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(54) Title: A SOLUTION FOR SURFACE TREATMENT PRIOR TO THE DEPOSITION OF A METAL LAYER AND A METHOD OF ITS PREPARATION

(57) Abstract: A solution for surface treatment prior to the deposition of a metal layer, in particular, to a solution for surface treatment prior to the deposition of a reflective layer of silver which contains at least one metal chloride and a reducing agent capable of oxidation by a metal chloride in dilute solution. A method of preparation of a solution for surface treatment prior to the deposition of a metal layer, in particular, of a solution for surface treatment prior to the deposition of a silver layer, according to which a solution of at least one metal chloride, distilled water, hydrochloric acid and a reducing agent capable of oxidation is mixed with the metal chloride in a dilute solution.

A Solution for Surface Treatment Prior to the Deposition of a Metal Layer and a Method of Its Preparation

Technical Field

The invention relates to a solution for surface treatment prior to the deposition of a metal layer, in particular, to a solution for surface treatment prior to the deposition of a layer of silver, and to a method of its preparation.

State of the Art

At the present time, there exist technologies to treat surfaces prior to chemical-reductive metal plating according to which surfaces are treated by polishing and washing. After that, the surfaces are sensitized and activated. It is concerns depositing a very thin layer of one or more metals. For example, when making mirrors, the glass sheet is first sensitized using acid solution of tin dichloride. Tin dichloride concentrate is first diluted with distilled water and then immediately applied (mostly by spraying) on the glass surface. After a couple of seconds, the solution is washed off with distilled water. The dilute solution of tin dichloride disproportionates when in contact with glass which means that one molecule of tin dichloride is reduced to tin that sticks firmly to the glass surface. The other molecule of tin dichloride is oxidized to tin tetrachloride and flows off into waste water. The resulting layer of tin metal is very thin, virtually invisible, but it is very important for the quality of the reflective layer of silver.

At the present time, a layer of platinum-group metals, e.g. palladium or a mixture of palladium and ruthenium, is added to this layer of tin. Chlorides of these platinum-group metals are available in the form of acidic water solutions and are applied on the glass surface in a highly distilled-water-dilute state. The principle of deposition of the thin monoatomic layer is the same as that with the deposition of tin, which means that one molecule of chloride of the platinum-group metal is reduced and the platinum-group metal sticks to the thin layer of tin while the other molecule of the platinum-group metal is oxidized and washed off into waste water. The process can be expressed by the following reaction: $2PdCl_2 = Pd + PdCl_4$.

The glass treated with the monoatomic layer of tin on which another monoatomic layer of palladium (or of mixture of palladium and ruthenium) is deposited is prepared for reductive silver plating. i.e. for the process during which a dilute silver concentrate and dilute alkaline reduction concentrate are deposited separately, several times to one spot. The nozzles spraying both the concentrates should be arranged in such a manner that the sprayed solutions mix just above the surface or even right on the surface of the glass. Thus, opaque and highly reflective layer of silver is formed. This layer is then again, after desiccation, treated by a thin monoatomic layer of tin which is, again, deposited out of dilute solution of tin dichloride through the disproportionation principle as described above.

The layer of silver treated in this manner is then coated with an adhesive bridge and with a protective paint to protect the mirror from mechanical damage. The aforementioned deposition of individual layers on the glass before silver plating as well as the later deposition of tin layers on the deposited layer of silver take place by means of thin dilution of the chloride solution which results in increase of the solution Ph. The solution stops to be stable and starts to deposit the metal through disproportionation.

It is also known that, when depositing thick reflective layers of metals, two-component solutions are used. The metal to be deposited is contained in the first solution and hydroxide of an alkaline metal with a reducing agent is contained in the second one. Without the hydroxide of an alkaline metal, the reduction of the deposited metal is not carried out well because, during the metal deposition process, the reducing agent is oxidized to acid and also the acidic nitrate ion is released. These phenomena lead to increasing the acidity of the bath and to stopping the deposition of the metal on the glass. When this alkaline reduction is used for sensitization or activation, the metal on the glass does not deposit out because tin or platinum-group metal hydroxide is deposited as a precipitate. Therefore, attempts to use the oxidation-reduction reaction for sensitization or activation have failed. Thus, the disproportionation reaction was used, where the chloride disproportionates in contact with the surface if the chloride is highly diluted with distilled water. This means that one mole of this metal chloride was oxidized and the other was reduced to the metal which adhered to the surface to be treated. This method had an undeniable advantage as it was carried out in a one-component process. Only one concentrate was used, which was diluted with distilled water just before use and applied to the surface to be treated. However, the disadvantage of this technology was the low efficiency, which was around 10%. Previously, only sensitization using tin dichloride was carried out. Tin was cheap and ecology was not a topic of discussion. In recent years, activation using platinum-group metal chloride has been introduced which has improved the quality of mirrors. Again, disproportionation was used. The platinum-group metal chloride was highly diluted with distilled water and sprayed on the surface. The price of platinum-group metals is many times higher than that of tin and requirements for heavy metal content in wastewater are strict at present. Therefore, the water from the activation and sensitisation process has to be expensively treated before being discharged into the sewage system.

