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(54) **A SENSITIZING SOLUTION AND METHOD OF ITS PREPARATION**

(57) A sensitizing solution, especially a sensitizing solution for sensitizing surfaces, containing a solution of tin(II) chloride SnCl₂ and distilled water, especially for sensitizing non-conductive surfaces, which further contains glycerine. A method of preparation of the sensitizing

solution, especially the method of preparation of the sensitizing solution, according to which the solution of tin(II) chloride SnCl₂ and distilled water is mixed with a reducing agent, which is glycerine.

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DescriptionField of the Invention

5 **[0001]** The present invention relates to a sensitizing solution, in particular to a sensitizing solution for sensitizing the surface of glass and plastics, especially for sensitizing glass panels, prior to applying further coatings, and the methods of its preparation.

Background of the Invention

10 **[0002]** Nowadays, a number of applications of various sensitizing solutions are known for increasing the sensitivity of various electrically non-conductive surfaces to accept different coatings layers such as Pd, Ru, Cu, Ag.

[0003] It is known from a patent document CS 112952 that for sensitizing surfaces is generally used a known sensitizing agent, namely an aqueous solution of tin(II) chloride at various concentrations or an aqueous solution of tin(II) chloride with a certain proportion of hydrochloric acid, which inhibits hydrolysis of the dissolved tin salt. Sensitization is used to form a continuous hydrophilic film of tin on the treated surface, which is determinative for a good progress of silvering process and for quality of deposited silver. Just before application on a glass surface, the sensitizing solution concentrate is diluted with distilled water, which raises the pH of the sensitizing solution and causes a disproportionation reaction, leading to the deposition of tin on the glass surface. This solution is then thoroughly rinsed off the surface with distilled water. The glass surface is thus ready for the application of additional coatings or for direct silvering. According to a method of preparing tin(II) chloride-based solutions for sensitizing electrically non-conductive objects intended to be chemically silvered, as disclosed in this patent document, solid SnCl_2 is oxidized by 1.0 to 10.0% H_2O_2 solution or 1.0 to 10.0% FeCl_3 solution or 0.5 to 5.0% KMnO_4 solution or 0.6 to 6.0% $\text{K}_2\text{Cr}_2\text{O}_7$ solution, obtaining at least 5% and the most 30% of SnCl_4 .

25 **[0004]** A method for increasing the sensitizing ability of solutions for the treatment of electrically non-conductive surfaces of objects of organic origin prior to silvering is described in a patent document CS 120550. A solution is prepared from tin(II) chloride with an addition of oxidizing agents, for example hydrogen peroxide, while ferric sulphate, ferric chloride or ferric hydroxide is also added to the solution in an amount corresponding to 0.2 to 0.7% of the used solid tin(II) chloride.

30 **[0005]** Currently, glass surface sensitization is usually performed using an acidic aqueous solution of tin(II) chloride (SnCl_2) in water. The tin deposited on the glass surface supports silvering process. Reducing silvering then proceeds faster, more evenly and the formed silver layer adheres better to the glass.

[0006] The tin(II) chloride solution is supplied as a concentrate containing 1,145 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 167 g of HCl in 1 litre of solution. This 1 litre of solution contains 600 g of tin. Hydrochloric acid is added for stabilization because the solution, especially diluted, tends to oxidise and thereby degrade. At the same time, the addition of hydrochloric acid ensures the solubility of tin(II) chloride at lower temperatures. Prior to application onto the glass, the concentrate is diluted with distilled water and dosed in amount of 50 to 70 mg Sn/m^2 of glass.

35 **[0007]** Currently, 1,570 m^2 of glass pass through the mirror production line per hour, during this time 600 g of Sn x $(2.5 \times 0.07) = 105$ g Sn is applied onto the glass per hour. Per 1 m^2 this makes 105,000 mg : 1,570 $\text{m}^2 = 66$ mg Sn per m^2 . The deposition on glass is around 3.5 to 4.1 mg Sn/m^2 . The effectiveness is therefore low, around 6% of tin is deposited on the glass and 94% is discharged into waste water.

[0008] The principle of deposition can be expressed by the following equation: $2\text{SnCl}_2 \rightarrow \text{Sn} + \text{SnCl}_4$. It is a disproportionation, where one molecule is reduced, the other one is oxidised. If everything proceeded perfectly, a maximum of 50% of tin would be deposited on a glass surface. However, it is necessary to use an even larger excess in order to cover the glass with the required layer of tin.

