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(54) Title: AN ACTIVATING SOLUTION AND METHOD OF ITS PREPARATION

(57) Abstract: An activating solution, particularly an activating solution for improving the corrosion resistance of surfaces, particularly for improving the corrosion resistance of mirrors, containing a solution of at least one platinum metal chloride, distilled water and glycerine. The method of preparation of the activating solution, according to which a solution of at least one platinum metal chloride, distilled water and glycerine is mixed.

An activating solution and method of its preparation

Field of the Invention

The invention relates to an activating solution, particularly an activating solution for improving the corrosion resistance of surfaces, particularly for improving the corrosion resistance of mirrors.

Background Art of the Invention

Several types of activating solutions are currently known to improve the corrosion resistance of surfaces. Activating solutions are also used to reduce the unevenness of a silver layer in mirror manufacturing. Activating solutions are used between a sensitizing zone and a silvering zone. After termination of the sensitization and rinsing off remaining sensitizing solution with demineralized water, the activating solution is applied onto the glass. The activating solution allows the creation of nucleation centres. After thoroughly rinsing off the remaining activating solution with demineralized water, and collecting it in a separate waste sump, a metallizing solution is applied onto the glass. This method of increasing the corrosion resistance of the silver layer appears to be rather effective, however, considerably expensive due to price of the activating solutions. Another disadvantage is the usage of additional metal in production and the resulting need to separate and capture it from waste water.

The activating solution most commonly consists of an aqueous solution of palladium dichloride in the acidic environment of hydrochloric acid. However, it can also consist of a number of other metal chlorides (titanium, copper, rhodium, ruthenium). Their protective factor varies. A mixture of ruthenium tetrachloride and palladium dichloride with a proportion of 20 to 50% ruthenium tetrachloride is also used. The reason is significantly lower price of ruthenium compared to palladium. These activating solutions are supplied in concentrated form, containing 10 to 100 g/l of platinum metals. These are aqueous solutions with the presence of hydrochloric acid, which ensures the stability of the concentrate. Prior to application, the concentrate is significantly diluted with distilled water, which results in an increase of the pH of the solution, causing a disproportionation reaction, thus deposition of part of the palladium on the sensitized glass surface. One of the two molecules of palladium dichloride is thus reduced and deposited as palladium metal, the other one is oxidized to palladium tetrachloride. In the case of ruthenium trichloride, this ratio is even less convenient. Four molecules of ruthenium trichloride are disproportionated to one molecule of ruthenium metal and three molecules of ruthenium tetrachloride. So, in theory, only 25% of ruthenium can be deposited on the glass and 75% of ruthenium is drained into the waste water.

The above-described state of art makes it obvious that it has numerous disadvantaged, especially the low efficiency of utilizing the activating metal content in the activating solution. This also involves another disadvantage, namely the high content of activating metals in the waste water, threatening the environment and increasing the carbon footprint of the mirrors produced.

The object of the invention is a solution enabling a substantially higher yield of platinum metals from the activating solution, while maintaining or improving the quality of the activation process.

Disclosure of the Invention

The above-described disadvantages are largely eliminated and the object of the invention is achieved by an activating solution, particularly an activating solution improving the corrosion resistance of surfaces, particularly the corrosion resistance of mirrors, according to the present invention, the subject matter of the invention is that it contains a solution of at least one platinum metal chloride, distilled water and glycerine. The advantage of this invention is in replacing the disproportionation reaction with an oxidation-reduction reaction. An organic reducing agent – glycerine – is added to the acidic solution of platinum metal chloride. In concentrated form, the acidity of this solution is sufficient and the solution is stable. Prior to application, the solution is again strongly diluted with distilled water, reducing its acidity, thus increasing its pH, which triggers an oxidation-reduction process. Glycerine is oxidized and platinum metals are completely reduced. This can theoretically enable a 100% effective deposition of platinum metals on the glass. Saving platinum metal brings both economic and environmental savings, reduces the burden on waste water as well as the carbon footprint of the mirrors produced.

In a preferred embodiment, the activating solution contains concentrated activating solution, which contains 20 to 215 g of platinum metal salts, 20 to 202 g of glycerine and distilled water in one litre.

In another preferred embodiment, the activating solution contains concentrated activating solution, which contains 13.8 to 138 g of ruthenium trichloride $RuCl_3$×HCl, 7.55 to 75.5 g of palladium dichloride $PdCl_2$, 20 to 202 g of glycerine and distilled water in one litre. Replacing a part of palladium with ruthenium increases the corrosion resistance of mirrors. The protective action of a layer containing a mixture of palladium and ruthenium is higher than the protective action of a layer of the same thickness containing only palladium. Given the current prices of palladium and ruthenium, substituting ruthenium for the considerably more expensive palladium is more beneficial.

