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# SOLUTION AND PROCESS FOR PRODUCING A PHOSPHATE COATING ON A METAL BODY

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The present invention relates to a process for producing phosphate coatings on surfaces of iron, steel, zinc or the alloys thereof by contacting said surfaces with a solution containing ions of zinc, alkali metals, phosphate, nitrate, nitrite and eventually alkaline earth metals, the portion of nitrate ions being at least as great as that of phosphate ions. The present invention furthermore relates to a composition of matter for preparing and replenishing the phosphatization solutions used. The phosphatization solutions used must contain the components $PO_4$, Zn and $NO_3$ in a very definite proportion, must have a limited content of total acid and a definite nitrite content must be maintained in order to suppress as far as possible the formation of free acid in the solution.

According to a preferred embodiment of the invention, the thickness of the phosphate coatings can be regulated by adding to the phosphatization solutions citric acid or tartaric acid or the corresponding salts.

It is already known to produce phosphate coatings on surfaces of iron, steel, zinc or the alloys thereof with the use of acid solutions of zinc phosphate which contain as accelerator a combination of nitrate and nitrite. In the said solutions the $NO_3$ content should be greater than the $P_2O_5$ content. Solutions of this type have, however, the drawback that owing to their low pH value, i.e. the amount of free acid present, the nitrite contained in the solutions decomposes very rapidly, thus loses its activity and evolves unhealthy nitrous gases from the solution.

The process of the invention for producing phosphate layers on surfaces of iron, steel, zinc or the alloys thereof avoids the disadvantages of the known processes, especially the undesired nitrite decomposition. The phosphatization solutions used contain zinc, alkali metal, phosphate, ntirate, nitrite and, if desired, alkaline earth metal ions, the portion of nitrate ions being at least as great as that of phosphate ions. According to the invention the metal surfaces are treated with the solutions at about 20° C. to about 45° C., preferably 35° C. to 40° C. In the solutions there is maintained a proportion of

$$PO_4:Zn:NO_3$$

of 1:(0.8 to 1.7):(1:5 to 3.2) and a total acid point number of about 8 to 14. The formation of free acid in the solution is suppressed by maintaining a nitrite content of about 0.1 to about 1 gram per liter of solution.

By "total acid point number" there is to be understood the amount of N/10 NaOH in cc. consumed in the titration of 10 cc. of the slurry-free solution (after it has been diluted with about 2 times the amount of water) with phenolphthalein as indicator. The acid point number is the measure for the total phosphoric acid present in the solution. Correspondingly, by "free acid" there is to be understood the amount of N/10 NaOH in cc. consumed in the titration of 10 cc. of solution with bromophenol blue as indicator. It indicates the amount of free acid present in the solution.

The present invention is based on the surprising observation that by maintaining the aforesaid conditions, the solutions practically do not contain free acid, they have a pH value in the range of about 3.5 to about 4.1 (determined with pH paper), the minor formation of free acid



in the solution can be substantially avoided during the treatment by the addition of nitrite and thus the undesired nitrite decomposition can be completely suppressed.

It has also been found that the thickness of the phosphate coatings can be adjusted or controlled by the addition of small amounts of citric acid or citrates and/or tartaric acid or tartrates to the phosphatization solutions.

When about 0.2 to 2 grams per liter of citric acid and/or 0.04 to 0.4 gram per liter of tartaric acid or the equivalent amounts of the salts of these acids are added to the solutions the thickness of the applied phosphate coatings can be adjusted, according to the requirement in each case, to about 2$\mu$ or less than 0.5$\mu$, the values obtained being extremely well reproducible. When the aforesaid acids are added in an amount near the lower limit of the indicated range a thickness of the coating of about 2$\mu$ is obtained, while an addition near the upper limit yields coatings having a thickness of 0.5$\mu$ and less, which coatings have a very fine grain structure. This fact offers all advantages of fine-grained phosphate layers, especially an excellent lacquer adhesion in the elastic or plastic shaping.

Solutions which have a content of free acid of about 0.5 point no longer give a satisfactory result. In order to obtain satisfactory phosphate coatings, care must, therefore, be taken that the formation of free acid in the solutions is substantially suppressed. In practice the solutions should contain at most an amount of free acid as corresponds to 0.3 point. The additions of citric acid or tartaric acid for regulating the thickness of the coatings are not prejudicial to the steps taken for suppressing the formation of free acid in the solution. When they are present in the solutions, unobjectionable results can still be obtained with a content of free acid up to 0.4 point. That means the acids may be added not only in the form of their salts but also in the form of the acids themselves.

