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(54) METHOD OF SURFACE PRE-TREATMENT OF STEEL COMPONENTS

(57) An invention relates to a method of pre-treating a surface of steel components, wherein the steel components are placed in an activation bath containing micro-structured zinc phosphate dispersed in a mechanically stirred distilled water solution having a concentration in the range of 0.2 to 0.3 wt%, wherein an activation time is 2 to 3 minutes at an activation bath temperature of 20 to 40 °C.

Processed by Luminess, 75001 PARIS (FR)

Description

Field of the Invention

[0001] The invention relates to realising fine-grained phosphate coatings with desired properties, i.e. primarily higher absorbency and ensuring higher adhesion for coating materials, preservative preparations and waxes. These properties can be ensured by the so-called technological activation rinse. Activation is essential to form fine-grained, more chemically resistant, i.e. higher resistance to alkaline environments, and more corrosion-resistant coatings of the so-called tri-cationic phosphate, mainly composed of the crystalline phase of phosphophyllites ($Zn_2Fe(PO_4)_2{\cdot}4H_2O$).

Background of the Invention

[0002] From the entire spectrum of phosphate coatings used by the industry, tri-cationic phosphating occupies an extraordinary position due to its application in the automotive industry as a standard in the pre-treatment of steel body profiles to ensure the highest corrosion resistance to atmospheric conditions and resistance to abrasive damage. At present, the industrial production of coatings from tri-cationic phosphate baths is ensured by employing an activation rinse using an aqueous suspension of α-polymer modification of titanophosphate ($Na_4TiO(PO_4)_2{\cdot}4H_2O$), see the Application Patent - Jernstedt 1943. It is a white-pink powdery substance whose activation potential for subsequent phosphating is ensured by the formation of a very diluted suspension in the form of an activation bath. During activation, the suspension is intensively stirred but not heated. The physically adsorbed particles of polymer modification of titanophosphate ensure the subsequent refinement of the morphology of the expelled phosphate coating, as the ion exchange of sodium cations from the titanophosphate molecule for zinc cations from the phosphating bath has been expertly demonstrated. The tri-cationic phosphate coating produced using a conventional activation process is the highest standard in the pre-treatment of automotive sheet metal surfaces before actual cataphoretic painting, which has excellent adsorption properties for various coating systems.

[0003] However, the use of α-polymer modification of titanophosphate ($Na_4TiO(PO_4)_2{\cdot}4H_2O$) for activation phosphate baths is currently associated with certain difficulties. The production of this substance using fluorotitanate (K_2TiF_6), sodium polyphosphate ($Na_4P_2O_7{\cdot}10H_2O$), phosphoric acid (H_3PO_4) and sodium hydrogenphosphate ($Na_2HPO_4{\cdot}2H_2O$) is very economically and environmentally demanding. Titanium minerals (K_2TiF_6) are costly and preferably used for producing high-strength composites, e.g., for centroplanes of aircraft and bioacceptable alloys used for joint prostheses. The production of α-polymer modification of titanophosphate is burdened by the necessity of realising and using phosphate substances, which must be ecologically disposed of - the initiation of overgrowth of cyanobacteria in waterways. In addition, the production is recemical; therefore, it is necessary to purify the mixture, which again increases the cost of preparing a suitable activator. Only the α-polymer modification has suitable activation properties, which are also related to the overall storage time. Impurities from production containing some metals and non-metals, e.g. Fe, As, Cu, Si and Al, significantly reduce the activation capacity of bulk mixtures. An essential problem of this activator is the significant reduction in activation capacity due to storage. This problem is related to the change in particle size distribution, i.e. conglomeration, as a result of air humidity. A slight destabilisation of the structure of the molecule by UV exposure has also been demonstrated for this substance. Considering the current geopolitical developments with a significant impact on the energy and raw materials industry, finding an alternative with a comparable activation effect is necessary.

