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(54) Method for coating tubes

Verfahren zur Beschichtung von Rohren

Procédé de revêtment des tubes

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Description

[0001] The invention relates to a method according to claim 1 for coating the inner surface of a tube made of copper or copper alloy.

[0002] Copper tubes are known to be coated internally by tin that provides a cathodic protection for copper. Specific quality requirements are set for tin-coated tubes with respect to strength, purity and coating porosity. In chemical tin coating, the process is known to be distinguished as two or three separate process steps comprising the activation of the surface to be coated, precoating and the coating step proper with the tin coating. In the surface activation, the surface to be coated is treated by certain chemicals in order to make the coating succeed. In the precoating after the activation, the solution is usually composed of an acidic solution, in which there is dissolved both a complexing agent participating in the coating reactions, as well as the tin source proper. The function of the precoating step is to form tin nuclei on the surface to be coated. In the coating step, a tin coating layer is deposited onto the tin nuclei. The actual coating step may be carried out either in an acidic or an alkaline solution.

[0003] Chemical tin coating is known to be carried out as an ion-exchange reaction, in which copper ions are dissolved from the basic metal, and simultaneously on the surface of the basic metal, from the tin coating solution there is deposited an equivalent quantity of tin ions on the basis of the tension between the tin coating solution and copper. An increased quantity of dissolved copper in the solution with respect to the quantity of tin slows down the ion exchange reaction. Consequently, also according to the quantity of deposited tin, the solution must from time to time be subjected to tin source regulation. When the surface of the basic metal is completely coated, the ion exchange reaction is slowed down and finally stops. If the tin coating becomes nonhomogeneous during the tin coating process, this may later result in that tin ions are disengaged for example to household water. The working life of a tin coating solution can be raised by adding so-called stabilizers into the solution. It is well known that the tin coating process is carried out in two separate steps, so that the solution of the first step is only used for transmission, and the solution of the second step is used for accumulating the tin layer.

[0004] According to the patent EP0848084, there is known a method for manufacturing a copper tube, according to which the tin coating of the copper tubes is carried out in two steps, so that the temperature of the tin coating solution is raised when proceeding to the second tin coating step.

[0005] Further, according to document US-A-5,769,129 a plating method has been known to coat the inner surface of a copper alloy pipe with Sn by means of a chemical plating solution. The plating method is carried out by using Tin(II)-chloride, Thiourea and Tartaric acid as the plating solution which is caused to flow through the copper pipe. According to document EP 0 851 041 A1 a coating method for a copper tube is disclosed which method is based on the same principal to let a chemical tin-solution flow through the pipe. Hereby, method is divided into two method steps which differ in the temperature of the solution to be fed through the pipe, respectively. Accordingly, one has to begin with a low temperature within the range of 35°C - 45°C. which first method step is followed by the second one using a temperature between 70°C and 85° C at the maximum temperature. At least it is proposed to alter the temperature during the plating process to realize the effect of the double-step process.

[0006] The object of the present invention is to introduce a novel solution that is more advantageous than the prior art for coating the inner wall of a tube made of copper or copper alloy with a tin layer, particularly so that the coating is carried out in one coating step.

[0007] The invention is characterized by what is set forth in the characterizing part of claim 1. Other preferred embodiments of the invention are characterized by what is set forth in the rest of the claims.

[0008] Remarkable advantages are achieved by the arrangement according to the invention. By means of the method according to the invention, the tin coating process of the interior tube wall is made more rapid, and the quantity of used chemicals is remarkably reduced in comparison with conventional tin coating. By means of the invention, there is formed a tin layer according to the regulations on the inner surface of a tube made of copper or copper alloy by carrying out the coating in one coating step, so that the tin layer is formed as the tin coating solution circulates on the inner tube surface. The one coating step according to the invention means that the coating solution is circulated to the inner tube surface at one end of the tube, and it is made to flow out of the other end of the tube, during which time there is created a tin layer by means of chemical tin coating according to an ion exchange reaction. Advantageously the multi-step activation of the inner tube surface, the precoating and the coating are made to take place by means of one and the same coating solution and essentially in one coating step, while the coating solution circulates on the inner tube surface.

[0009] The coating solution according to the invention, circulated on the inner tube surface, includes at least pH adjustment agent, to the extent that the pH of the coating solution <1, tin source for creating bivalent tin ions (Sn^{2+}) in the coating solution and complexing agent. According to an embodiment of the invention, the employed tin source is tin chloride ($SnCl_2$), and the employed complexing agent is thiourea $(NH_2)_2CS$, in which case the ratio of the contents of tin chloride and thiourea in the coating solution is 1:(1-10), preferably, however, 1:4. According to an embodiment of the invention, the employed pH adjustment agent is hydrochloric acid (HCl). The employed tin source can be for example tin (II) sulfate or some other tin source, by using which the tin ion can be

made to be present as bivalent (Sn^{2+}) in the above mentioned coating solution. According to an embodiment of the invention, the employed pH adjustment agent is sulfuric acid (H_2SO_4). The content of thiourea in the coating solution is 2 - 20 percentages by weight (w-%), preferably 10 percentages by weight. When the content of thiourea in the coating solution is relatively low, the tubes are easier to clean after coating.

