

DESCRIPTION

Title: METHOD FOR TREATING WASTE WATERS AND RESIDUE SLUDGE BY MEANS OF DECARBONATION IN A CHEMICAL INSTALLATION FOR NITRIDATION IN A MOLTEN SALT BATH

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Technical field of the invention

The present invention relates to a method for treating waste waters, and residue sludge from the oxidation bath, to recover oxidation salts, carbonate salts and water,
10 in a chemical installation for nitridation in a molten salt bath.

Prior art

In automotive, aeronautical, or industrial applications, the mechanical parts are generally subjected to significant stresses in operation.

15 Conventionally, the mechanical parts can receive treatments of a physico-chemical nature, making it possible to improve some of their properties, among which appear, in particular, friction properties, resistance to wear, resistance to fatigue, resistance to seizing, or also resistance to corrosion.

A treatment known from the prior art is nitridation. Nitridation consists of
20 immersing a ferrous metal part in a medium which is able to transfer nitrogen, which can be, in particular, a molten salt bath. In the present text, nitridation also includes nitrocarburising, which is a variant of nitridation, in which carbon diffuses in the part in addition to nitrogen. The ARCOR® method, designed and implemented by the Applicant, is a preferred example of the nitridation method.

25 In reference to figure 1 which represents an installation for nitridation according to the prior art, such an installation 1 comprises several successive baths, among which, from upstream to downstream, a nitridation bath 2, an oxidation bath 3, and a stop bath 4, also called “water stop bath”. Upstream of the nitridation bath, a degreasing bath 5, or one or more washing baths 6, and a drying device 7 such as an oven are

usually provided. Downstream of the stop bath 4, one or more washing baths 8, and a device 9 for drying parts are usually provided.

The mechanical parts are first degreased, washed, and heating by successively passing into the degreasing bath 5, into the washing baths 6, and into the drying
5 device 7, respectively. The parts are then immersed in the nitridation bath 2, which is a molten salt bath, containing, among others, carbonates. As needed, adding regeneration salts will lead to the transformation of carbonates into cyanates, which are reactive species. Nitrogen (and optionally carbon) diffuses in the parts and precipitates in the form of nitrides, which leads to the formation of a combination
10 layer mainly comprising iron nitrides (or other alloy elements), and an underlying diffusion zone, in which nitrogen is present between the iron atoms (solid solution) or nitrogen reacts with the alloy elements contained in steel to form nitrides.

The combined effect of the combination layer and the diffusion layer makes it possible to obtain a nitrided part having good friction properties, as well as an
15 excellent resistance to wear.

After nitridation, the parts are immersed in the oxidation bath 3 comprising oxidising salts, typically hydroxides and/or nitrates, to improve their resistance to corrosion and give them a uniform black appearance.

After oxidation, the parts are immersed in the stop bath 4 which contains cold water,
20 which stops oxidation, then are cleaned by several successive washes in the washing baths 8, before being dried in the drying device 9, then discharged.

For certain treatments, the oxidation step is not required, the parts are transferred from the nitridation bath directly to a dedicated stop bath. The waters from this stop bath are nitridation salt-enriched (and no longer in oxidation salts).

25 Although nitridation is an effective method for improving the properties of the mechanical parts, it has the disadvantage of generating liquid and solid waste (sometimes called effluents), and requires water. This represents a significant

ecological impact, and can cause relatively high production costs, in particular due to the treatment of waste described below.

During an ARCOR treatment, nitridation salts are entrained by the parts and pollute the oxidation bath, then salts from the oxidation bath are entrained and transferred
5 into the stop bath. Secondary chemical reactions also create sludge/waste even in treatment baths (nitridation and oxidation).

It is also possible that the line is used alternatively with or without oxidation and that the stop bath thus alternatively serves as a stop bath for nitridation then for oxidation. Nitridation salts and oxidation salts are thus alternatively transferred into
10 the same stop bath.

This waste is represented in figure 1. These are solid effluents B, but also liquid effluents E.