45 **[0009]** From the above-mentioned state of art, it is clear that it has a number of disadvantages, the main disadvantage is very low yield of tin forming the sensitizing layer. The redundant sensitizing solution is discharged to waste water together with a large amount of unused tin. This represents a major environmental burden, with significant disposal and recycling costs.

50 **[0010]** The object of the invention is to prepare a sensitizing solution enabling a substantially higher yield of tin from the sensitizing solution, while maintaining or improving the quality of the sensitization process.

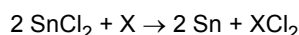
Summary of the Invention

55 **[0011]** The above-mentioned disadvantages are significantly eliminated and the object of the invention is realized by a sensitizing solution, particularly a sensitizing solution for sensitizing of surfaces, containing a solution of tin(II) chloride SnCl_2 and distilled water, particularly for sensitizing non-conductive surfaces such as glass panel surfaces prior to applying silvering solution, or for sensitizing a silvered surface prior to applying silane solution, or for sensitizing plastics,

according to the invention, the subject matter of the invention is that it further contains glycerine. The advantage of adding glycerine is that during sensitization occurs a reduction reaction, while all tin is reduced and an organic agent is oxidized.

[0012] In a preferred embodiment, the diluted sensitizing solution prior to application contains 0.01 to 1 wt.% of tin(II) chloride SnCl_2 , 0.01 to 1 wt. % of glycerine, and the rest consists of distilled water.

[0013] The above-mentioned disadvantages are further significantly eliminated and the object of the invention realized by the preparation method of the sensitizing solution, especially the method of preparation of the above-mentioned sensitizing solution according to the invention, the subject matter of the invention is that the solution of tin(II) chloride SnCl_2 and distilled water is mixed with a reducing agent, which is glycerine. Subsequently, during the sensitization of the surface, all the tin is reduced and the organic agent is oxidized according to the following equation:



where X is an organic reducing agent, which is glycerine. The advantage is that theoretically almost 100% of Sn can be deposited on the surface.

[0014] In a preferred embodiment, glycerine is firstly pre-heated to 35 °C. Subsequently for 1 litre of the resulting sensitizing solution, 45 to 450 ml of acidic solution of tin(II) chloride with a temperature of 20 °C and a concentration of 1,145 g of tin(II) chloride dihydrate per 1 litre is slowly added under constant stirring to 50 to 500 g of glycerine. Furthermore, distilled water is added and all components are stirred again, forming 1 litre of concentrated sensitizing agent.

[0015] In a preferred embodiment, prior to application onto the surface, the concentrated sensitizing agent is diluted with distilled water in a ratio of 1:500 to 1:5,000. The advantage is that such previously prepared concentrate can be diluted at the place of application, which saves both transport and storage costs.

[0016] The main advantage of the invention is a significant cost saving thanks to considerably higher yield of tin from the sensitizing agent. Using the sensitizing solution according to this invention, as the mirror production line also processes 1,570 m² of glass per hour, and onto 1 m² is applied only 10 mg Sn/ m², while deposited is only 4 mg Sn/m² on the glass. The Sn deposition rate on the glass is thus around 40%. The used sensitizing solution per 1 m² of glass, containing the remaining 6 mg of Sn, is discharged into waste water. When using conventional sensitizing agent, 66 mg - 4 mg = 62 mg of Sn is discharged into waste water per 1 m² of glass. Therefore, when using the sensitizing solution according to this invention, 56 mg of Sn is saved per 1 m² of mirror produced. The significant advantage is not only the economic effect, but also the environmental effect. While using the sensitizing solution according to this invention, 90% less of tin is discharged into waste water compared to the use of conventional sensitization.

Preferred embodiments of the Invention

Example 1

[0017] A sensitizing solution for sensitizing glass panel surface, prior to applying a silvering solution, contains 1 wt.% of tin(II) chloride SnCl_2 , 1 wt.% of glycerine, and the rest consists of distilled water.

[0018] According to the preparation method of the above-mentioned sensitizing solution containing a reducing agent, which is glycerine, the first step was to pre-heat glycerine to 35 °C. Subsequently for 1 litre of the resulting sensitizing solution, to 500 g of glycerine under constant stirring was slowly added 450 ml of acidic solution of tin(II) chloride with a temperature of 20 °C and a concentration of 1,145 g of tin(II) chloride dihydrate per 1 litre. Furthermore, distilled water was added and all components were stirred again, forming 1 litre of concentrated sensitizing agent, which prior to application onto the surface to be sensitized, was diluted with distilled water in a ratio of 1: 500.

