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(54) **METHOD FOR ZERO-DISCHARGE PHOSPHATIZATION AND SAPONIFICATION BASED ON HIGH-PRESSURE CLOSED CIRCULATION SYSTEM**

VERFAHREN ZUR ENTLADUNGSFREIEN PHOSPHATIERUNG UND VERSEIFUNG AUF DER BASIS EINES GESCHLOSSENEN HOCHDRUCK-KREISLAUFSYSTEMS

PROCÉDÉ DE PHOSPHATATION ET DE SAPONIFICATION À DÉCHARGE NULLE BASÉ SUR UN SYSTÈME DE CIRCULATION FERMÉE HAUTE PRESSION

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Description

FIELD OF THE INVENTION

[0001] The invention relates to the field of phosphatization and saponification pretreatment in the metal cold-working industry, and particularly to a method for zero-discharge phosphatization and saponification based on a high-pressure closed circulation system.

BACKGROUND OF THE INVENTION

[0002] In the metal cold-working industry, when procedures such as wire drawing, extrusion, deep drawing, etc. are performed, the phosphatization-saponification treatment is first performed on the surface of a workpiece, and then the friction between the workpiece and a mold can be reduced to achieve a good lubricating effect.

[0003] The specific phosphatization process flow is as follows: firstly, the surface of a metal workpiece is degreased and derusted by an acid and a base, and the surface of the treated metal workpiece is washed with water; secondly, zinc-series phosphorization is performed, and the surface of the treated metal workpiece is washed with water; and thirdly, the surface of the metal workpiece is saponified with sodium stearate and then dried. The reasons for zinc-series phosphatization are as follows: firstly, a zinc-series phosphatized film is saponified to form a zinc stearate layer with excellent lubricity; and secondly, zinc-series phosphatization is carried out at a relatively low operating temperature and can be performed at 40, 60 or 90°C.

[0004] When a metal workpiece is derusted by the above process, derusting is performed by washing respectively with hydrochloric acid, nitric acid and sulfuric acid according to different metals, which produces toxic and smoky yellow and red smog, causes serious corrosive three-waste pollution, and easily allows that an outer layer of the metal of the washed workpiece is dissolved to form over-etching and the inside of the metal itself undergoes hydrogen permeation to cause hydrogen embrittlement, thus endangering the safety in use and shortening the service life. In addition, the whole process requires water washing for multiple times, and washing with water to dilute the waste working liquid may consume and lose a lot of water resources, resulting in serious pollution and great waste.

[0005] EP1314799A1 relates to a novel electrochemical reaction method and an electrochemical reaction apparatus thereof with small or zero in amount of generation of liquid waste such as electrolytic solution, using matter shifted into a supercritical or subcritical state and an electrolytic solution.

[0006] CN1283710C relates to a process for phosphonating iron and steel includes pickling, water washing, phosphonating, drying in air, saponifying and natural drying and CN105018920A discloses a phosphorus saponification production process to improve the production

efficiency, the safety, the reliability, the heating efficiency, the quality, to save energy and reduce the production cost. These processes are not in a closed circulation system, causing the problem of pollution and waste.

SUMMARY OF THE INVENTION

[0007] To solve the problems existing in the prior art, the invention provides a high-pressure closed circulation system and a method for zero-discharge phosphatization and saponification using the system.

[0008] To achieve the above object, the invention employs the following technical solution:

a method for zero-discharge phosphatization and saponification based on a high-pressure closed circulation system comprises an autoclave, a separation kettle, a buffer kettle, a hydraulic pump and a recovery vat. The method comprises the following steps:

step 1: a workpiece is fed into the autoclave and then sealed such that the pressure range of the autoclave is above 20 MPa;

step 2: degreasing and derusting by CO₂: carbon dioxide is buffered by the buffer kettle and then delivered to the autoclave by the hydraulic pump, and then the workpiece is derusted and degreased by spraying a high-pressure carbon dioxide gas stream via a Venturi nozzle in the autoclave;