The disadvantage of current methods of sensitization or activation of surfaces, such as glass in silver plating, is the low efficiency of disproportionation reactions where at least 90% of the applied metals are not retained on the surface and flow into the wastewater. This results in significant economic losses, given the price of these metals and, of course, the environmental effect is very unfavourable with heavy metals entering the waste water.

The goal of the invention is to prepare a solution for surface treatment prior to the deposition of a metal layer which will allow a substantial increase in the yield of platinum-group metals and a related reduction in the environmental burden of the newly proposed technology.

Principle of the Invention

The aforementioned disadvantages are, to a large extent, eliminated and the goals of the invention accomplished by a solution for surface treatment prior to the deposition of the metal layer, in particular a solution for surface treatment prior to the deposition of the reflective silver layer according to the invention, the nature of which consists in containing at least one metal chloride and a reducing agent capable of oxidation by a metal chloride in dilute solution. Advantageously, thanks to said solution, the disproportionation reaction of the metal chloride can be replaced by an oxidation-reduction reaction. In contrast to reflective layers, the thickness of the sensitizing or activating layer is several orders of magnitude smaller. It forms a completely transparent film on the glass which is not visible. A standard acidic metal chloride (tin or platinum-group metal) solution is used to produce the supersensitizing and superactivating solution and an aqueous solution of a pure neutral reducing agent is added. In the concentrate which is acidic, the reducing agent is not activated and the solution is stable. At the high dilution of this solution (used in sensitization and activation) with distilled water, the Ph changes and the solution reduces out metal on the glass when it hits the surface to be treated. Sensitization and, by the same principle, surface activation will occur. The process is carried out with a high efficiency exceeding 95% of the deposited metal on the glass. The process can be described by the following reaction: $SnCl_2 + X = Sn + XCl_2$, where X are the reducing agents we have found.

It is advantageous if the concentrate of the solution for surface treatment prior to the deposition of the metal layer comprises 20 to 800g of metal chlorides and 20 to 300g of metal chloride oxidizable reducing agents in dilute solution, 0.5 to 15g of hydrochloric acid and distilled water in one litre. This concentrate must be diluted with distilled water at a ratio of 1 to 400 to 1 to 7000 before application on the glass.

According to the first variant, it is advantageous if the reducing agent capable of oxidation by metal chloride in dilute solution is a substance from the group of aliphatic polyols, which may be, for example, ethylene glycol, or diethylene glycol, or triethylene glycol, or propylene glycol, or dipropylene glycol, or sorbitol, or meglumine.

According to the second variant, it is advantageous if the reducing agent capable of oxidation by metal chloride in dilute solution is a substance from the group of reducing sugars, which may be, for example, glucose, fructose or maltose.

According to the third variant, it is advantageous if the reducing agent capable of oxidation by metal chloride in dilute solution is a substance from the group of acid salts formed by oxidation of aldoses and their neutralization by metal hydroxide, which may be, for example, sodium gluconate.

An advantage is the fact that the reductants capable of oxidation by the metal chloride in dilute solution according to the above variants do not reduce the metal in the acidic environment of the metal chloride concentrate and that this single-component concentrate is stable for a long time. A further advantage of these substances is the fact that, when diluted, oxidation-reduction reaction leading to metal elimination over disproportionation reactions is preferred. This results in high yields of deposited metals on glass or on silver. Another advantage resulting from the high yield of the oxidation-reduction reaction is the economic savings with respect to the amount of metal saved. This is particularly evident when using platinum-group metals. Another considerable advantage is the very low metal content in wastewaters which means that the technology is very environmentally friendly. A significantly lower carbon footprint is another advantage of this technology. The solutions have a 3 to 10 times lower carbon footprint due to the saving of the metal chlorides used.

It is most preferable to use tin dichloride for sensitizing solutions and platinum-group metal chlorides, most commonly palladium chloride and ruthenium trichloride, or a mixture thereof, for activating solutions.

The aforementioned disadvantages are, to a large extent, eliminated and the goals of the invention further accomplished by the method for preparing a solution for surface treatment prior to the deposition of a metal layer, in particular a solution for surface treatment prior to the deposition of a silver layer according to the invention the nature of which consists in mixing a solution of at least one metal chloride, distilled water, hydrochloric acid and a reducing agent capable of oxidation with the metal chloride in a dilute solution.