The solid effluents B are called “residue sludge”. They are mainly collected in the oxidation bath 3 and in the nitridation bath 2 (after performing the method), and are
15 generally sent into salt mines to be treated and stored there. They contain insoluble species and salt. For the two types of salts (nitridation salt and oxidation salt), metals and metal oxides coming from the parts to be treated (iron and alloy metals) constitute insolubles. For the oxidation salt, carbonates constitute a large portion of insolubles. Residue sludge is physically removed during regular maintenance
20 operations.

The liquid effluents E are called “waste waters”. They are collected at the outlet of the stop bath 4, and are generally sent into purification stations or managed by companies specialising in waste treatment.

In addition, the purchase costs of raw materials are themselves also relatively high,
25 it is therefore interesting to optimise their consumption.

Brief description of the invention

Faced with this situation, the Applicant has therefore sought a solution to reduce the environmental impact and to control the costs associated with nitridation methods.

The Applicant has quite specifically focused their research on reducing waste, and limiting waste for both renewable resources such as water, and non-renewable
5 resources, such as raw materials used in nitridation and oxidation baths, i.e. nitridation and oxidation salts.

The Applicant has arrived at developing a treatment method which makes it possible to overcome all of the abovementioned disadvantages, and this, without modifying the architecture of the nitridation chains, therefore being able to be implemented on
10 current lines.

To this end, the invention proposes a method for treating waste waters (E), and/or residue sludge (B) from the oxidation bath, to recover oxidation salts and carbonates, in at least one installation for nitridation in a molten salt bath comprising a nitridation bath, an oxidation bath, and a stop bath,
15 the treatment method comprising: the following steps:

- decarbonation of waste waters and/or residue sludge by precipitation of carbonate ions CO_3^{2-} ,
- separation of a liquid phase containing oxidation salts and of a solid phase containing a carbonate precipitate,
- 20 - recovery, on the one hand, of oxidation salts and, on the other hand, of carbonates.

According to the treatment method of the invention, the waste waters at the outlet of the stop bath and the residue sludge from the oxidation bath are treated in order to separately recover the oxidation salts, carbonates and water. Advantageously, the
25 recovered water can supply the stop bath and/or the washing baths when a water recycling step as described below is carried out.

Carbonate ions CO_3^{2-} come from the entrainment of the salts from the nitridation salts and are formed in the reaction medium. They constitute a “contaminating”

species for the oxidation bath. The decarbonation step aims to remove the carbonate ions by precipitation, in order to be able to isolate the oxidising species (nitrates and/or hydroxides) necessary for the correct operation of the oxidation bath.

The removing of carbonate ions is advantageously used to produce enhanceable
5 carbonates. This enhancement contributes to reducing the cost of nitridation in a salt bath. At the same time, it reduces the ecological impact.

After solid/liquid separation, the oxidation salts are recovered. The latter can thus be reinjected into the oxidation bath or be re-enhanced, and water is advantageously reinjected into the stop bath and/or the washing/rinsing baths.

10 In doing so, the oxidation and waste effluents supply the oxidation bath and advantageously, the different water tanks, in particular, the washing baths and/or the stop bath.

The re-enhancement of the oxidation salts and the carbonat salts, and if necessary, their recycling, drastically reduces the environmental impact of the industrial
15 nitridation method, by reducing solid and liquid waste, while reusing the latter, in order to supply the method, due to this reducing the quantities and the costs of raw materials, which are oxidising salts.

The method of the invention therefore offers a double ecological and economic advantage.

20 It is specified that the parts can only undergo one nitridation, without oxidation, in which case the stop bath serves to stop the nitridation reaction. The method of the invention does not apply to a single nitridation line, without oxidation bath, as in this case, the recovery of carbonates can be done by simply filtering the waste waters.

25 The nitridation installation can comprise several nitridation baths and/or several oxidation baths and/or several stop baths.

The nitridation installation is used in the present text in its more general acceptance. The different baths that it comprises, can in practice, be installed in a same location or in different locations. For example, the decarbonation of waste waters and/or waste sludge can be carried out with a first chemical installation in a first place, and
 5 the separation of the liquid phase and the solid phase can be carried out with a second chemical installation in a second place different from the first. In addition, a same place may comprise several nitridation installations, i.e. several nitridation lines.