step 3: cyclic separation: supercritical CO₂ is delivered to the autoclave for cyclic cleaning by means of the buffer kettle and the hydraulic pump until the autoclave is clean, and oil stains and solid residues are pushed into the separation kettle by the supercritical CO₂;

step 4: high-pressure phosphatization: a phosphatizing solution is pressurized and injected into the autoclave by the hydraulic pump, and then mixed and diluted with high-pressure fluid in the autoclave under the action of a stirrer of the autoclave; the autoclave is warmed up to the reaction temperature to phosphatize the surface of the workpiece; the phosphatizing solution undergoes a chemical reaction on the surface of the workpiece to form a phosphatized film; and after the reaction is completed, the fluid in the autoclave is discharged to the separation kettle to separate and collect residues obtained after phosphatization;

step 5: cyclic separation II: supercritical CO₂ is delivered to the autoclave for cyclic cleaning by means of the buffer kettle and the hydraulic pump until the autoclave is clean;

step 6: high-pressure saponification: a saponifying solution is pressurized and injected into the autoclave by the hydraulic pump, and then mixed and diluted with high-pressure fluid in the autoclave under the action of the stirrer of the autoclave; the autoclave is warmed up to the reaction temperature to saponify the surface of the workpiece; the saponify-

ing solution undergoes a chemical reaction on the surface of the workpiece to form a saponified film; and after the reaction is completed, the fluid in the autoclave is discharged to the separation kettle to separate and collect residues obtained after saponification;

step 7: cyclic separation III: supercritical CO₂ is delivered to the autoclave for cyclic cleaning by means of the buffer kettle and the hydraulic pump until the autoclave is clean; and

step 8: drying: the autoclave is opened for aeration drying.

[0009] A further improvement is that the carbon dioxide separated from the separation kettle in the step 5 and the step 7 is refrigerated, pressurized and then introduced to the autoclave for cyclic washing.

[0010] Compared with the prior art, the invention has the following beneficial effects: after the technical solution of the present application is employed, the solubility of oil stains, phosphoric acid, phosphate and sodium stearate can be changed by adjusting the temperature and pressure changes to achieve the purpose of cyclic separation and collection, the amount of acids, bases and industrial water used is greatly reduced, the chemical solution flows in a closed pipeline without volatilization and leakage, no sewage and waste liquid are discharged to the environment, good working conditions are provided, and production residues can be conveniently collected and treated without environmental pollution.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011]

Fig. 1 is a functional block diagram showing the steps of a method for zero-discharge phosphatization and saponification based on a high-pressure closed circulation system; and

Fig. 2 is a functional block diagram of the system for the method for zero-discharge phosphatization and saponification based on a high-pressure closed circulation system.

DETAILED DESCRIPTION OF THE INVENTION

[0012] A preferred embodiment of the invention will be further described below with reference to the drawings.

[0013] As shown in Figs. 1 and 2, a method for zero-discharge phosphatization and saponification based on a high-pressure closed circulation system comprises an autoclave, a separation kettle, a buffer kettle, a hydraulic pump and a recovery vat. The method comprises the following steps:

step 1: a workpiece is fed into the autoclave and then sealed such that the pressure range of the autoclave is above 20 MPa;

step 2: degreasing and derusting by CO₂: carbon dioxide is buffered by the buffer kettle and then delivered to the autoclave by the hydraulic pump, and then the workpiece is derusted and degreased by spraying a high-pressure carbon dioxide gas stream via a Venturi nozzle in the autoclave; wherein, in this step, mainly the kinetic energy and momentum of the generated carbon dioxide "snow" (containing small particles of dry ice) are used for derusting, and the chemical dissolution action of the carbon dioxide "snow" is used for degreasing; and then supercritical carbon dioxide fluid is introduced, and the dissolution and scouring actions of the supercritical fluid allow oil stains and solid particles in the container to be discharged to the separation kettle for separation and collection;