Still further, it has been found that the addition of citric acid and/or tartaric acid or the salts thereof enables the periods of treatment to be reduced. Tests have revealed, for example, that with a solution containing per liter about 0.5 gram of citric acid the period of treatment in the immersion process could be reduced from 60 seconds to 45 seconds.

The narrow range of the proportion $PO_4:Zn:NO_3$ is critical because too high a content of primary zinc phosphate in the solution would lead to the formation of free acid by hydrolysis.

It is advantageous to add to the solutions a weakly foaming emulsifier, for example hydroxyethylated tall oil fatty acid, whereby the metal articles to be treated are simultaneously degreased and phosphatized. Thus, the metal articles can be treated in one operation.

In addition to the usual advantage of an acceleration with nitrate/nitrite, the process of the invention offers the further advantages that nitrite need not be added continuously since a decomposition of the nitrite is substantially avoided when the aforesaid conditions are maintained and, if necessary, the nitrite may be contained in a solid or concentrated dissolved starting product which does not contain free acid capable of decomposing the nitrite. It is known that in phosphatization processes using nitrite this component must be added continuously, but not in concentrated form because this would involve a spontaneous decomposition of the nitrite.

The phosphate coatings produced by the process of the invention provide a very good protection against corrosion on metal surfaces; they are well suitable as adhesive base for lacquers and for preparing the metal articles for cold working. The metal articles can be treated by the immersion process or by the spraying process, the latter being especially suitable for preparing metal parts,

such as wires and bands of iron or steel, for cold-working because it simplifies the operation.

It is a further advantage of the process of the invention that for preparing and replenishing the treatment solutions solid products or concentrated aqueous solutions can be used.

The composition of matter for preparing and replenishing the treatment solutions is suitably composed of primary or secondary phosphates or nitrates which may contain crystal water.

If different compositions of matter are used for preparing and replenishing the solutions, in the replenishing composition the proportion $PO_4$:Zn:$NO_3$ is suitably 1:(0.6–0.8):(0.6–1.5).

In most cases, however, it is more advantageous to use the same composition of matter for preparing and replenishing the treatment solution. It is then necessary that the composition of matter contain $PO_4$, Zn and $NO_3$ in a proportion of 1:(0.6–1.7):(0.8–3.2) and, if desired, the required amount of nitrite. In the preparation of the solution a starting salt is then added in order to adjust the required concentration of the individual components, which starting salt has such a composition that the required proportion is present from the beginning.

When citric acid or tartaric acid or the salts thereof are added in accordance with the invention the composition of the replenishing agent with respect to the proportion of $PO_4$ to Zn is not restricted to the narrow limit defined above. In this case the said limit of 1:(0.6–0.8) can be enlarged to about 1:(0.3–0.8), without any detrimental effect being observed.

The composition of matter in solid or concentrated aqueous form for preparing and replenishing the solutions used for treating metal parts according to the invention is characterized by a content of about 15–40% of $PO_4$, 9–36% of Zn, 12–55% of $NO_3$, 4.0–20% of alkali metal, calculated as sodium, and, if desired, 2.0–10% of $NO_2$. For regulating the thickness of the coating the composition of matter may furthermore contain 0.08–8% of citric acid and/or 0.02–2% of tartaric acid or equivalent amounts of citrate or tartrate.

For special purposes it may be advantageous if the phosphatization solution and correspondingly the composition of matter for preparing same additionally contains alkaline earth metal ions.

The following examples serve to illustrate the invention but they are not intended to limit it thereto.

*Example 1*

Cold-worked automobile body sheet iron was sprayed for 1½ minutes at 40° with a solution containing per liter:

3.57 grams of $PO_4$
3.61 grams of Zn
6.87 grams of $NO_3$
0.4 gram of $NO_2$

and having a pH value of 3.8–4, determined with an indicator paper for measuring the hydrogen ion concentration ("Lyphan"). The solution had a total acid content corresponding to 9.6 points and a proportion of $PO_4$:Zn:$NO_3$ of 1:1:1.9.