According to the first variant, it is advantageous if the first solution of a reducing agent capable of oxidation by metal chloride in dilute solution which is a substance from the group of aliphatic polyols or a substance from the group of reducing sugars or a substance from the group of salts of acids formed by oxidation of aldoses and their neutralization by metal hydroxide with distilled water is prepared as the first by mixing 20 to 300g of a reducing agent capable of oxidation by metal chloride in dilute solution with 20 to 300g of distilled water, and the second solution is prepared by mixing 20 to 800g of metal chlorides, 300 to 500ml of distilled water with 0,5 to 15g of hydrochloric acid, and then the first solution and the second solution are mixed and replenished with distilled water up to 1 litre of the resulting solution concentrate, which is diluted with distilled water at a ratio of 1 : 400 to 1 : 7000 before application.

According to the second variant, it is advantageous if the solution concentrate is first prepared by heating the substance capable of oxidation by metal chloride in dilute solution, which is a substance of the group of aliphatic polyols, or a substance of the group of reducing sugars, or a substance of the group of salts of acids formed by oxidation of aldoses and their neutralization, to a temperature of 30 to 35°C. Further, for one litre of the resulting solution concentrate, 20 to 200g of a substance capable of oxidation by metal chloride in dilute solution and 20 to 200g of metal chlorides are mixed with 100ml of distilled water containing 0,5g of hydrochloric acid, the solution being stirred until all the metal chloride is dissolved is then supplemented with distilled water up to one litre of the resulting solution concentrate which is, before application, diluted with distilled water at a ratio of 1 : 1500 to 1 : 2500.

According to the third variant, it is advantageous if the solution concentrate is first prepared by heating the substance capable of oxidation by metal chloride in dilute solution, which is a substance of the group of aliphatic polyols or a substance of the group of reducing sugars or a substance of the group of salts of acids formed by oxidation of aldoses and their neutralization, to a temperature of 35°C, further, 150 to 400ml of a 20°C warm solution of metal chlorides in distilled water at a concentration of 1145 g of metal chlorides per litre is slowly added to 80 to 200 g of the substance capable of oxidation by metal chloride in dilute solution, with constant stirring, and the solution is further supplemented up to 1 litre with distilled water containing 0.5g of hydrochloric acid per litre, all is again mixed and distilled water is further supplemented up to 1 litre of the resulting solution concentrate, which is diluted with distilled water at a ratio of 1 : 1500 to 1 : 7000.

The main advantage of the invention is the fact that the composition of the solution allows, thanks to suitable reducing agents, the reductive deposition of metals on the surface of the glass in a dilute state. The metal chloride concentrate with the reducing agent is stable and is not subject to reductive metal deposition, thus not degrading the metal chloride concentrate. The solution is one component and no modification of the technology is required. The reducing agent must be active only at high dilution, and it has been shown in extensive tests that suitable reducing agents are substances from the group of aliphatic polyols, substances from the group of reducing sugars or substances from the group of salts of acids formed by oxidation of aldoses and their neutralization. Acidic solutions of metal chlorides, for example tin dichloride, palladium chloride or a mixture of ruthenium trichloride and palladium chloride, are added to a substance of the aliphatic polyol group or to a substance of the reducing sugar group or to a substance of the group of salts of acids formed by oxidation of aldoses and their neutralization. The concentrate is diluted with distilled water to make the resulting solution suitable for the customer. The great advantage is the fact that the customer can thus directly replace the previously used metal chloride solution without having to change dosage ratios and without making other modifications of the line. Thus, substances from the group of aliphatic polyols, substances from the group of reducing sugars or substances from the group of salts of acids formed by oxidation of aldoses and their neutralization increase the efficiency of metal deposition by a factor of several times, while this allows for a 95 % deposition of said metals on the glass. They improve the economy and protect waste water from heavy metals while the quality of products, e.g. mirrors, is the same or even higher.

Substances from the group of aliphatic polyols, substances from the group of reducing sugars or substances from the group of salts of acids formed by oxidation of aldoses and their neutralization will provide a more efficient way of elimination of metals such as Sn, Pd, Ru on glass, replacing the disproportionation reaction by an oxidation-reduction reaction. The fact that the reducing agent is directly contained in the metal chloride solution and that the application does not require any modification of the technology is very advantageous. In other words, both the metal and the reducing agent are in one concentrate.

The solutions for pre-treating glass and plastic surfaces prior to reductive silvering in the manufacture of mirrors according to the invention also facilitate the treatment of the reflective silver layer prior to the application of the adhesion bridge and the protective varnish, thus ensuring better corrosion resistance of the reflective layers. These solutions are more than 9 times more effective in depositing metal on the surface if compared to the original solutions containing only metal chloride.

Examples of the Performance of the Invention

Example 1

The solution for surface treatment prior to the deposition of a metal layer, which is the silver layer, comprises a solution of an activating solution concentrate containing 13g of ruthenium trichloride $RuCl_3xHCl$, 7g of palladium chloride $PdCl_2$, 20g of diethylene glycol and 0.5 g of HCl in solution with distilled water in one litre.

The resulting activating solution when applied to glass contains 1 part of the activating solution concentrate in 1500 parts of the diluting distilled water.