step 3: cyclic separation: supercritical CO₂ is delivered to the autoclave for cyclic cleaning by means of the buffer kettle and the hydraulic pump until the autoclave is clean, and oil stains and solid residues are pushed into the separation kettle by the supercritical CO₂;

step 4: high-pressure phosphatization: a phosphatizing solution is pressurized and injected into the autoclave by the hydraulic pump, and then mixed and diluted with high-pressure fluid in the autoclave under the action of a stirrer of the autoclave; the autoclave is warmed up to the reaction temperature to phosphatize the surface of the workpiece; the phosphatizing solution undergoes a chemical reaction on the surface of the workpiece to form a phosphatized film; and after the reaction is completed, the fluid in the autoclave is discharged to the separation kettle to separate and collect residues obtained after phosphatization;

step 5: cyclic separation II: supercritical CO₂ is delivered to the autoclave for cyclic cleaning by means of the buffer kettle and the hydraulic pump until the autoclave is clean; and the carbon dioxide separated from the separation kettle is refrigerated, pressurized and then introduced to the autoclave for cyclic washing;

step 6: high-pressure saponification: a saponifying solution is pressurized and injected into the autoclave by the hydraulic pump, and then mixed and diluted with high-pressure fluid in the autoclave under the action of the stirrer of the autoclave; the autoclave is warmed up to the reaction temperature to saponify the surface of the workpiece; the saponifying solution undergoes a chemical reaction on the surface of the workpiece to form a saponified film; and after the reaction is completed, the fluid in the autoclave is discharged to the separation kettle to separate and collect residues obtained after saponification;

step 7: cyclic separation III: supercritical CO₂ is delivered to the autoclave for cyclic cleaning by means of the buffer kettle and the hydraulic pump until the

autoclave is clean; and the carbon dioxide separated from the separation kettle is refrigerated, pressurized and then introduced to the autoclave for cyclic washing; and

step 8: drying: the autoclave is opened for aeration drying.

Claims

1. A method for zero-discharge phosphatization and saponification based on a high-pressure closed circulation system, comprising an autoclave, a separation kettle, a buffer kettle, a hydraulic pump and a recovery vat; the method comprising the following steps:

step 1: a workpiece is fed into the autoclave and then sealed such that the pressure range of the autoclave is above 20 MPa;

step 2: degreasing and derusting by CO₂: carbon dioxide is buffered by the buffer kettle and then delivered to the autoclave by the hydraulic pump, and then the workpiece is derusted and degreased by spraying a high-pressure carbon dioxide gas stream via a Venturi nozzle in the autoclave;

step 3: cyclic separation: supercritical CO₂ is delivered to the autoclave for cyclic cleaning by means of the buffer kettle and the hydraulic pump until the autoclave is clean, and oil stains and solid residues are pushed into the separation kettle by the supercritical CO₂;

step 4: high-pressure phosphatization: a phosphatizing solution is pressurized and injected into the autoclave by the hydraulic pump, and then mixed and diluted with high-pressure fluid in the autoclave under the action of a stirrer of the autoclave; the autoclave is warmed up to the reaction temperature to phosphatize the surface of the workpiece; the phosphatizing solution undergoes a chemical reaction on the surface of the workpiece to form a phosphatized film; and after the reaction is completed, the fluid in the autoclave is discharged to the separation kettle to separate and collect residues obtained after phosphatization;

step 5: cyclic separation II: supercritical CO₂ is delivered to the autoclave for cyclic cleaning by means of the buffer kettle and the hydraulic pump until the autoclave is clean;

step 6: high-pressure saponification: a saponifying solution is pressurized and injected into the autoclave by the hydraulic pump, and then mixed and diluted with high-pressure fluid in the autoclave under the action of the stirrer of the autoclave; the autoclave is warmed up to the reaction temperature to saponify the surface of

the workpiece; the saponifying solution undergoes a chemical reaction on the surface of the workpiece to form a saponified film; and after the reaction is completed, the fluid in the autoclave is discharged to the separation kettle to separate and collect residues obtained after saponification;

step 7: cyclic separation III: supercritical CO₂ is delivered to the autoclave for cyclic cleaning by means of the buffer kettle and the hydraulic pump until the autoclave is clean; and

step 8: drying: the autoclave is opened for aeration drying.