In another preferred embodiment, the activating solution contains concentrated activating solution, which contains 20 to 200 g of palladium dichloride $PdCl_2$, 20 to 200 g of glycerine and distilled water in one litre.

In another preferred embodiment, the activating solution further contains 0.005 to 0.05 g of hydrochloric acid HCl, which increases the solution's stability, preventing unwanted metal deposition in the piping and application nozzles. Platinum metal is only expelled on the glass surfaces.

The improved activating solution contains concentrated activating solution and distilled water in ration of 1:500 to 1:10,000. The advantage is that using the concentrate reduces storage and transporting costs of the activating solution, because only the concentrate needs to be transported and stored.

The above-described disadvantages are further largely eliminated and the object of the invention is achieved by the preparation method of the activating solution, particularly the preparation method of the activating solution above-mentioned, according to the invention, the subject matter of the invention is that a solution of at least one platinum metal chloride, distilled water and glycerine is mixed.

When the activating solution contains two platinum metal chlorides, more precisely ruthenium trichloride $RuCl_3$×HCl and palladium dichloride $PdCl_2$, it is advantageous to prepare a concentrated activating solution by heating up glycerine to 30 °C first, then preparing a first solution by mixing 20 to 202 g of glycerine, 13.8 to 138 g of ruthenium trichloride $RuCl_3$×HCl and 20 to 200 ml of distilled water, for 1 litre of the resulting activating solution concentrate. At the same time a second solution is prepared by mixing 7.55 to 75.5 g of palladium dichloride $PdCl_2$, 0.005 to 0.05 g HCl and 40 to 400 ml of distilled water, for 1 litre of the resulting activating solution concentrate, further the first and the second solutions are mixed under constant stirring and distilled water is added to obtain 1 litre of the resulting activating solution concentrate, which is prior to application further diluted with distilled water in a ratio of 1:500 to 1:10,000.

When the activating solution contains only one platinum metal chloride, or more precisely if it contains palladium dichloride $PdCl_2$, it is advantageous to prepare a concentrated activating solution by heating up glycerine to 30 °C first, and then for 1 litre of the resulting activating solution is mixed 20 to 200 g of glycerine, 20 to 200 g of palladium dichloride $PdCl_2$, 20 to 400 ml of distilled water and 0.005 to 0.05 g of HCl, and then distilled water is added up to the total volume of 1 litre of the resulting activating solution, which is prior to application diluted with distilled water in a ratio of 1:500 to 1:10,000.

The advantage of the invention is a significant cost saving owing to the considerably higher yield of the platinum metal. For 1 m^2 of mirrors, 0.0287 ml of conventional activation solution concentrate is applied, corresponding to 2.064 mg of platinum metal per 1 m^2 of mirrors. 0.79 mg of platinum metal per 1 m^2 of mirrors is deposited on the glass and 1.274 mg of platinum metal is drained into waste water. The deposition efficiency on glass is therefore slightly over 38%. Theoretically, the yield of disproportionation reaction could achieve 50% with palladium dichloride, however, at the above dosage it practically only reaches 38%. The advantage of using the activating solution according to the invention is that 0.024 ml of the concentrate is used to produce 1 m^2 of mirrors, thus 0.956 mg of platinum metals per 1 m^2. 0.91 mg of metal is deposited on the glass per 1 m^2 and 0.046 mg of platinum metals flow into waste water. Utilizing the reducing properties of glycerine can theoretically allow to deposit 100% of metal on the glass. Practically, the above-mentioned example shows that it is possible to deposit 95.18% of the platinum metals applied by spraying onto sensitized glass. Although the waste water is treated according to the current state of the art, and some of the platinum metals are recovered, the use of the activating solution according to the invention still significantly reduces the cost of producing mirrors. Another advantage is a large increase in the quality of mirrors, as the conventional method captures only 0.79 mg of platinum metals per 1 m^2. Using the new formulation, 0.91 mg of platinum metal per 1 m^2 is captured. This increase contributes significantly to a higher quality of mirrors. Another advantage is the aforementioned reduction of wasting platinum metals into waste water, thus reducing waste water treatment costs and introducing a positive environmental effect.

Preferred embodiments of the Invention

Example 1

One litre of activating solution concentrate contains 13.8 g of ruthenium trichloride $RuCl_3 \times HCl$, 7.55 g of palladium dichloride $PdCl_2$, 20 g of glycerine and 0.005 g of HCl in a solution with distilled water.