[0010] In a coating solution according to the invention, the complexing agent participates in the tin coating reactions as a complexing agent at least by binding free copper ions in said coating solution. When carrying out the coating in one step by a coating solution according to the invention, the inner tube surface is also cleaned of possible impurities that are accumulated on the inner surface in earlier treatments of the inner tube surface. When using a coating solution according to the invention, the use of many other chemicals, such as for example stabilizers, can be completely avoided. When the use of many other chemicals is avoided, the further treatment of the coating solution is remarkably cheaper. In addition, the when using a coating solution according to the invention, harmful sedimentation of the solution at high temperatures can be avoided. The coating reaction time is remarkably shortened at the achieved high temperatures. Advantageously also when using a coating solution according to the invention, the solution expenses are reduced, and the time required for preparing the solution remains short in comparison with the manufacturing of multi-step coating solutions. Likewise, the use of rinsing waters circulated between various steps can be avoided, and savings can be achieved in the further treatment expenses of the solution.

[0011] According to the invention, the temperature of the coating solution is adjusted to be within the range 35 - 100ºC when feeding the coating solution onto the inner tube surface. By using this temperature, on the inner tube surface there is accumulated an advantageous tin layer according to the regulations. According to an embodiment of the invention, the tube is preheated before coating, which further enhances a successful coating. Preheating can be carried out from outside the tubes, or for instance by rinsing the inside of the tube by warm water or warm compressed air. According to the invention, the coating circulates on the inner tube surface for less than 30 minutes.

[0012] According to the invention, the coating is carried out in an oxygen-free atmosphere, so that the coating solution and the coating equipment are insulated against the effects of oxygen, for example by arranging them in oxygen-free protective gas and by preventing the access of oxygen into the coating solution. According to an embodiment of the invention, oxygen is removed from the coating solution, for instance before coating or during the coating step, in which case the effects of oxygen contained in the various ingredients of the solution can be avoided. Thus the oxidation of tin in the solution is advantageously prevented. Tin oxidation binds tin as a component, which means that the quantity of free tin ions in the solution is reduced. When the oxidation of tin is prevented in the tin coating solution, the working age and resistance of the solution is improved. According to the invention, the stabilizer can thus be advantageously replaced by various equipment arrangements. The function of the stabilizer is to prevent the oxidation of tin ions (Sn^{2+}) in the solution. After coating, the inner tube surface is cleaned of solution residues, for example by means of rinsing by air and water. The inner surface of the tube to be coated can be either treated or untreated. According to the invention, the inner surface of the tube to be coated is oxidized, in which case the tube can be semi-hard or soft. Advantageously by means of the coating solution according to the invention, both pickling and coating are carried out in the same coating solution. According to an embodiment of the invention, the tube to be coated is hard. The tube can also be pickled. The tube to be coated can be a tube coil, or a straight tube, and can have a length of even 1,000 meters.

[0013] The invention is described in more detail below with reference to an example.

EXAMPLE

[0014] The following example describes a method according to the present invention for coating a tube made of copper by a tin layer. According to the example, the tube to be coated is a semi-hard, straight tube with an oxidized inner surface. The coating for forming the tin layer can be carried out by feeding the coating solution simultaneously either onto the inner surfaces of several tubes, or to one tube at a time. Onto the inner tube surface, there is fed coating solution from a separate solution tank by pressurizing the coating solution into the tube. According to the example, the coating solution contains hydrochloric acid (HCl) as the pH adjustment, tin chloride ($SnCl_2$) as the tin source, and thiourea ($(NH_2)_2CS$) as the complexing agent. pH adjustment agent is added into pure water to that extent that the acidity (pH) in the coating solution is below 1, whereafter thiourea is added so that the content of thiourea in the final coating solution is 10 percentages by weight. Tin chloride is added to the coating solution to the extent that the ratio of the tin chloride and thiourea contents in the coating solution is 1:4, i.e. the quantity of thiourea is 4 times as much as the quantity of tin chloride. In the coating solution, tin is present in ion form (Sn^{2+}). According to the example, the temperature of the coating solution is 75 ºC, when it is fed onto the inner tube surface. The solution tank and the rest of the equipment are protected so that the access of oxygen into the coating solution is prevented for example by protective gas. According to the example, oxygen is removed from the coating solution. The temperature of the coating solution kept in the solution tank is maintained constant. Before feeding the coating solution in the tube, the tubes are rinsed by warm liquid. According to the example, the coating solution is fed into the preheated