For replenishing the solution a solid mixture was used in which the components $PO_4$, Zn, $NO_3$ and $NO_2$ were present in a proportion of 1:0.2:0.60:0.45.

The sheets treated with the aforesaid solution were subsequently treated with an aqueous acid solution containing 0.01% of $CrO_3$. One part of the sheets was lacquered with a commercial test lacquer and the other part was oiled with a commercial corrosion inhibiting oil.

The following test values were obtained:

(1) Salt water spray test according to DIN 50,907 (German Industrial Standard) with oiled sheets: the sheets were sprayed for 5 minutes at room temperature with a 3% sodium chloride solution, the test was repeated in intervals of 55 minutes. After 400 hours the oiled sheets showed less than 1% of rust.



(2) Salt water spray test with unoiled sheets: the sheets were still rust-free after 25 hours and showed about 1% of rust after 75 hours.

(3) Sea water test according to DIN 50,907: the lacquered sheets provided with 2 cross-wise incisions down to the metal were immersed for 72 hours at room temperature into a 3% sodium chloride solution. Evaluation: 5.5 points with a scale of 1 to 6 points, 1 being the lowest and 6 the highest evaluation.

(4) Condensed water climate test according to DIN 50,017: the lacquered sheets were alternately placed for 8 hours in a steam-saturated atmosphere of 40–45° C. and for 16 hours at room temperature in air with normal humidity (each of the 24 hour periods is called one round and each test comprises 10 rounds). After 10 rounds the lacquered sheets did not show any corrosion phenomena.

(5) Grid division test according to DIN 53,151: with a special knife a grid was cut into the lacquered surface of the sheets. The test is negative if squares, formed by the incisions, of the lacquer film scale off. In the present case the lacquer adherence was good.

(6) Mandrel bending test according to DIN 53,152: a lacquered sheet with grid division was bent over a 6 mm. mandrel. The test is negative if the lacquer scales off. In the present case the lacquer adherence was good.

*Example 2*

Cold-worked automobile body sheet iron was treated as described in Example 1. Instead of the phosphatization solutions used in said example, the following solutions were used:

| Solution A | Solution B | Solution C |
|---|---|---|
| 4.47 g./l. $PO_4$<br>4.52 g./l. Zn<br>8.58 g./l. $NO_3$<br>0.5 g./l. $NO^2$<br>pH 3.8* | 4.9 g./l. $PO_4$<br>6.4 g./l. Zn<br>12.1 g./l. $NO_3$<br>0.6 g./l. $NO_2$<br>pH 3.8–4* | 3.25 g./l. $PO_4$<br>3.0 g./l. Zn<br>4.9 g./l. $NO_3$<br>0.9 g./l. $NO_2$<br>pH 3.5* |
| TOTAL ACID | | |
| 12 points | 13.2 points | 8 points |
| $PO_4$:Zn:$NO_3$ | | |
| 1:1:1.92 | 1:1.3:2.47 | 1:0.92:1.5 |

*Determined with indicator paper "Lyphan."

The sheets treated with solutions A, B and C, respectively, were after-treated as described in Example 1 and subjected to the tests indicated in said example. The results obtained were as good as those of the preceding example.

*Example 3*

Highly elastic steel bands for measuring purposes were treated by immersion with a solution having the following concentrations:

4.97 g./l. Zn, total acid ..... 10.5 points.
1.45 g./l. Na, free acid ..... 0.2 point.
10.10 g./l. $NO_3$, pH value ..... 3.2–3.6.
9.94 g./l. $PO_4$, treatment time ..... 45 seconds.
0.4 g./l. $NO_2$, treatment temperature ..... 38° C.
0.15 g./l. tartaric acid, $PO_4$:Zn:$NO_3$ ..... 1:1:2.03.

The applied phosphate coating had a thickness of about 0.8$\mu$. The anti-corrosion and lacquer adherence tests gave excellent results.

The above phosphatization solution was replenished by a composition of matter containing the components $PO_4$:Zn:$NO_3$:tartaric acid in a proportion of 1:0.6:0.52:0.0085.

*Example 4*

In order to illustrate the regulability of the thickness of the phosphate coatings produced by the process of the invention highly elastic steel bands for measuring purposes were treated with the solution used in Example 3 in which the content of tartaric acid had been reduced to 0.06 g./l. The coatings obtained with this solution had a thickness of 1.5$\mu$.