The resulting activating solution contains 1 portion of concentrated activating solution to 500 portions of distilled water.

According to the preparation method for 1 litre of concentrate of the above-mentioned activating solution, the activating solution concentrate is prepared first by heating up glycerine to 30 °C, then the first solution is prepared to form 1 litre of the resulting activating solution concentrate by mixing 20 g of glycerine, 13.8 g of ruthenium trichloride $RuCl_3 \times HCl$ and 20 ml of distilled water. The mixture is stirred until the crystalline ruthenium trichloride is dissolved. At the same time, a second solution is prepared by mixing 7.55 g of palladium dichloride $PdCl_2$, 40 ml of distilled water and 0.005 g of HCl to prepare 1 litre of the resulting activating solution concentrate. The solution is again stirred until the salt is dissolved completely. The resulting activating solution concentrate is obtained by mixing the first and the second solution under constant stirring and then adding distilled water to the total volume of 1 litre.

The application solution is prepared by diluting the activating solution concentrate with distilled water in a ratio of 1:500 just before the application.

Such prepared activating solution is applied onto sensitized and rinsed glass panel surface prior to applying the silver layer.

Example 2

One litre of activating solution concentrate contains 138 g of ruthenium trichloride $RuCl_3 \times HCl$, 75.5 g of palladium dichloride $PdCl_2$, 202 g of glycerine and 0.05 g of HCl in a solution with distilled water.

The resulting activating solution contains 1 portion of concentrated activating solution to 10,000 portions of distilled water.

According to the preparation method for 1 litre of concentrate of the above-mentioned activating solution, the activating solution concentrate is prepared first by heating up glycerine to 30 °C, then the first solution is prepared to form 1 litre of the resulting activating solution concentrate by mixing 202 g of glycerine, 138 g of ruthenium trichloride $RuCl_3 \times HCl$ and 200 ml of distilled water. The mixture is stirred until the crystalline ruthenium trichloride is dissolved. At the same time, a second solution is prepared by mixing 75.5 g of palladium dichloride $PdCl_2$, 400 ml of distilled water and 0.05 g of HCl to prepare 1 litre of the resulting activating solution concentrate. The solution is again stirred until the salt is dissolved completely. The resulting activating solution concentrate is obtained by mixing the first and the second solution under constant stirring and then adding distilled water to the total volume of 1 litre.

The application solution is prepared by diluting the activating solution concentrate with distilled water in a ratio of 1:10,000 just before the application.

Such prepared activating solution is applied onto sensitized and rinsed glass panel surface prior to applying the silver layer.

Example 3

One litre of activating solution concentrate contains 58 g of ruthenium trichloride $RuCl_3 \times HCl$, 35 g of palladium dichloride $PdCl_2$, 100 g of glycerine and 0.01 g of HCl in a solution with distilled water.

The resulting activating solution contains 1 portion of concentrated activating solution to 2,500 portions of distilled water.

According to the preparation method for 1 litre of concentrate of the above-mentioned activating solution, the activating solution concentrate is prepared first by heating up glycerine to 30 °C, then the first solution is prepared to form 1 litre of the resulting activating solution concentrate by mixing 100 g of glycerine, 58 g of ruthenium trichloride $RuCl_3 \times HCl$ and 100 ml of distilled water. The mixture is stirred until the crystalline ruthenium trichloride is dissolved. At the same time, a second solution is prepared by mixing 35 g of palladium dichloride $PdCl_2$, 400 ml of distilled water and 0.01 g of HCl to prepare 1 litre of the resulting activating solution concentrate. The solution is again stirred until the salt is dissolved completely. The resulting activating solution concentrate is obtained by mixing the first and the second solution under constant stirring and then adding distilled water to the total volume of 1 litre.

The application solution is prepared by diluting the activating solution concentrate with distilled water in a ratio of 1:2,500 just before the application.

Such prepared activating solution is applied onto sensitized and rinsed glass panel surface prior to applying the silver layer.

Example 4

One litre of activating solution concentrate contains 75 g of palladium dichloride $PdCl_2$, 100 g of glycerine and 0.005 g of HCl in a solution with distilled water.

The resulting activating solution contains 1 portion of concentrated activating solution to 2,500 portions of distilled water.