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2. The method for zero-discharge phosphatization and saponification based on a high-pressure closed circulation system according to claim 1, wherein the carbon dioxide separated from the separation kettle in the step 5 and the step 7 is refrigerated, pressurized and then introduced to the autoclave for cyclic washing.

Patentansprüche

1. Verfahren zur entladungsfreien Phosphatierung und Verseifung auf der Basis eines geschlossenen Hochdruck-Kreislaufsystems, das einen Autoklaven, einen Trennkessel, einen Pufferkessel, eine Hydraulikpumpe und einen Rückgewinnungsbehälter umfasst; wobei das Verfahren die folgenden Schritte umfasst:

Schritt 1: ein Werkstück wird in den Autoklaven eingeführt und dann so verschlossen, dass der Druckbereich des Autoklaven über 20 MPa liegt; Schritt 2: Entfetten und Entrosten durch CO₂: Kohlendioxid wird durch den Pufferkessel gepuffert und dann durch die Hydraulikpumpe in den Autoklaven gefördert, und dann wird das Werkstück entrostet und entfettet, indem ein Hochdruck-Kohlendioxid-Gasstrom über eine Venturi-Düse in den Autoklaven gesprüht wird; Schritt 3: zyklische Trennung: Überkritisches CO₂ wird zur zyklischen Reinigung über den Pufferkessel und die Hydraulikpumpe in den Autoklaven gefördert, bis der Autoklav sauber ist und Ölflecken und feste Rückstände durch das überkritische CO₂ in den Trennkessel gedrückt werden;

Schritt 4: Hochdruck-Phosphatierung: eine Phosphatierlösung wird unter Druck gesetzt und durch die Hydraulikpumpe in den Autoklaven eingespritzt, und dann mit Hochdruckflüssigkeit im Autoklaven unter der Wirkung eines Rührers des Autoklaven gemischt und verdünnt; der Autoklav wird auf die Reaktionstemperatur erwärmt, um die Oberfläche des Werkstücks zu

phosphatieren; die Phosphatierlösung durchläuft eine chemische Reaktion auf der Oberfläche des Werkstücks, um einen phosphatierten Film zu bilden; und nach Beendigung der Reaktion wird die Flüssigkeit im Autoklaven in den Trennkessel abgelassen, um die nach der Phosphatierung erhaltenen Rückstände zu trennen und zu sammeln;

Schritt 5: zyklische Trennung II: überkritisches CO₂ wird dem Autoklaven zur zyklischen Reinigung mittels des Pufferkessels und der Hydraulikpumpe zugeführt, bis der Autoklav sauber ist;

Schritt 6: Hochdruck-Verseifung: eine Verseifungslösung wird unter Druck gesetzt und durch die Hydraulikpumpe in den Autoklaven eingespritzt und dann im Autoklaven unter der Wirkung des Rührers des Autoklaven mit Hochdruckflüssigkeit gemischt und verdünnt; der Autoklav wird auf die Reaktionstemperatur erwärmt, um die Oberfläche des Werkstücks zu verseifen; die Verseifungslösung durchläuft eine chemische Reaktion auf der Oberfläche des Werkstücks, um einen verseiften Film zu bilden; und nachdem die Reaktion abgeschlossen ist, wird die Flüssigkeit im Autoklaven in den Trennkessel abgelassen, um die nach der Verseifung erhaltenen Rückstände abzutrennen und zu sammeln;

Schritt 7: zyklische Trennung III: überkritisches CO₂ wird dem Autoklaven zur zyklischen Reinigung mittels des Pufferkessels und der Hydraulikpumpe zugeführt, bis der Autoklav sauber ist; und

Schritt 8: Trocknung: der Autoklav wird zur Belüftungstrocknung geöffnet.

