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[54] **PROCESS FOR MANUFACTURING ZINC COATED STEEL SHEET, AND STEEL SHEET OBTAINED BY THIS PROCESS**

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[58] **Field of Search**...148/6.15 R, 6.15 Z, 6.16, 31.5, 148/195

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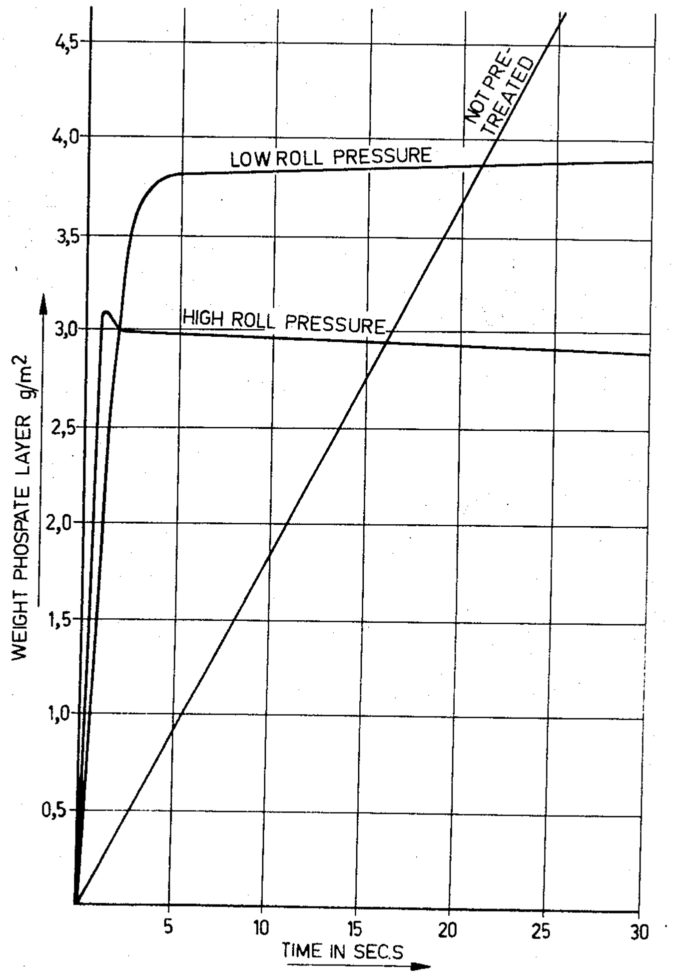
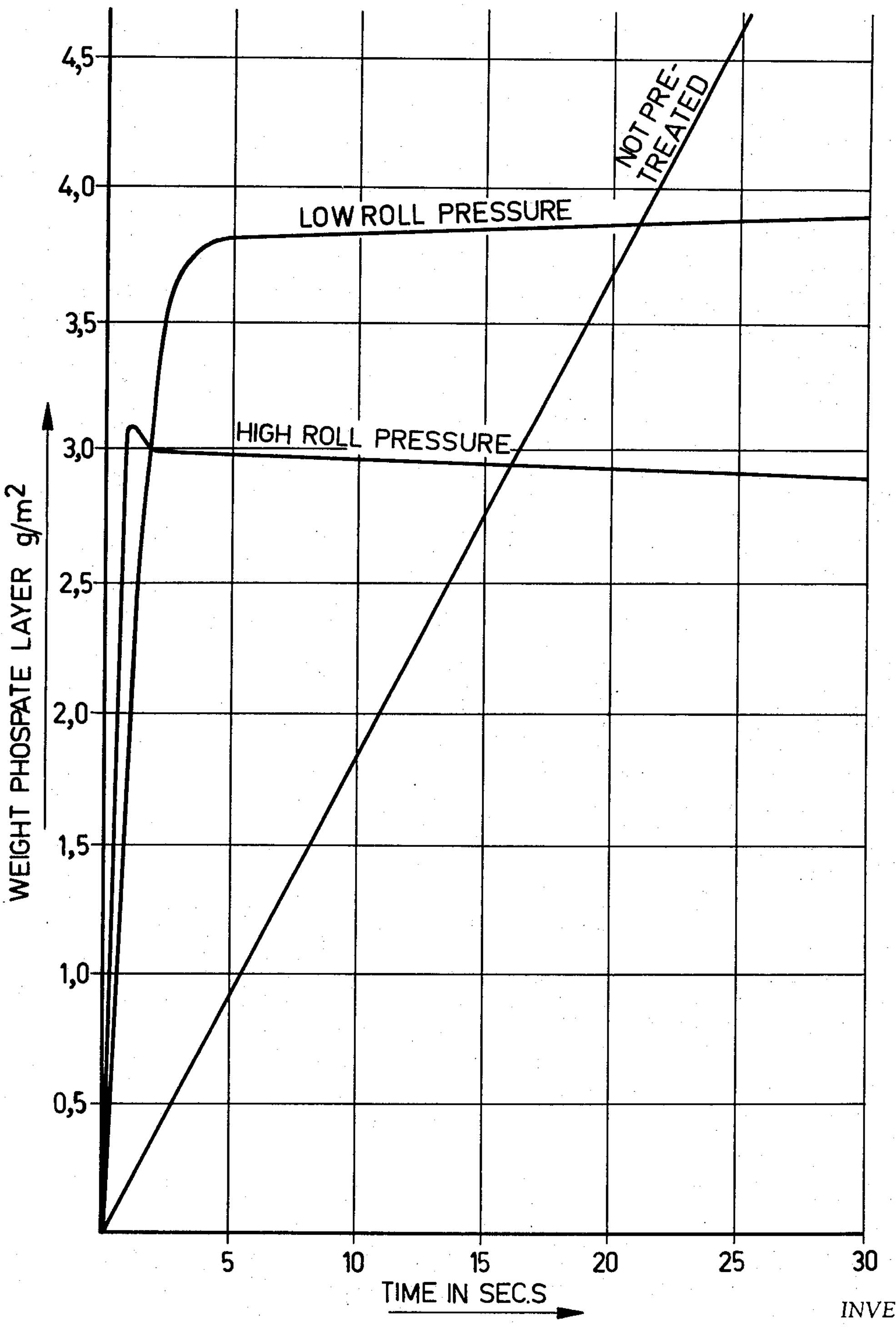
[57] **ABSTRACT**