According to the method of preparing the solution for surface treatment before the silver metal layer is deposited, 1 litre of the solution concentrate is first prepared by heating diethylene glycol to a temperature of 30°C, then the first solution is formed by mixing 20g of diethylene glycol, 13g of ruthenium trichloride $RuCl_3$ xHCl and 200ml of distilled water per 1 litre of the resulting activating solution concentrate. The mixture should be stirred until all the crystalline ruthenium trichloride has dissolved. At the same time, the second solution is made by mixing 7g of palladium chloride $PdCl_2$ and 400ml of distilled water with 0,5g of HCl per 1 litre of the resulting activating solution concentrate. The solution should be stirred again until the salt is completely dissolved. The resulting concentrate of the activating solution is obtained by mixing the first and second solutions, while continuous stirring, and by replenishing the mixture with distilled water up to 1 litre.

The application solution is prepared by diluting the concentrate of the activating solution with distilled water at a ratio of 1 : 1500 just before application.

The activating solution thus prepared is applied on the sensitized and rinsed surface of glass plates before the silver layer is applied.

Example 2

The solution for surface treatment prior to the deposition of a metal layer, which is the silver layer, comprises a solution of a solution concentrate containing 184g of tin dichloride dihydrate, 80g of diethylene glycol and 0.5 g of HCl in solution with distilled water in one litre.

The resulting activating solution contains 1 part of the activating solution concentrate in 1500 parts of the diluting distilled water.

According to the method of preparation of the above sensitizing solution containing the reducing agent which is diethylene glycol, it is first heated to a temperature of 35°C, then, for 1 litre of the resulting sensitizing solution, 150ml of 20°C warm acidic tin dichloride solution at a concentration of 1230g of tin dichloride dihydrate per 1 litre is slowly added to the 80g of diethylene glycol, while continuous stirring, and distilled water with 0.5g of HCl is added. The mixture should be stirred again to produce 1 litre of sensitising solution concentrate which is diluted with distilled water to 1 : 1500.

The sensitizing solution thus prepared is applied to the surface of glass plates, after a while it is important to rinse the remaining solution thoroughly with distilled water, in this way the surface is ready for the application of the activating solution or for reductive silvering.

Example 3

The solution for surface treatment prior to the deposition of a metal layer, which is the silver layer, comprises a solution of an activating solution concentrate containing 58g of ruthenium trichloride $RuCl_3$ xHCl, 35g of palladium chloride $PdCl_2$, 100g of ethylene glycol and 0.1 g of HCl in solution with distilled water in one litre.

The resulting activating solution contains 1 part of the activating solution concentrate in 2500 parts of distilled water.

According to the method of preparation of 1 litre of the concentrate of the above activating solution, the concentrate of the activating solution is first prepared by heating the ethylene glycol to a temperature of 30°C, then the first solution is made by mixing 100g of ethylene glycol, 58g of ruthenium trichloride $RuCl_3xHCl$ and 200ml of distilled water for 1 litre of the resulting concentrate of the activating solution. The mixture should be stirred until all the crystalline ruthenium trichloride has dissolved. At the same time, the second solution is made by mixing 35g of palladium chloride $PdCl_2$ and 400 ml of distilled water with 0.1 g of HCl for 1 litre of the resulting activating solution concentrate. The solution should be stirred again until the salt is completely dissolved. The resulting concentrate of the activating solution is obtained by mixing the first and second solutions, while continuous stirring, and by replenishing the mixture with distilled water up to 1 litre.

The application solution is prepared by diluting the concentrate of the activating solution with distilled water at a ratio of 1 : 2500 just before application.

The activating solution thus prepared is applied to the sensitized and rinsed surface of glass plates before the silver layer is applied.

Example 4

The solution for surface treatment prior to the deposition of a metal layer, which is the silver layer, comprises a solution of an activating solution concentrate containing 75g of palladium chloride $PdCl_2$, 100 g of diethylene glycol and 0.5 g of hydrochloric acid in solution with distilled water in one litre.

The resulting activating solution contains 1 part of the activating solution concentrate in 2500 parts of distilled water.

According to the method of preparation of 1 litre of the concentrate of the above activating solution, the concentrate of the activating solution is first prepared by heating the diethylene glycol to a temperature of 30°C, further, the solution is made by mixing 100g of diethylene glycol, 75g of palladium chloride $PdCl_2$ and 100ml of distilled water with 0.5 g of HCl for 1 litre of the resulting concentrate of the activating solution. The solution should be stirred until the palladium chloride is completely dissolved and then the solution replenished with distilled water up to 1 litre.

The application solution is prepared by diluting the concentrate of the activating solution with distilled water at a ratio of 1 : 2500 just before application.

Alternatively, activating solution concentrates may be prepared which may contain 20 to 230g of palladium chloride $PdCl_2$, 20 to 200g of glycerin and distilled water in one litre of the resulting activating solution concentrate.

The activating solution thus prepared is applied to the sensitized and rinsed surface of glass plates before the silver layer is applied.