[0019] The sensitizing solution thus prepared is then applied onto the glass panel surface; after a while, the remaining solution has to be thoroughly rinsed by distilled water, so the treated surface is ready for applying the silvering solution.

Example 2

[0020] A sensitizing solution for sensitizing silvered glass panel surface, prior to applying a silane solution, contains 0.01 wt.% of tin(II) chloride SnCl_2 , 0.01 wt.% of glycerine, and the rest consists of distilled water.

[0021] According to the preparation method of the above-mentioned sensitizing solution, containing a reducing agent, which is glycerine, the first step was to pre-heat glycerine to 35 °C. Subsequently for 1 litre of the resulting sensitizing solution, 50 g of glycerine under constant stirring was slowly added 45 ml of acidic solution of tin(II) chloride with a temperature of 20 °C and a concentration of 1,145 g of tin(II) chloride dihydrate per 1 litre. Furthermore, distilled water was added and all components were stirred again, forming 1 litre of concentrated sensitizing agent, which prior to application onto the surface to be sensitized, was diluted with distilled water in a ratio of 1: 5,000.

[0022] The sensitizing solution thus prepared is applied onto the silvered glass panel surface, previously rinsed with

distilled water. Next the surface is rinsed with distilled water again and the silane solution is applied.

Example 3

[0023] A sensitizing solution for sensitizing plastics, prior to applying a silver coating, contains 0.02 wt.% of tin(II) chloride SnCl_2 , 0.02 wt.% of glycerine, and the rest consists of distilled water.

[0024] According to the preparation method of the above-mentioned sensitizing solution, containing a reducing agent, which is glycerine, the first step was to pre-heat glycerine to 35 °C. Subsequently for 1 litre of the resulting sensitizing solution, 100 g of glycerine under constant stirring was slowly added 90 ml of acidic solution of tin(II) chloride with a temperature of 20 °C and a concentration of 1,145 g of tin(II) chloride dihydrate per 1 litre. Furthermore, distilled water was added and all components were stirred again, forming 1 litre of concentrated sensitizing agent, which prior to application onto the surface to be sensitized, was diluted with distilled water in a ratio of 1: 5,000.

[0025] The sensitizing solution thus prepared is applied onto the plastic surface prior to rinsing by distilled water and applying the silvering solution.

Industrial applicability

[0026] The sensitizing solution according to the present invention can be used for sensitizing various types of surfaces, especially glass panels in mirror production, to sensitize silver coating before applying silane, and for treating plastics prior to silvering their surfaces.

Claims

1. A sensitizing solution, especially a sensitizing solution for sensitizing surfaces, containing a solution of tin(II) chloride SnCl_2 and distilled water, especially for sensitizing non-conductive surfaces, **characterized in that** it further contains glycerine.
2. The sensitizing solution according to claim 1, **characterized in that** it contains 0.01 to 1 wt.% of tin(II) chloride SnCl_2 , 0.01 to 1 wt.% of glycerine and distilled water.
3. A method of preparation of the sensitizing solution, especially the preparation method of the sensitizing solution according to claim 1 or 2, **characterized in that** a solution of tin(II) chloride SnCl_2 and distilled water is mixed with a reducing agent, which is glycerine.
4. The method of preparation of the sensitizing solution according to claim 3, **characterized in that** firstly glycerine is pre-heated to 35 °C, and secondly for 1 litre of the resulting sensitizing solution, 45 to 450 ml of tin(II) chloride SnCl_2 solution with a temperature of 20 °C and a concentration of 1,145 g of tin(II) chloride dihydrate per 1 litre is slowly added under constant stirring to 50 to 500 g of glycerine, and finally, distilled water is added and all components are stirred again, forming concentrated sensitizing solution.
5. The method of preparation of the sensitizing solution according to claim 4, **characterized in that** the sensitizing solution concentrate is diluted with distilled water in a ratio of 1:500 to 1:5,000 before applying onto a surface to be sensitized.



EUROPEAN SEARCH REPORT

Application Number

EP 22 17 2222

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Place of search

Date of completion of the search

Examiner

Munich

3 January 2023

Heer, Stephan

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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