[0004] The significant disadvantages of the existing steel activation, i.e. the use of the so-called α-polymorphic modification $Na_4TiO(PO_4)_2{\cdot}4H_2O$, before the actual phosphating include considerable economic and ecological demands associated with the production of titanophosphate. The economic demands are mainly reflected in the costly input raw materials for the production of titanophosphate and technological needs of the production itself, when intensive purification of the synthetically produced polymorphic modification from other polymorphic modifications and compounds accompanying the mineral raw materials of titanium - based on Fe, As, Cu, Si - is required. The environmental demands of titanophosphate production are associated with the need to dispose of phosphate-rich compounds. Other major disadvantages of the use of this activation are the gradual reduction of the effect due to storage, e.g. conglomeration of particles, UV degradation, as well as the necessity of a high level of surface pretreatment before activation, especially a high degree of degreasing and pickling of the steel surface, because the presence of even small amounts of oxo-hydroxide impurities, grease or residual salts can completely block the activation process.

Summary of the Invention

[0005] The above deficiencies are largely eliminated by the method of pre-treating the surface of steel components according to the present invention. In this method of surface pre-treatment, the components are placed in an activation bath containing micro-structured zinc phosphate dihydrate dispersed in a mechanically stirred distilled water solution having a concentration in the range of 0.2 to 0.3 wt%, wherein the activation time is 2 to 3 minutes at an activation bath temperature of 20 to 40 °C.

[0006] It is a dry micronised powdered zinc phosphate dihydrate designed to activate the steel surface before phosphating. The given dimensions of the particle size distribution [μm] are achieved by a specific method of grinding on a so-called jet mill.

[0007] The most significant advantage is the use of the so-called dry milling when it is not necessary to disperse the phosphate into a liquid. This results in a considerable increase in the lifetime of the powder prepared in this way. Commercially available products have a limited shelf life, after which recrystallisation occurs, and are sensitive to temperatures below 0 °C. It is also preferred in terms of transport, with regard to weight reduction, when no "water" is transported.

[0008] A very interesting option in this respect is the use of available so-called lacquer pigment from $Zn_3(PO_4)_2 \cdot 2H_2O$. This pigment is produced in various purities in an incomparably more economical and environmentally friendly way to fill primer, mainly epoxy, coatings in implementing modern anti-corrosion coating systems for steel. In this case, zinc phosphate dihydrate acts as a corrosion inhibitor in the primer. Its partial hydration ensures the blocking of cathodic corrosion sites, i.e. local phosphating, and thus significantly slows the corrosion process under atmospheric conditions. In principle, only partially soluble $Zn_3(PO_4)_2 \cdot 2H_2O$ can be used as a suitable activator since the ion exchange of the adsorbed molecule, i.e. Zn for Na in the case of titanophosphate, will not be necessary. The stability of $Zn_3(PO_4)_2 \cdot 2H_2O$ against UV and air humidity is significantly higher than that of the α-polymer modification of titanophosphate ($Na_4TiO(PO_4)_2 \cdot 4H_2O$). The partial solubility of the lacquer pigment also ensures a reduction in the conglomeration properties of the mixture. Impurities in the lacquer pigment cannot affect the activation process in this case.

[0009] However, the morphology of individual particles of all commercially available $Zn_3(PO_4)_2 \cdot 2H_2O$-based lacquer pigments is unsuitable for the actual activation process due to their considerable size. According to current literature sources, the activation ability of the micronised pigment is greater than that of the conventionally used titanophosphate ($Na_4TiO(PO_4)_2 \cdot 4H_2O$); therefore, it is possible to consider the reduction of the content of heavy metals, primarily Co, secondarily Ni, in the phosphating baths of tri-cationic phosphate, with the formation of comparably suitable conversion coatings.

[0010] The uniqueness of the phosphate precipitate from the tri-cationic phosphate bath is assured by the high P/H index of the majority representation of phosphophyllite versus hopeite-$Zn_3(PO_4)_2 \cdot 4H_2O$) and thus by the increased resistance of the coating to alkaline environments. Significant increase in alkalinity in the vicinity of coated phosphated sheet due to application of potential during cataphoretic painting in automotive paint shops.