Example 5

The solution for surface treatment prior to the deposition of a metal layer, which is the silver layer, comprises a solution of a solution concentrate containing 800g of tin dichloride dihydrate, 300g of ethylene glycol and distilled water in one litre.

The resulting activating solution prior to application contains 1 part of the activating solution concentrate in 7000 parts of the diluting distilled water.

According to the method of preparation of the above sensitizing solution containing a reducing agent, which is ethylene glycol, the ethylene glycol is first heated to a temperature of 35°C, further, to make 1 litre of the resulting sensitizing solution, 650ml of a 20°C warm acidic solution of tin dichloride at a concentration of 1230g of tin dichloride dihydrate per litre is slowly added to 300g of ethylene glycol, while continuous stirring, then distilled water is added and the mixture should be stirred again.

The application solution is prepared by diluting the concentrate of the activating solution with distilled water at a ratio of 1 : 7000 just before application on the sensitized surface.

The sensitizing solution prepared in this way is applied to the surface of plastics before washing with distilled water and applying the silvering solution.

Example 6

The solution for surface treatment prior to the deposition of a metal layer, which is the silver layer, comprises a solution of an activating solution concentrate containing 13g of ruthenium trichloride $RuCl_3xHCl$, 7 g of palladium chloride $PdCl_2$, 20g of triethylene glycol and 0.5 g of HCl in solution with distilled water in one litre.

The resulting activating solution contains 1 part of the activating solution concentrate in 500 parts of the diluting distilled water.

According to the method of preparation of 1 litre of the concentrate of the above activating solution, the concentrate of the activating solution is first prepared by heating triethylene glycol to a temperature of 30°C, then the first solution is made by mixing 20g of triethylene glycol, 13g of ruthenium trichloride $RuCl_3xHCl$ and 20ml of distilled water for 1 litre of the resulting concentrate of the activating solution. The mixture should be stirred until all the crystalline ruthenium trichloride has dissolved. At the same time, the second solution is made by mixing 7g of palladium chloride $PdCl_2$ and 400ml of distilled water with 0.5g of HCl for 1 litre of the resulting activating solution concentrate. The solution should be stirred again until the salt is completely dissolved. The resulting concentrate of the activating solution is obtained by mixing the first and second solutions, while continuous stirring, and by replenishing the mixture with distilled water up to 1 litre.

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

The activating solution thus prepared is applied to the sensitized and rinsed surface of glass plates before the silver layer is applied.

Example 7

The solution for surface treatment prior to the deposition of a metal layer, which is the silver layer, comprises a solution of a sensitizing solution concentrate containing 200g of tin dichloride dihydrate, 80 g of triethylene glycol and 5 g of HCl in solution with distilled water in one litre.

The resulting sensitizing solution contains 1 part of the sensitizing solution concentrate in 1500 parts of diluting distilled water.

According to the method of preparation of the above sensitizing solution containing the reducing agent which is triethylene glycol, it is first heated to a temperature of 35°C, then, to make 1 litre of the resulting sensitizing solution, 160ml of 20°C warm acidic tin dichloride solution at a concentration of 1230 g of tin dichloride dihydrate per 1 litre is slowly added to 80 g of triethylene glycol, while continuous stirring, and distilled water with 5g of HCl is added and mixed again to produce 1 litre of sensitising solution concentrate which is diluted with distilled water at a ratio of 1 : 1500 before application on sensitized surface.

The sensitizing solution thus prepared is applied to the surface of glass plates, after a while it is important to rinse the remaining solution thoroughly with distilled water, in this way the surface is ready for the application of the activating solution or for reductive silvering.

Example 8

The solution for surface treatment prior to the deposition of a metal layer, which is the silver layer, comprises a solution of an activating solution concentrate containing 13g of ruthenium trichloride $RuCl_3$ xHCl, 7g of palladium chloride $PdCl_2$, 20g of propylene glycol and 0.5 g of HCl in solution with distilled water in one litre.

The resulting activating solution contains 1 part of the activating solution concentrate in 500 parts of the diluting distilled water.

According to the method of preparation of 1 litre of the concentrate of the above activating solution, the concentrate of the activating solution is first prepared by heating the propylene glycol to a temperature of 30°C, then the first solution is formed by mixing 20g of propylene glycol, 13g of ruthenium trichloride $RuCl_3$xHCl and 20ml of distilled water for 1 litre of the resulting concentrate of the activating solution. The mixture should be stirred until all the crystalline ruthenium trichloride has dissolved. At the same time, the second solution is made by mixing 7g of palladium chloride $PdCl_2$ and 400ml of distilled water with 0.5g of HCl for 1 litre of the resulting activating solution concentrate. The solution should be stirred again until the salt is completely dissolved. The resulting concentrate of the activating solution is obtained by mixing the first and second solutions, while continuous stirring, and by replenishing the mixture with distilled water up to 1 litre.