tube at a turbulent speed. The coating solution circulates on the inner tube surface for about 20 minutes, during which time a tin layer is formed. The tin layer grows on the inner surface according to the ion exchange reaction, so that metallic copper is dissolved from the inner tube surface to the tin coating solution to ions, and the tin ion contained in the coating solution is deposited on the inner tube surface, forming a metallic coating. The tin layer is formed as a homogeneous layer with a thickness of about 1 - 2 micrometers. When the coating solution has circulated from one end of the tube to the other end, and the tin layer is formed, the tube is emptied of the coating solution. The tin-coated tubes are cleaned of coating solution residues for example by rinsing the tubes with water. When necessary, the tin-coated tubes are dried before their further treatment, such as storage or transport.

[0015] For a man skilled in the art, it is obvious that the various embodiments of the invention are not restricted to the examples given above, but may vary within the scope of the appended claims.

Claims

1. A method for coating the inner surface of a tube made of copper or copper alloy by a tin layer, according to which method the tin layer is formed by chemical tin coating, and the coating solution circulated on the inner tube surface contains at least a pH adjustment agent to the extent that the pH of the coating solution is < 1, a tin source for forming bivalent tin ions (Sn^{2+}) in the coating solution, as well as a complexing agent,
   characterized in that the inner surface of the tube to be coated is oxidized and that the coating of the inner tube surface is carried out in one coating step by said coating solution, the method being arranged in oxygen-free protective gas, wherein the tin layer is formed as the coating solution having a temperature within the range of 35 - 100°C circulates on the inner tube surface for less than 30 minutes.

2. A method according to claim 1, **characterized in that** the employed tin source is tin chloride.

3. A method according to claim 1, **characterized in that** the employed complexing agent is thiourea.

4. A method according to claim 2 or 3, **characterized in that** the ratio of the tin chloride and thiourea contents in the coating solution is 1:(1-10)

5. A method according to claim 4, **characterized in that** the ratio of the tin chloride and thiourea contents in the coating solution is preferably 1:4.

6. A method according to claim 1, **characterized in that** the employed pH adjustment agent is hydrochloric acid.

7. A method according to claim 1, **characterized in that** the employed pH adjustment agent is sulfuric acid.

8. A method according to claim 1, **characterized in that** the employed tin source is tin sulfate.

9. A method according to claim 3, 4 or 5, **characterized in that** the content of thiourea in the coating solution is 2 - 20 percentages by weight.

10. A method according to claim 9, **characterized in that** the content of thiourea in the coating solution is preferably 10 percentages by weight.

11. A method according to any of the preceding claims, **characterized in that** the tube is preheated before coating.

12. A method according to any of the preceding claims, **characterized in that** the inner tube surface is cleaned after coating.

13. A method according to claim 1 - 12, **characterized in that** the tube to be coated is semi-hard.

14. A method according to claim 1 - 12, **characterized in that** the tube to be coated is soft.

15. A method according to claim 1 - 14, **characterized in that** the tube to be coated is pickled.

Patentansprüche

1. Verfahren zum Beschichten der Innenfläche eines aus Kupfer oder einer Kupferlegierung gefertigten Rohres mit einer Zinnschicht, gemäß welchem Verfahren die Zinnschicht mittels einer chemischen Zinnbeschichtung gebildet wird, und die an der Innenrohrfläche zirkulierte Beschichtungslöschung zumindest ein pH-Reguliermittel enthält, in dem Maße, dass der pH der Beschichtungslösung < 1 ist, ferner eine Zinn-Stammquelle zur Bildung von bivalenten Zinn-Ionen (Sn^{2+}) in der Beschichtungslösung, ferner einen Komplexbildner,
   dadurch gekennzeichnet, dass die zu beschichtende Innenfläche des Rohres oxidiert wird und dass die Beschichtung der Innenrohrfläche in einem einzelnen Beschichtungsschritt mit Hilfe der Beschichtungslösung ausgeführt wird, wobei das Verfahren in einem sauerstofffreien Schutzgas durchgeführt wird, und die Zinnschicht gebildet wird, wenn die Beschichtungslösung eine Temperatur innerhalb des Bereiches von 35 - 100°C hat und auf der Innenrohrfläche für weniger als 30 Minuten zirkuliert.

2. Verfahren nach Anspruch 1,
dadurch gekennzeichnet, dass die verwendete Zinn-Stammquelle Zinnchlorid ist.

3. Verfahren nach Anspruch 1,
dadurch gekennzeichnet, dass der verwendete Komplexbildner Thiocarbamid ist.

4. Verfahren nach Anspruch 2 oder 3,
dadurch gekennzeichnet, dass das Verhältnis von Zinnchlorid und den Thiocarbamid-Anteilen in der Beschichtungslösung ist 1 : (1-10).