The decarbonation step can, in particular, be carried out, in several ways:

- decarbonation of only waste waters, or
- 10 - decarbonation of residue sludge, previously leached in water, or more generally, in an aqueous solution, for example, mains water, or industrial water, or more generally, in an aqueous solution, or
- decarbonation of residue sludge, previously leached in the waste waters.

According to other aspects, the treatment method according to the invention has the
 15 following different features taken individually or according to their technically possible combinations:

- decarbonation is done by reaction between the carbonate ions CO_3^{2-} and the monovalent or divalent cations chosen from among: calcium ions Ca^{2+} (CaCO_3 precipitate), lithium Li^+ (Li_2CaO_3 precipitate), barium Ba^{2+} (BaCO_3 precipitate),
 20 magnesium Mg^{2+} (MgCO_3 precipitate), iron (II) Fe^{2+} (FeCO_3 precipitate), copper Cu^{2+} (CuCO_3 precipitate), manganese Mn^{2+} (MnCO_3 precipitate), cobalt Co^{2+} (CoCO_3 precipitate), or their mixtures. Poorly soluble species capable of precipitating in solution are targeted;
- decarbonation is done with hydroxides and/or alkaline and/or alkaline earth
 25 metal nitrates, in order to form carbonates of these alkaline and/or alkaline earth metals;
- decarbonation is done with lime Ca(OH)_2 and/or calcium nitrate $\text{Ca(NO}_3)_2$, to form calcium carbonate CaCO_3 , according to either of following respective reactions (1) and (2):

[Chem. 1]



[Chem. 2]



- 5 Choosing the decarbonation reaction makes it possible to select the carbonate that is sought to be produced (according to the cation used) for enhancement and/or recycling. It is thus possible to adapt the method to the carbonate demand.
- the method further comprises, before the decarbonation step, a step of leaching
10 the residue sludge by adding water;
 - leaching residue sludge is done at least partially with waste waters;
 - the method further comprises, before the decarbonation step, a step of separating metal particles or metal oxides present in the waste waters and/or the residue sludge, for example, by filtration. This makes it possible to optimise the
15 purity of the carbonate precipitate with a view to its re-enhancement;
 - the step of separating the liquid phase containing the oxidation salts and the solid phase is carried out by decantation then filtration;
 - the method further comprises, after the step of separating the liquid phase and the solid phase, a step of separating water and oxidation salts in the liquid phase,
20 to recover the oxidation salts in solid form;
 - the step of separating water and oxidation salts in the liquid phase is done by drying the liquid phase, for example, in a vacuum evaporator;
 - the method further comprises, after separating water and oxidation salts, a step of recycling water to the stop bath and/or at least one washing bath;
 - 25 - the method further comprises, after the step of separating the liquid phase and the solid phase, a step of reinjecting oxidation salts into the oxidation bath. Preferably, when a separation of water and oxidation salts in the liquid phase to recover the oxidation salts in solid form is done, the step of reinjecting oxidation salts is done after the latter;

- the nitridation bath comprises cyanate ions CNO^- and carbonate ions CO_3^{2-} ;
 - the nitridation bath further comprises alkaline ions, preferably lithium ions Li^+ , and/or potassium ions K^+ , and/or sodium ions Na^+ ;
 - the oxidation bath comprises hydroxide ions OH^- and/or nitrate ions NO_3^- , and
- 5 optionally carbonate ions.

Description of the figures

Other advantages and features of the invention will appear upon reading the following description given as a non-limiting, illustrative example, in reference to

10 the following accompanying figures:

[Fig. 1] Figure 1 is a diagram which illustrates an industrial installation for nitridation in a molten salt bath according to the prior art.

[Fig. 2] Figure 2 is a diagram which illustrates an industrial installation for nitridation in a molten salt bath according to the invention, in which only nitridation,

15 oxidation, and stop baths are represented.

[Fig. 3] Figure 3 is a diagram which illustrates, in detail, the reaction of decarbonation of residue sludge and/or waste waters, according to an embodiment.

Detailed description of embodiments of the invention

20 The method of the invention will now be described in detail in reference to figure 2, which is a simplified representation of a installation 10 for nitridation in a molten salt bath, in that only the main elements of the installation are preserved, namely a nitridation bath 11, and oxidation bath 12, and a stop bath 13, with the aim of simplifying the present text.