According to the preparation method for 1 litre of concentrate of the above-mentioned activating solution, the activating solution concentrate is prepared first by heating up glycerine to 30 °C, then the solution is prepared to form 1 litre of the resulting activating solution concentrate by mixing 100 g of glycerine and 75 g of palladium dichloride $PdCl_2$, 100 ml of distilled water and 0.005 g of HCl. The solution is stirred until the palladium dichloride is dissolved completely and then then adding distilled water to the total volume of 1 litre.

The application solution is prepared by diluting the activating solution concentrate with distilled water in a ratio of 1:2,500 just before the application.

Alternatively, concentrates of activating solution can be prepared using 20 to 200 g of palladium dichloride $PdCl_2$, 20 to 200 g of glycerine and distilled water in one litre of the final activating solution concentrate.

Such prepared activating solution is applied onto sensitized and rinsed glass panel surface prior to applying the silver layer.

Industrial Applicability

The activating solution according to this invention can be used for improving the corrosion resistance of the applied surfaces, especially to improve the corrosion resistance of mirrors. The activating solution is mostly applied on sensitized and rinsed glass surface before the actual silvering. This solution can also be applied onto sensitized plastic surface before applying the silver layer by means of reducing agents.

CLAIMS

1. An activating solution, particularly the activating solution for improving the corrosion resistance of surfaces, particularly for improving the corrosion resistance of mirrors, **characterized in that** it contains a solution of at least one platinum metal chloride, distilled water and glycerine.

2. The activating solution according to claim 1, **characterized in that** it contains an activating solution concentrate, containing in one litre 20 to 215 g of platinum metal salts, 20 to 202 g of glycerine and distilled water.

3. The activating solution according to any of claims 1 to 2, **characterized in that** it contains an activating solution concentrate, which in one litre of the solution contains 13.8 to 138 g of ruthenium trichloride $RuCl_3 \times HCl$, 7.55 to 75.5 g of palladium dichloride $PdCl_2$, 20 to 202 g of glycerine and distilled water.

4. The activating solution according to any of claims 1 to 2, **characterized in that** it contains an activating solution concentrate, which in one litre of the solution contains 20 to 200 g of palladium dichloride $PdCl_2$, 20 to 200 g of glycerine and distilled water.

5. The activating solution according to any of claims 3 to 4, **characterized in that** it further contains 0.005 to 0.05 g of HCl.

6. The activating solution according to any of claims 2 to 5, **characterized in that** it contains an activating solution concentrate and distilled water in a ratio of 1:500 to 1:10,000.

7. The method of preparation of the activating solution, especially the method of preparation of the activating solution according to any of claims 1 to 6, **characterized in that** a solution of at least one platinum metal chloride, distilled water and glycerine is mixed.

8. The method of preparation of the activating solution according to claim 7, **characterized in that** firstly an activating solution concentrate is prepared by heating up glycerine to 30 °C, then a first solution is made by mixing 20 to 202 g of glycerine, 13.8 to 138 g of ruthenium trichloride $RuCl_3 \times HCl$ and 20 to 200 ml of distilled water per litre of the resulting

activating solution concentrate, while at the same time a second solution is prepared by mixing 7.55 to 75.5 g of palladium dichloride $PdCl_2$, 0.005 to 0.05 g of HCl and 40 to 400 ml of distilled water per litre of resulting activating solution concentrate, and then the first and the second solutions are mixed under constant stirring and distilled water is added to obtain 1 litre of resulting activating solution concentrate, which is prior to application diluted with distilled water in a ratio of 1:500 to 1:10,000.

9. The method of preparation of the activating solution, according to claim 7, **characterized in that** the activating solution concentrate is first prepared by heating up glycerine to 30°C, and then 20 to 200 g of glycerine, 20 to 200 g of palladium dichloride $PdCl_2$, 20 to 400 ml of distilled water and 0.005 to 0.05 g of HCl are mixed to obtain 1 litre of the resulting activating solution concentrate, after that distilled water is added up to the volume of 1 litre for the resulting activating solution concentrate, which is prior to application diluted with distilled water in a ratio of 1:500 to 1:10,000.

INTERNATIONAL SEARCH REPORT

International application No
PCT/CZ2022/050083

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C18/18 C03C17/10 C23C18/20 C23C18/30
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/088653 A1 (CHOU CHIA WEI [TW] ET AL) 12 April 2012 (2012-04-12)	1,2,4,6,7
Y	example 1.1	3,5
A		8,9

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A	paragraph [0302]	8,9

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Y	example 26	5
A		8,9

Y	US 5 212 138 A (KRULIK GERALD A [US] ET AL) 18 May 1993 (1993-05-18)	3,5
A	example 1	8,9

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/CZ2022/050083

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