*Example 5*

Cold-worked automobile body sheet iron was treated with the following solution in order to show the action of citric acid:

| | |
|---|---|
| 4.68 g./l. Zn, total acid | 12.0 points. |
| 4.15 g./l. Na, free acid | 0.1 point. |
| 15.9 g./l. $NO_3$, pH value | 3.5–3.8. |
| 5.59 g./l. $PO_4$, treatment time | 60 seconds. |
| 0.4 g./l. $NO_2$, treatment temperature | 38° C. |
| 0.15 g./l. citric acid, thickness of coating | 1.5$\mu$. |

$PO_4$:Zn:$NO_3$=1:0.8:2.84.

A composition of matter suitable for replenishing the phosphatization solution contained the components $PO_4$:Zn:$NO_3$:citric acid in a proportion of 1:0.35:0.95:0.012.

*Example 6*

In order to prove the regulating action of citric acid on the thickness of the phosphate coating the same solution as in Example 5 was used in which the content of citric acid had been increased to 1.5 g./l. The phosphate coating obtained had a thickness of at most 0.8$\mu$.

I claim:

**1.** In a process of producing phosphate coatings on surfaces of a metal selected from the group consisting of iron, steel, zinc, and alloys of the said metals by contacting the metal surfaces with phosphatization solutions containing zinc ions, alkali metal ions, phosphate ions, nitrate ions and nitrite ions, in which solutions the portion of nitrate ions is at least as great as that of phosphate ions, the improvement of contacting the metal surfaces with the phosphatization solution at a temperature in the range of about 20° C. to about 45° C., maintaining in the solution a proportion by weight of $PO_4$:Zn:$NO_3$ of 1:0.8 to 1.7:1.5 to 3.2, and a point number of total acid of about 8 to about 14 and suppressing the formation of free acid in the solution by maintaining a nitrite content of about 0.1 to about 1 g. per liter of solution.

**2.** The process of claim **1**, wherein the solution additionally contains alkaline earth metal ions.

**3.** The process of claim **1**, wherein the metal surfaces are treated with the solution at a temperature in the range of 35 to 40° C.

**4.** The process of claim **1**, wherein the thickness of the phosphate coatings is regulated by adding to the solution at least one substance selected from the group consisting of citric acid and tartaric acid, the amount of citric acid ranging from about 0.2 to 2.0 g. per liter of solution and the amount of tartaric acid ranging from 0.04 to 0.4 g. per liter of solution.



**5.** The process of claim **4**, wherein, the citric acid and tartaric acid are added in the form of citrate and tartrate.

**6.** The process of claim **1**, wherein for simultaneously degreasing and phosphatizing the metal surfaces, the solution additionally contains hydroxyethylated tall oil fatty acid.

**7.** The process of claim **1**, wherein solid products are used for preparing and replenishing the phosphatization solution.

**8.** The process of claim **1**, wherein concentrated aqueous solutions are used for preparing and replenishing the phosphatization solutions.

**9.** The process of claim **1**, wherein different compositions of matter are used for preparing and replenishing the phosphatization solutions, the proportion of $PO_4$:Zn:$NO_3$ in the replenishing preparation being 1:0.6–0.8:0.6–1.5.

**10.** The process of claim **1**, wherein the same composition of matter is used for preparing and replenishing the phosphatization solution, the proportion of $PO_4$:Zn:$NO_3$ in the composition being 1:0.6–1.7:0.8–3.2, and the composition contains the required amount of nitrite.

**11.** The process of claim **10**, wherein for adjusting the required concentration of the individual components in the phosphatization solution when it is prepared a starting salt is added having such a composition that the solution contains $PO_4$, Zn and $NO_3$ from the onset in the proportion of 1:0.8 to 1.7:1.5 to 3.2.

**12.** A phosphatization solution for producing phosphating coatings on surfaces of a metal selected from the group consisting of iron, steel, zinc and alloys thereof consisting essentially of a solution containing zinc ions, alkali metal ions, phosphate ions, nitrate ions and nitrite ions in which solution the portion of nitrate ions is at least as great as that of phosphate ions, the proportions by weight of $PO_4$:Zn:$NO_3$ is 1:0.8 to 1.7:1.5 to 3.2, the point number of total acid being between about 8 to about 14 and the solution containing from about 0.1 to about 1 g. per liter of nitrate.


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