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

The activating solution thus prepared is applied to the sensitized and rinsed surface of glass plates before the silver layer is applied.

Example 9

The solution for surface treatment prior to the deposition of a metal layer, which is the silver layer, comprises a solution of a sensitizing solution concentrate containing 200g of tin dichloride dihydrate, 80g of propylene glycol and 5g of HCl in solution with distilled water in one litre.

The resulting sensitizing solution contains 1 part of the sensitizing solution concentrate in 1500 parts of the diluting distilled water.

According to the method of preparation of the above sensitizing solution containing the reducing agent which is propylene glycol, it is first heated to a temperature of 35°C, then, to obtain 1 litre of the resulting sensitizing solution, 160ml of a 20°C warm acidic solution of tin dichloride at a concentration of 1230 g of tin dichloride dihydrate per 1 litre is slowly added to 80g of propylene glycol, while continuous stirring, and distilled water with 5g of HCl is added and mixed again to produce 1 litre of sensitising solution concentrate, which is diluted with distilled water at a ratio of 1 : 1500 just before application on the sensitized surface.

The sensitizing solution thus prepared is applied to the surface of glass plates, after a while it is important to rinse the remaining solution thoroughly with distilled water, in this way the surface is ready for the application of the activating solution or for reductive silvering.

Example 10

The solution for surface treatment prior to the deposition of a metal layer, which is the silver layer, comprises a solution of an activating solution concentrate containing 13g of ruthenium trichloride $RuCl_3xHCl$, 7.55g of palladium chloride $PdCl_2$, 20 g of dipropylene glycol and 0.5 g of HCl in solution with distilled water in one litre.

The resulting activating solution contains 1 part of the activating solution concentrate in 500 parts of the diluting distilled water.

According to the method of preparation of 1 litre of the concentrate of the above activating solution, the concentrate of the activating solution is first prepared by heating the dipropylene glycol to a temperature of 30°C, then the first solution is formed by mixing 20g of dipropylene glycol, 13g of ruthenium trichloride $RuCl_3xHCl$ and 20ml of distilled water for 1 litre of the resulting concentrate of the activating solution. The mixture should be stirred until all the crystalline ruthenium trichloride has dissolved. At the same time, the second solution is made by mixing 7.55g of palladium chloride $PdCl_2$ and 400ml of distilled water with 0,5g of HCl for 1 litre of the resulting activating solution concentrate. The solution should be stirred again until the salt is completely dissolved. The resulting concentrate of the activating solution is obtained by mixing the first and second solutions, while continuous stirring, and by replenishing the mixture with distilled water up to 1 litre.

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

The activating solution thus prepared is applied to the sensitized and rinsed surface of glass plates before the silver layer is applied.

Example 11

The solution for surface treatment prior to the deposition of a metal layer, which is the silver layer, comprises a solution of a sensitizing solution concentrate containing 200g of tin dichloride dihydrate, 80g of dipropylene glycol and 5g of HCl in solution with distilled water in one litre.

The resulting sensitizing solution contains 1 part of the sensitizing solution concentrate in 1500 parts of the diluting distilled water.

According to the method of preparation of the above sensitizing solution containing the reducing agent which is dipropylene glycol, it is first heated to a temperature of 35°C, then, to obtain 1 litre of the resulting sensitizing solution, 160ml of a 20°C warm acidic solution of tin dichloride at a concentration of 1230g of tin dichloride dihydrate per 1 litre is slowly added to 80g of dipropylene glycol, while continuous stirring, and distilled water with 5g of HCl is added and mixed again to produce 1 litre of sensitizing solution concentrate, which is diluted with distilled water at a ratio of 1 : 1500 just before application on the sensitized surface.

The sensitizing solution thus prepared is applied to the surface of glass plates, after a while it is important to rinse the remaining solution thoroughly with distilled water, in this way the surface is ready for the application of the activating solution or for reductive silvering.

Example 12

The solution for surface treatment prior to the deposition of a metal layer, which is the silver layer, comprises a solution of an activating solution concentrate containing 13g of ruthenium trichloride $RuCl_3xHCl$, 7.55g of palladium chloride $PdCl_2$, 20 g of tripropylene glycol and 0.5 g of HCl in solution with distilled water in one litre.

The resulting activating solution contains 1 part of the activating solution concentrate in 500 parts of the diluting distilled water.

According to the method of preparation of 1 litre of the concentrate of the above activating solution, the concentrate of the activating solution is first prepared by heating the tripropylene glycol to a temperature of 30°C, then the first solution is formed by mixing 20g of tripropylene glycol, 13g of ruthenium trichloride $RuCl_3xHCl$ and 20ml of distilled water for 1 litre of the resulting concentrate of the activating solution. The mixture should be stirred until all the crystalline ruthenium trichloride has dissolved. At the same time, the second solution is made by mixing 7.55g of palladium chloride $PdCl_2$ and 400ml of distilled water with 0.5g of HCl for 1 litre of the resulting activating solution concentrate. The solution should be stirred again until the salt is completely dissolved. The resulting concentrate of the activating solution is obtained by mixing the first and second solutions, while continuous stirring, and by replenishing the mixture with distilled water up to 1 litre.