2. Verfahren zur entladungsfreien Phosphatierung und Verseifung auf der Basis eines geschlossenen Hochdruck-Kreislaufsystems nach Anspruch 1, wobei das im Schritt 5 und im Schritt 7 aus dem Trennkessel getrennt Kohlendioxid gekühlt, unter Druck gesetzt und dann dem Autoklaven zum zyklischen Waschen zugeführt wird.

Revendications

1. Procédé de phosphatation et de saponification à décharge nulle basé sur un système à circulation fermée haute pression, comprenant un autoclave, un récipient de séparation, un récipient tampon, une pompe hydraulique et une cuve de récupération, le procédé comprenant les étapes suivantes :

étape 1 : une pièce est introduite dans l'autoclave, puis scellée de telle sorte que la plage de pression de l'autoclave est au-dessus de 20 MPa ;

étape 2 : dégraissage et décapage par CO₂ : le dioxyde de carbone est tamponné par le récipient tampon, puis adressé à l'autoclave par la pompe hydraulique, puis la pièce est décapée et dégraissée par pulvérisation d'un courant de dioxyde de carbone gazeux haute pression par l'intermédiaire d'une buse Venturi dans l'autoclave ;

étape 3 : séparation cyclique : du CO₂ supercritique est adressé à l'autoclave pour un nettoyage cyclique au moyen du récipient tampon et de la pompe hydraulique jusqu'à ce que l'autoclave soit propre, et des taches d'huile et des résidus solides sont poussés dans le récipient de séparation par le CO₂ supercritique ;

étape 4 : phosphatation haute pression : une solution de phosphatation est mise sous pression et injectée dans l'autoclave par la pompe hydraulique, puis mélangée et diluée avec un fluide haute pression dans l'autoclave sous l'action d'un agitateur de l'autoclave ; l'autoclave est chauffé jusqu'à la température de réaction pour phosphater la surface de la pièce ; la solution de phosphatation subit une réaction chimique sur la surface de la pièce pour former un film phosphaté ; et, après la fin de la réaction, le fluide dans l'autoclave est déchargé dans le récipient de séparation pour séparer et collecter des résidus obtenus après phosphatation ;

étape 5 : séparation cyclique II : du CO₂ supercritique est adressé à l'autoclave pour un nettoyage cyclique au moyen du récipient tampon et de la pompe hydraulique jusqu'à ce que l'autoclave soit propre ;

étape 6 : saponification haute pression : une solution de saponification est mise sous pression et injectée dans l'autoclave par la pompe hydraulique, puis mélangée et diluée avec du fluide haute pression dans l'autoclave sous l'action de l'agitateur de l'autoclave ; l'autoclave est chauffé jusqu'à la température de réaction pour saponifier la surface de la pièce ; la solution de saponification subit une réaction chimique sur la surface de la pièce pour former un film saponifié ; et, après la fin de la réaction, le fluide dans l'autoclave est déchargé dans le récipient de séparation pour séparer et collecter des résidus obtenus après saponification ;

étape 7 : séparation cyclique III : du CO₂ supercritique est adressé à l'autoclave pour un nettoyage cyclique au moyen du récipient tampon et de la pompe hydraulique jusqu'à ce que l'autoclave soit propre ; et

étape 8 : séchage : l'autoclave est ouvert pour un séchage par aération.

2. Procédé de phosphatation et de saponification à décharge nulle basé sur un système à circulation fer-

mée haute pression selon la revendication 1, dans lequel le dioxyde de carbone séparé du récipient de séparation dans l'étape 5 et l'étape 7 est réfrigéré, mis sous pression, puis introduit dans l'autoclave pour un lavage cyclique.