Phosphated zinc coated steel sheet characterized by a phosphate layer with a mass of less than 4 g/m^2 and with a structure which closes the zinc layer 90 percent or more, and process for improving phosphating of zinc coated steel sheet which essentially comprises passing the zinc coated sheet between elastically surfaced rollers prior to phosphating.

7 Claims, 1 Drawing Figure





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PROCESS FOR MANUFACTURING ZINC COATED STEEL SHEET, AND STEEL SHEET OBTAINED BY THIS PROCESS

This invention relates to a process for manufacturing an improved zinc coated steel sheet, in which such a steel sheet is submerged in a phosphate solution. This invention also relates to phosphated zinc coated steel sheet.

Phosphating of zinc coated steel sheet is frequently applied for electrolytically zinc coated steel strip, although it is also possible to use it for steel strip which is zinc coated by submerging in a zinc bath and for zinc coated steel sheet which is not in long strip form. During submerging in the phosphate bath a layer is formed on the surface of the zinc layer, which mainly consists of $Zn_3(PO_4)_2 \cdot 4H_2O$. This is formed in part from the bath, which among others consists of phosphoric acid and zinc phosphate, and in part from the zinc layer, which is partly dissolved in the bath.

The phosphating of the zinc coated steel sheet has the object to give to the sheet an electrochemical insulation, so that the adhering of lacquer thereon is improved. Moreover the corrosion resistance of the zinc layer is improved, so that the occurrence of so-called white rust is counteracted.

In general phosphate layers have a crystalline structure. It is assumed that the phosphate layer may be thinner when the phosphate crystallites become smaller. About the influence of the thickness of the layer of the phosphate on the corrosion resistance little was known. It is, however, obvious to assume that a thinner phosphate layer will be better deformable than a thicker one and that thereby also the adhering of paints or lacquers on the sheet will be more favorable for a thinner phosphate layer.

It is known from literature (for instance from "Yawata Technical Report", Nr. 254, pages 106–107, March 1966) that a zinc coated sheet which is rubbed with the fingers or with a brush obtained a finer crystal structure in the phosphate layer after phosphating.

This finer structure was found in those zones which had been rubbed.

Up to now it has not appeared possible to develop on this basis a process which was reproduceable as to its results and in which the crystallite structure of the phosphate layer was sufficiently fine and uniform throughout. It was neither possible to obtain a phosphate layer which was uniform in thickness, so that no effective influence of rubbing or brushing on the corrosion resistance, on the deformability and on the adhering of lacquers or paints on the sheet was obtained.

It is remarked that not only phosphating of the sheet was known, but also chromating as a means to counteract corrosion of the sheet and to improve adhering of the lacquer or paint. In general the chromated and thereafter painted or lacquered sheets are superior as far as deformability is concerned without cracks occuring in the lacquer or paint. However, the corrosion resistance is better for phosphated sheets.

