concentration and the ion composition of an electrolyte.
6. Method according to one or more of Claims 1-5, characterized in that cations in the electrolyte are exchanged with hydrogen ions of the cation exchanger.
7. Method according to one or more of Claims 1-5, characterized in that potassium ions in the electrolyte are exchanged with hydrogen ions of the cation exchanger.
8. Method according to one or more of Claims 1-7, characterized in that the ion exchanger is regenerated.
9. Method according to one or more of Claims 1-8, characterized in that the density of the electrolyte is regulated at least partially by means of the ion exchanger.

10. Method according to one or more of Claims 1-9, characterized in that the electrolyte is led through the ion exchanger by means of transport devices and then fed back into the bath.
11. Method according to one or more of Claims 1-10, characterized in that the eluate is fed to recovery processes.
12. Method according to one or more of Claims 1-11, characterized in that the ion exchanger to be used and also the associated parameters, such as regeneration steps, or the like, are adapted to the electrolyte to be maintained.
13. Method according to one or more of Claims 1-12, characterized in that the electrolyte to be cleaned is led in a continuous cycle process through the ion exchanger, which achieves a constant preparation of the electrolyte.
14. Method according to one or more of Claims 1-13, characterized in that the transport rate and thus the amount of the electrolyte to be prepared can be selected.
15. Method according to one or more of Claims 1-14, characterized in that measurement devices compare the important actual values of the electrolyte with the corresponding desired values and adjust the velocity and flow rate of the electrolyte through the ion exchanger.
16. Device for care and maintenance of an electrolyte, characterized by an ion exchanger that exchanges ions from the electrolyte with its counterions.
17. Device for care and maintenance of an electrolyte according to Claim 16, characterized in that it has collecting means that collect the regenerated electrolyte, wherein this collected fluid is fed back to the electrolyte bath by means of guidance means.

18. Device for care and maintenance of an electrolyte according to Claim 16 or 17, characterized by measurement devices that measure the relevant parameters of the electrolyte to be maintained in the form of actual values, storage devices that store the desired values of the relevant parameters of the electrolyte to be maintained, at least one calculation unit that compares the measured actual value with the stored desired value, a control unit that controls the means in order to adjust the actual value of the electrolyte to the desired value, an ion exchanger, transport devices that lead the electrolyte fluid to the ion exchanger and back into the electrolyte bath, and flushing devices that regenerate the ion exchanger.