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

The activating solution thus prepared is applied to the sensitized and rinsed surface of glass plates before the silver layer is applied.

Example 13

The solution for surface treatment prior to the deposition of a metal layer, which is the silver layer, comprises a solution of a sensitizing solution concentrate containing 200g of tin dichloride dihydrate, 80g of tripropylene glycol and 5g of HCl in solution with distilled water in one litre.

The resulting sensitizing solution contains 1 part of the sensitizing solution concentrate in 1500 parts of the diluting distilled water.

According to the method of preparation of the above sensitizing solution containing the reducing agent which is tripropylene glycol, it is first heated to a temperature of 35°C, then, to obtain 1 litre of the resulting sensitizing solution, 160ml of a 20°C warm acidic solution of tin dichloride at a concentration of 1230g of tin dichloride dihydrate per 1 litre is slowly added to 80g of tripropylene glycol, while continuous stirring, and distilled water with 5g of HCl is added and mixed again to produce 1 litre of sensitising solution concentrate, which is diluted with distilled water at a ratio of 1 : 1500 just before application on the sensitized surface.

The sensitizing solution thus prepared is applied to the surface of glass plates, after a while it is important to rinse the remaining solution thoroughly with distilled water, in this way the surface is ready for the application of the activating solution or for reductive silvering.

Example 14

The solution for surface treatment prior to the deposition of a metal layer, which is the silver layer, comprises a solution of an activating solution concentrate containing

13g of ruthenium trichloride $RuCl_3$ xHCl, 7g of palladium chloride $PdCl_2$, 20g of sorbitol and 1g of hydrochloric acid HCl in distilled water in one litre.

The resulting activating solution contains 1 part of activating solution concentrate in 500 parts of the diluting distilled water.

One litre of activating solution concentrate is prepared by mixing two aqueous solutions. The first is made by dissolving 20g of sorbitol in 300ml of distilled water. The second solution is prepared by dissolving successively 13g of ruthenium trichloride and 7g of palladium chloride in 500ml of distilled water acidified with 1g of hydrochloric acid. Both the solutions are mixed and replenished with distilled water up to 1 litre.

This concentrate of the activating solution is diluted at a ratio of 1:500 with distilled water before application to a glass sheet.

Example 15

The solution for surface treatment prior to the deposition of a metal layer, which is the silver layer, comprises a solution of an activating solution concentrate containing 50g of ruthenium trichloride $RuCl_3$ xHCl, 40g of palladium chloride $PdCl_2$, 100 g of glucose and 10 g of hydrochloric acid HCl in distilled water in one litre.

The resulting activating solution contains 1 part of activating solution concentrate in 3000 parts of diluting distilled water.

One litre of the activating solution concentrate is prepared by mixing two aqueous solutions. The first is made by dissolving 100g of glucose in 300ml of distilled water. The second solution is prepared by dissolving 50g of ruthenium trichloride and 40g of palladium chloride successively in 500ml of distilled water acidified with 10g of hydrochloric acid. Both the solutions are mixed and replenished with distilled water up to 1 litre.

This concentrate of the activating solution is diluted with distilled water at a ratio of 1:3000 before application to a glass sheet.

Example 16

The solution for surface treatment prior to the deposition of a metal layer, which is the silver layer, comprises a solution of a sensitizing solution concentrate containing 800g of tin dichloride dihydrate, 10 g of hydrochloric acid HCl, 300g of meglumine and distilled water in one litre.

The resulting sensitizing solution contains 1 part of the sensitizing solution concentrate in 7000 parts of diluting distilled water.

One litre of sensitizing solution concentrate is prepared by mixing two aqueous solutions. The first is made by dissolving 300g of meglumine in 300ml of distilled water. The second solution is prepared by dissolving successively 650ml of a solution of tin dichloride dihydrate containing 1230g of $SnCl_2 . 2 H_2O$ and 10g of hydrochloric acid in 500ml of distilled water. Both the solutions are mixed and replenished with distilled water up to 1 litre.

This concentrate of the sensitizing solution is diluted with distilled water at a ratio of 1:7000 before application to the glass sheet.

Example 17

The solution for surface treatment prior to the deposition of a metal layer, which is the silver layer, comprises a solution of a sensitizing solution concentrate containing 170g of tin dichloride dihydrate, 10g of hydrochloric acid HCl, 100g of sodium gluconate and distilled water in one litre.

The resulting sensitizing solution contains 1 part of sensitizing solution concentrate in 1500 parts diluting distilled water.

One litre of sensitizing solution concentrate is prepared by mixing two aqueous solutions. The first is made by dissolving 100g of sodium gluconate in 300ml of distilled water. The second solution is prepared by dissolving successively 170g of tin dichloride dihydrate and 10g of hydrochloric acid in 500ml of distilled water. Both the solutions are mixed and replenished with distilled water up to 1 litre.