[0011] The main advantages of the activation, according to the present invention, clearly include the economy and ecological parameters of $Zn_3(PO_4)_2 \cdot 2H_2O$ production, which are significantly lower than in the case of the α-titanophosphate output. Zinc phosphate dihydrate is produced as a secondary raw material in the production of phosphoric acid and also in the production of phosphate fertilisers. The ecological parameters of production are also lower compared to the production of $Na_4TiO(PO_4)_2 \cdot 4H_2O$, and the overproduction of this raw material is ensured within the production of primary corrosion inhibitors into the primer organic base, coating systems on steel usually on epoxy base. The use of micronised pigment is more environmentally and human-health friendly because the presence of arsenic (As) in the bulk material is eliminated. Furthermore, the highest degree of surface pre-treatment, especially degreasing and pickling, is not required before $Zn_3(PO_4)_2 \cdot 2H_2O$-based activation because the activation process does not proceed with ion exchange. The activation potency is related to the particle size distribution of micronised zinc phosphate dihydrate and is significantly higher in the proposed concept. According to the proposed powder preparation concept, there is no risk of a decrease in potency, i.e. activation capacity, due to prolonged storage time. UV degradation is also excluded.

Description of Embodiments of the Invention

[0012] Only the description of the activation pre-rinse or the activation is essential to include innovative activation for the surface protection of steel parts against corrosion in the automotive industry or in the light engineering and construction industry. The actual activation bath is classified as an intermediate bath before the phosphating. After activation, industrial phosphating occurs immediately without the introduction of distilled water rinsing. The essence of the activation process is based on the surface adsorption of micronised $Zn_3(PO_4)_2 \cdot 2H_2O$ particles on a steel substrate with a high degree of surface occupancy. The activation process is carried out in tanks in which the concentration in the form of the mass fraction of micronised $Zn_3(PO4)_2 \cdot 2H_2O$ is 0.25 wt% when dissolved in distilled water. The activation takes place at a temperature of 20 to 40 °C for 2 to 3 minutes and the bath is stirred intensively before and during the activation, so that particles do not settle to the bottom of the tank. Stirring is provided by an immersion stirrer with speed adjustment so that there is no turbulent flow around the activated steel component, i.e. there must be no central vortex. The dimensions of the tanks for activation on this basis are adapted to the dimensions of the subsequently phosphated parts, i.e. the dimensions of these tanks for activation rinse do not differ from those of the tanks for phosphating. The volume of the activation bath depends on the choice of the dimensions of the parts, which is influenced by the size of the phosphated parts, with the proviso that there must be a space around the edges of the parts for the bath to flow around and static and/or dynamic shaking of the coated part must not occur during activation. Before the actual activation, a suitable pretreatment of the surface of the parts must be chosen so that the parts are free of grease in case of hydrophobic particles of all kinds, scale and possibly precipitates of corrosion products formed by electrochemical corrosion of metals. The methods and types of solutions for these purposes are selected individually with regard to the overall line process of surface pre-treatment before the application of coatings, waxes, etc. Unless sufficient efficiency of surface pretreatment, i.e., removal of impurities, corrosion precipitate, and grease from the metal surface, is ensured, the activation potency for forming a fine-grained and well-adhered structure of the subsequently expelled phosphate coating may be severely limited.

Industrial Applicability

[0013] The general application of the innovative activation bath will have an impact primarily on the automotive industry, where it can be used primarily for the inclusion of a conventional line for tri-cationic phosphate before the application of cataphoretic paints in the treatment of car bodies or the painting of automotive shock absorber components. The light engineering industry can also use this activation bath to treat transformer plates or components, usually gears sets, to reduce run-in or drag friction. Within the construction industry, this activation bath can be used for coating components intended for the application of organic coatings with increased demands on durability, i.e. resistance to under-corrosion. From this point of view, these can be column footings, anchors for steel structures, additional fasteners, etc.

Claims

1. A method of pre-treating a surface of steel components, ***characterised in that*** the steel components are placed in an activation bath containing micro-structured zinc phosphate dihydrate dispersed in a mechanically stirred distilled water solution having a concentration in the range of 0.2 to 0.3 wt%, wherein an activation time is 2 to 3 minutes at an activation bath temperature of 20 to 40 °C.

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EUROPEAN SEARCH REPORT

Application Number
EP 23 20 1369

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	26 March 2024	Fodor, Anna

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82