5. Verfahren nach Anspruch 4,
dadurch gekennzeichnet, dass das Verhältnis von Zinnchlorid und den Thiocarbamid-Bestandteilen in der Beschichtungslösung vorzugsweise 1 : 4 ist.

6. Verfahren nach Anspruch 1,
dadurch gekennzeichnet, dass das verwendete pH-Reguliermittel Salzsäure ist.

7. Verfahren nach Anspruch 1,
dadurch gekennzeichnet, dass das eingesetzte pH-Reguliermittel Schwefelsäure ist.

8. Verfahren nach Anspruch 1,
dadurch gekennzeichnet, dass die verwendete Zinnstammquelle Zinnsulfat ist.

9. Verfahren nach Anspruch 3, 4 oder 5,
dadurch gekennzeichnet, dass der Anteil an Thiocarbamid in der Beschichtungslösung 2 - 20 Gewichtsprozent beträgt.

10. Verfahren nach Anspruch 9,
dadurch gekennzeichnet, dass der Anteil an Thiocarbamid in der Beschichtungslösung vorzugsweise 10 Gewichtsprozent beträgt.

11. Verfahren nach einem der vorangehenden Ansprüche,
dadurch gekennzeichnet, dass der Rohr vor dem Beschichten erwärmt wird.

12. Verfahren nach einem der vorangehenden Ansprüche,
dadurch gekennzeichnet, dass die Innenrohrfläche nach dem Beschichten gereinigt wird.

13. Verfahren nach Anspruch 1 - 12,
dadurch gekennzeichnet, dass das zu beschichtende Rohr halbhart ist.

14. Verfahren nach Anspruch 1-12,
dadurch gekennzeichnet, dass das zu beschichtende Rohr weich ist.

15. Verfahren nach Anspruch 1-14,
dadurch gekennzeichnet, dass das zu beschichtende Rohr gebeizt ist.

Revendications

1. Procédé de revêtement de la surface interne d'un tube constitué de cuivre ou d'un alliage de cuivre par une couche d'étain, selon lequel la couche d'étain est formée par un revêtement d'étain chimique, et la solution de revêtement mise en circulation sur la surface interne du tube contient au moins un agent d'ajustement de pH, dans la mesure où le pH de la solution de revêtement est inférieur à 1, une source d'étain pour former des ions d'étain bivalents (Sn^{2+}) dans la solution de revêtement, ainsi qu'un agent complexant,
caractérisé en ce que la surface interne du tube à revêtir est oxydée et que le revêtement de la surface intérieure du tube est réalisé en une seule étape de revêtement par ladite solution de revêtement, le procédé étant réalisé dans un gaz protecteur sans oxygène, dans lequel la couche d'étain est formée lorsque la solution de revêtement ayant une température comprise dans la gamme de 35 à 100°C, circule sur la surface interne du tube pendant moins de 30 minutes.

2. Procédé selon la revendication 1, **caractérisé en ce que** la source d'étain utilisée est le chlorure d'étain.

3. Procédé selon la revendication 1, **caractérisé en ce que** l'agent complexant utilisé est la thiourée.

4. Procédé selon les revendications 2 ou 3, **caractérisé en ce que** le rapport entre les teneurs en chlorure d'étain et en thiourée dans la solution de revêtement sont de 1 : (1-10).

5. Procédé selon la revendication 4, **caractérisé en ce que** le rapport entre les teneurs en chlorure d'étain et de thiourée dans la solution de revêtement est de préférence de 1 :4.

6. Procédé selon la revendication 1, **caractérisé en ce que** l'agent d'ajustement de pH utilisé est l'acide chlorhydrique.

7. Procédé selon la revendication 1, **caractérisé en ce que** l'agent d'ajustement de pH utilisé est l'acide sulfurique.

8. Procédé selon la revendication 1, **caractérisé en ce que** la source d'étain utilisée est le sulfate d'étain.

9. Procédé selon les revendications 3, 4 ou 5, **carac-**

térisé en ce que la teneur en thiourée dans la solution de revêtement est de 2-20 pour cent en poids.

10. Procédé selon la revendication 9, **caractérisé en ce que** la teneur en thiourée dans la solution de revêtement est de préférence de 10 pour cent en poids.

11. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le tube est préchauffé avant revêtement.

12. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la surface intérieure du tube est nettoyée après revêtement.

13. Procédé selon la revendication 1-12, **caractérisé en ce que** le tube à revêtir est semi-dur.

14. Procédé selon la revendication 1-12, **caractérisé en ce que** le tube à revêtir est mou.

15. Procédé selon la revendication 1-14, **caractérisé en ce que** le tube à revêtir est décapé.

REFERENCES CITED IN THE DESCRIPTION

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