25 The mechanical parts to be treated, previously degreased, then rinsed and dried in an oven, are immersed in the nitridation bath 11. The nitridation bath 11 is composed of molten nitridation salts which are brought to a temperature which is typically between 500°C and 630°C.

Nitridation aims to give the parts a greater hardness, and to improve their mechanical properties, in particular resistance to seizing and to wear, by diffusion of nitrogen, and optionally carbon in steel, in the case of a nitrocarburising.

The nitridation bath 11 mainly comprises cyanate ions CNO^- and carbonate ions CO_3^{2-} . Regeneration salts are added if needed in the nitridation bath to rapidly convert the carbonate ions CO_3^{2-} into cyanate ions CNO^- .

The nitridation bath 11 further comprises alkaline ions, preferably lithium ions Li^+ , and/or potassium ions K^+ , and/or sodium ions Na^+ .

After the nitridation step, the mechanical parts are immersed in the oxidation bath 12. The oxidation bath 12 is composed of molten oxidising salts brought to a temperature typically of around 450°C . The oxidation salts are composed among others of hydroxides.

Oxidation aims to improve resistance to corrosion of parts, and to give them a uniform black appearance.

After the oxidation step, the parts are immersed in the stop bath 13, which contains cold water (waste water), then are cleaned in washing baths, preferably successive cascading washes, before being dried in an oven, then discharged.

As can be seen in figure 2, the oxidation of parts generates sludge that is extracted by degreasing the bath, leading to the formation of residue sludge B, and the stopping water generate waste waters E, which respectively constitute solid and liquid waste that the method of the invention makes it possible to recycle.

The recovery of oxidation salts is based on the decarbonation of residue sludge and/or waste waters by precipitation of carbonate ions CO_3^{2-} .

In the preferred embodiment shown in figures 2 and 3, decarbonation is done by precipitation of carbonate ions CO_3^{2-} of residue sludge E and/or of waste waters B with lime $\text{Ca}(\text{OH})_2$ and/or calcium nitrate $\text{Ca}(\text{NO}_3)_2$, to form calcium carbonate

CaCO₃. For example, calcium carbonate may be enhanced as a base material for building materials.

Carbonate ions CO₃²⁻ react with lime Ca(OH)₂ according to the following equation (1):

5 [Chem. 1]



Thus, hydroxide ions and calcium carbonate are obtained.

Carbonate ions CO₃²⁻ react with calcium nitrate Ca(NO₃)₂ according to the following equation (2):

10 [Chem. 2]



In this case, nitrate ions and calcium carbonate are obtained.

When lime Ca(OH)₂ and/or calcium nitrate Ca(NO₃)₂ are both added into the reaction medium, the reactions (1) and (2) both occur. Carbonate ions CO₃²⁻ react
15 therefore both with lime Ca(OH)₂ and calcium nitrate Ca(NO₃)₂.

When only lime Ca(OH)₂ is added into the reaction medium, only the reaction (1) occurs. When only calcium nitrate Ca(NO₃)₂ is added into the reaction medium, only the reaction (2) occurs.

After a decantation phase, the liquid phase containing oxidation salts 23 and the
20 solid phase containing calcium carbonate precipitate CaCO₃ are separated. Preferably, the separation is done by filtration, for example on a filter press.

In the liquid phase, water and oxidation salts 23 are then separated, preferably by drying, in order to obtain oxidation salts 23 in solid form.

The oxidation salts 23 in solid form can be preserved to be enhanced, or can be
25 reinjected into the oxidation bath.

The decarbonation is illustrated in more detail in figure 3.

In this figure, the residue sludge B is put into a solution under stirring in a leaching step. A leaching solution 14 is obtained.

It is specified that the leaching solution 14 can be prepared by solvation of only
5 residue sludge B, by adding water, or by solvation of residue sludge B with waste waters E.

According to a preferred embodiment of the invention, the leaching solution 14 is formed by solvation of residue sludge B by waste waters E. This embodiment is particularly advantageous in that it makes it possible to recycle waste waters E while
10 using the latter as a solvent to solvate the residue sludge B, which makes it possible to reduce water consumption.