This concentrate of the sensitizing solution is diluted with distilled water at a ratio of 1:1500 before application to a glass sheet.

Industrial Application

The solution for surface treatment prior to the deposition of the metal layer according to the invention can be used as a sensitizing and activating solution for the treatment of glass and plastic surfaces prior to the chemical-reductive metal plating and also, for example, for the treatment of the Ag layer prior to the application of an adhesion bridge in the production of mirrors.

Patent Claims

1. A solution for surface treatment prior to the deposition of the metal layer, in particular a solution for surface treatment prior to the deposition of the reflective silver layer, **characterized in that** it contains at least one metal chloride and a reducing agent capable of oxidation by the metal chloride in dilute solution.
2. The solution for surface treatment prior to the deposition of the metal layer according to Claim 1, **characterized in that** it contains a solution concentrate which contains 20 to 800g of metal chlorides and 20 to 300g of a reducing agent capable of oxidation by metal chloride in dilute solution, 0.5 to 15 g of hydrochloric acid and distilled water in one litre, and distilled water at a ratio of 1 : 400 to 1 : 7000 to the solution concentrate.
3. The solution for surface treatment prior to the deposition of the metal layer, according to any one of Claims 1 and 2, **characterized in that** the reducing agent capable of oxidation by metal chloride in the dilute solution is a substance from the group of aliphatic polyols.
4. The solution for surface treatment prior to the deposition of a metal layer, according to any one of Claims 1 and 2, **characterized in that** the reducing agent capable of oxidation by metal chloride in the dilute solution is a substance from the group of reducing sugars.
5. The solution for surface treatment prior to the deposition of a metal layer, according to any one of Claims 1 and 2, **characterized in that** the reducing agent capable of oxidation by metal chloride in the dilute solution is a substance from the group of acid salts formed by oxidation of aldoses and their neutralization by metal hydroxide.
6. A method of preparation of a solution for surface treatment prior to the deposition of a metal layer, in particular a solution for surface treatment prior to the deposition of a silver layer, according to any one of Claims 1 through 5, **characterized in that** a solution of at least one metal chloride, distilled water, hydrochloric acid and a reducing agent capable of oxidation is mixed with a metal chloride in a dilute solution.
7. The method of preparation of the solution according to Claim 6, **characterized in that** a first solution of a reducing agent capable of oxidation by metal chloride in dilute solution which is a substance from the group of aliphatic polyols or a

substance from the group of reducing sugars or a substance from the group of salts of acids formed by oxidation of aldoses and their neutralization by metal hydroxide is prepared with distilled water by mixing 20 to 300g of a reducing agent capable of oxidation by metal chloride in dilute solution with 20 to 300g of distilled water, and then a second solution is prepared by mixing 20 to 800g of metal chlorides, 300 to 500ml of distilled water with 0.5 to 15g of hydrochloric acid after which the first solution and the second solution are mixed and supplemented with distilled water to 1 litre of the resulting solution concentrate, which is, before application, diluted with distilled water at a ratio of 1 : 400 through 1 : 7000.

8. The method of preparing the solution according to Claim 6, **characterized in that,** at first, a concentrate of the solution is prepared by heating a substance capable of oxidation by a metal chloride in dilute solution which is a substance from the group of aliphatic polyols or a substance from the group of reducing sugars or a substance from the group of salts of acids formed by oxidation of aldoses and their neutralization to a temperature of 30 to 35°C, further, for one litre of the resulting solution concentrate, 20 to 200g of the substance capable of oxidation by a metal chloride in dilute solution and 20 to 200g of metal chlorides are mixed with 100ml of distilled water containing 0.5 g of hydrochloric acid, the solution being stirred until all the metal chloride is dissolved, and then the solution is replenished with distilled water up to one litre of the resulting solution concentrate which is, before application, diluted with distilled water at a ratio of 1 : 1500 to 1 : 2500.

9. The method of preparing the solution according to Claim 6, **characterized in that,** at first, a concentrate of the solution is prepared by heating a substance capable of oxidation by metal chloride in dilute solution, which is a substance from the group of aliphatic polyols, a substance from the group of reducing sugars or a substance from the group of salts of acids formed by oxidation of aldoses and their neutralization to a temperature of 35°C, then 150 to 400ml of a 20°C warm solution of metal chlorides in distilled water at a concentration of 1145 g of metal chlorides per litre is slowly added to 80 to 200g of the substance capable of oxidation by metal chloride in dilute solution, while continuous stirring, and the solution is then further supplemented up to 1 litre with distilled water containing 0.5 g of hydrochloric acid per litre, and all is mixed again, and

distilled water is further added to make 1 litre of the resulting solution concentrate, which is diluted with distilled water at a ratio of 1 : 1500 to 1 : 7000 before application on the respective surface.