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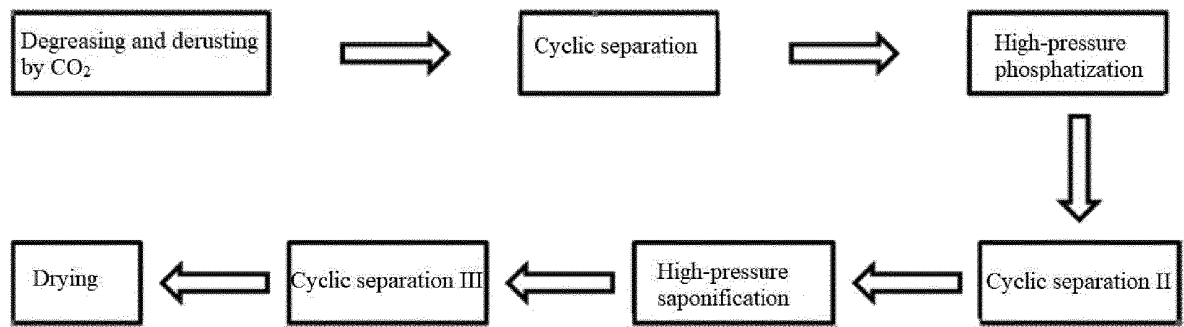


Fig. 1

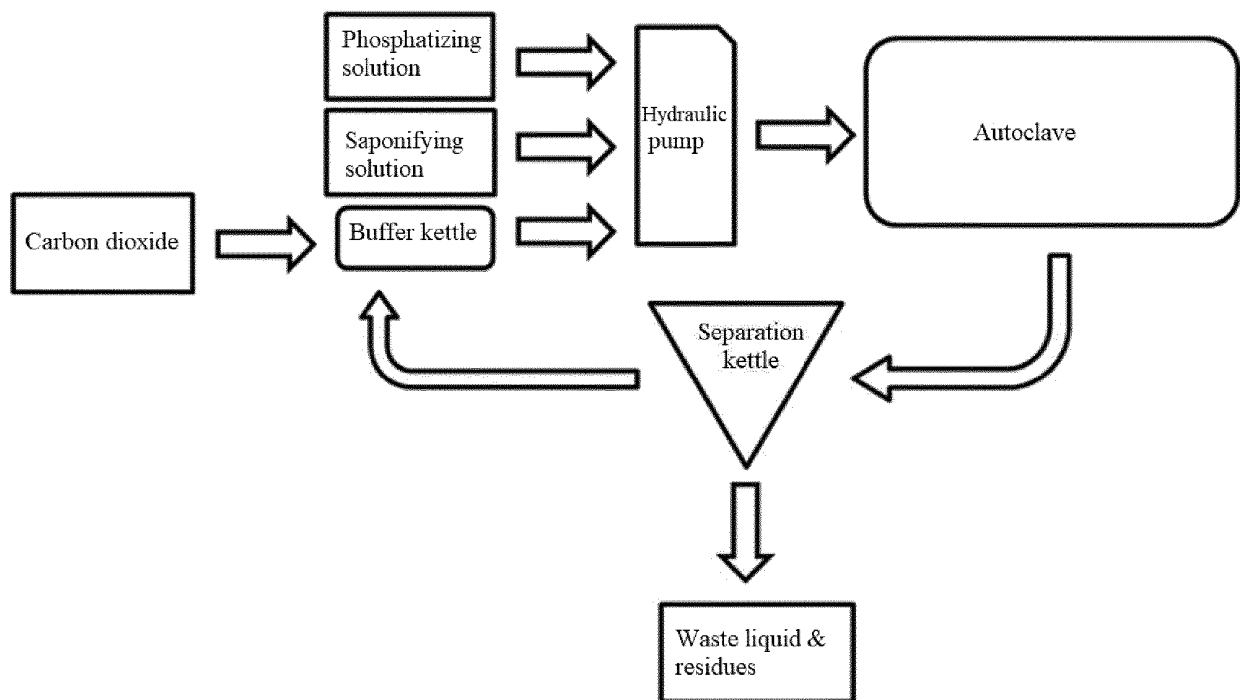


Fig. 2

REFERENCES CITED IN THE DESCRIPTION

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