According to an embodiment, this solution passes, before decarbonation, a first filtration step in order to remove the metal particles and metal oxides.

The leaching solution 14 is transferred into a reactor 15, supplied with lime $\text{Ca}(\text{OH})_2$
15 and/or calcium nitrate $\text{Ca}(\text{NO}_3)_2$, and stirred.

A calcium carbonate CaCO_3 precipitate is formed in a solution. The mixture is thus composed of a solid phase, calcium carbonate precipitate CaCO_3 , and a liquid phase containing oxidation salts.

After decantation, a solid/liquid separation of the settled solids 16, preferably by
20 filtration of the mixture as figure 3 illustrates using a filtration device 17.

The residue 18 comprising calcium carbonate precipitate CaCO_3 is put aside, and can be subsequently enhanced. The filtrate 19 is preferably reinjected into the reactor in order to maximise the yield of the decarbonation.

The supernatant 20 of the reactor is thus transferred into a drying device 21, such as
25 an oven, for example.

Preferably, the drying condensates 22 are reinjected into the leaching solution 14, or in the stop bath, or in the washing baths, in order to reduce water consumption.

Drying makes it possible to obtain recycled oxidation salts 23, which are thus preserved or reinjected into the oxidation bath.

- 5 The method according to the invention thus makes it possible, not only to reduce nitridation and oxidation waste, but also to reload the oxidation bath with oxidation salts, which is conveyed by an economic and ecological recycling, in line with the current environmental standards and technicalities.

CLAIMS

1. Method for treating waste waters (E), or residue sludge (B) from the oxidation bath or waste waters and residue sludge from the oxidation bath, including oxidation salts, such as hydroxides and/or nitrates, and carbonate salts to recover said salts, in at least one installation (10) for nitridation in a molten salt bath comprising a nitridation bath (11), an oxidation bath (12), and a stop bath (13),
the treatment method comprising the following steps:
 10 - decarbonation of waste waters (E) and/or residue sludge (B) by precipitation of carbonate ions CO_3^{2-} , said decarbonation is done by reaction between the carbonate ions CO_3^{2-} and the monovalent or divalent cations chosen from among: lithium Li^+ (Li_2CaO_3 precipitate), iron (II) Fe^{2+} (FeCO_3 precipitate), copper Cu^{2+} (CuCO_3 precipitate), manganese Mn^{2+} (MnCO_3 precipitate), cobalt Co^{2+} (CoCO_3 precipitate), or their mixtures, or
 15 by reaction with hydroxides and/or alkaline and/or alkaline earth metal nitrates, in order to form carbonates of these alkaline and/or alkaline earth metals;
 - separation of a liquid phase containing oxidation salts (23) and of a solid phase containing a carbonate precipitate,
 20 - recovery, on the one hand, of oxidation salts of the liquid phase and, on the other hand, of carbonates in a precipitate form.

2. Method according to claim 1, wherein decarbonation is done with lime $\text{Ca}(\text{OH})_2$ and/or calcium nitrate $\text{Ca}(\text{NO}_3)_2$, to form calcium carbonate CaCO_3 , according to either of following respective reactions (1) and (2):
 25 [Chem. 1]



[Chem. 2]



3. Method according to any one of the preceding claims, further comprising, before the precipitation step, a step of leaching the residue sludge (B), the precipitation being done in the leaching solution (14).
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4. Method according to claim 3, wherein the leaching of the residue sludge (B) is done with the waste waters (E).
- 10 5. Method according to any one of the preceding claims, further comprising, before the decarbonation step, a step of separating metal particles or metal oxides present in the waste waters (E) and/or the residue sludge (B).
- 15 6. Method according to any one of the preceding claims, further comprising, after the step of separating the liquid phase and the solid phase, a step of separating water and oxidation salts (23) in the liquid phase, to recover the oxidation salts in solid form.
- 20 7. Method according to claim 6, further comprising, after separating water and oxidation salts (23), a step of recycling water to the stop bath (13) and/or at least one washing bath (6, 8).
- 25 8. Method according to any one of the preceding claims, further comprising, after the step of separating the liquid phase and the solid phase, a step of reinjecting oxidation salts (23) into the oxidation bath (12).