A disadvantage occuring in the phosphating process of zinc coated sheet occurs when a steel sheet moving through a phosphate solution is brought to a standstill or is braked to a lower speed. It appears that the phosphate layer will in that case become thicker, approximately linnearly with the time of stay of the steel sheet in the bath. In extreme cases of a disturbance of the process too much zinc or even all zinc could have been merged into the solution from the zinc coated steel sheet, through the phase of the zinc phosphate.

An improved phosphated zinc coated steel sheet is according to the invention obtained by the steps to be described below, in such a way that the said disadvantages do not occur and that several advantages are obtained.

In this respect the invention consists in that the zinc coated steel sheet, before being submerged into the phosphate solution, is passed through at least one pair of rolls, which are pressed towards one another during this passage so as to exert on the steel sheet a force of at least 0.4 kgs per cm of roll length and preferably of about 20 kgs per cm of roll length, and that rolls are used which at least at the surface consists of rubbery material, i.e. an elastic material with rubber-like mechanical characteristics, with a hardness of 40° to 90° shore, and preferably of 60° to 80° shore.

It is remarked that without particular measures the forming of an entirely closed phosphate layer takes about 30 seconds. Apart from the fact that in such a time interval usually a far too thick phosphate layer will be formed, this time duration is also in other respect much too long for a treatment of a continuous steel strip, particularly because at a certain speed of the strip a very long bath is necessary. In this respect it is desired to have a treatment time of less than 10 seconds and preferably even less than 6 seconds. It is possible to obtain such time intervals when applying the process according to this invention.

In order to form a supremely good phosphate layer at a high speed of the zinc coated steel sheet through the phosphate bath it is preferred according to this invention to keep this sheet submerged in the phosphate solution during about 3 seconds at a temperature of about 70°C.

Although, as remarked before, it is possible in essence to influence the formation of the phosphate layer also by brushing of the zinc coated sheet, such a method is not preferable. This is so because it has not appeared possible to obtain in this way a uniform surface.

It has also been tried before to accelerate the formation of the phosphate layer by spraying the sheet with a watery dispersion of $Zn_3(PO_4)_2$ particles. In this way it is neither possible to accelerate the phosphating sufficiently to obtain a satisfactory phosphate layer at a strip speed of about 100 m/min. Moreover the costs of such a process are very high and up to now it has not appeared possible to obtain a reproduceable sufficiently uniform quality in this way.

It has appeared that by the process according to the invention a very fine crystal structure of the phosphate layer is obtained, which moreover is highly uniform over the entire surface of the steel sheet. Particularly surprising and remarkable is, however, that the phosphate layer is formed according to a quite different program in time, which results in a phosphate layer with an extremely high uniformity of thickness and with characteristics unknown up to now for such layers. It has in this respect appeared that the phosphate layer will build up, after the described treatment of the strip or sheet between the rolls, much more rapidly in the beginning than without such a roll treatment (10 to 20 times faster). However, when approaching a weight of the layer of about 2–3 grams per m^2 the growth of the phosphate layer is considerably decelerated and shortly thereafter substantially no further increase in thickness of the layer takes place. It seems to be that the phosphate layer has closed itself over the zinc layer so that the zinc coated steel sheet cannot react any further with the phosphate bath.

In relation therewith disturbances or retardings in the speed of running of a steel sheet through the phosphate bath can no more cause deviating and inferior parts in the sheet or strip.

The inspection and checking of the finished product is thereby facilitated considerably, which saves labor. More important is, however, that disturbances and retardations do not cause loss of first quality material any more. The importance thereof will be the more clear when it is kept in mind that with the processes usual up to now at least the part of the steel strip or sheet at the beginning of each coil, which has to be beaded through the phosphating device, should be rejected as waste.

Another advantage of the invention is that less deposits are formed in the phosphate bath. This is so because the quantity of deposit is proportional to the weight of the phosphate layer. As a result thereof the composition of the phosphate bath will not change as rapidly as in known processes, which considerably promotes the economy and efficiency of the entire process.

A last advantage of the new process may be seen in the fact that less zinc is dissolved, so that it is possible to apply a thinner zinc layer on the steel.

The "closed" phosphate layer obtained is extremely thin, so that it is adequately deformable and thus is also better suited to be painted or lacquered as the adhering of the paint layers is better when the phosphate layer is better deformable.

As the phosphate layer is "closed" it surprisingly appears also to give a better resistance of the sheet or strip against corrosion ("white rust"). Moreover the sheet phosphated according to this invention appears to have a deformability which is substantially the same as that of a chromated sheet.

A further improvement of the corrosion resistance and the paint adhering appears to be obtainable according to the invention by submerging the sheet or strip in a manner known per se, in subsequence to the submerging in the phosphate solution, into a solution on a chromate basis. As such the so-called pacifying of a phosphate layer with the aid of for instance a chromate solution is known. This may be Deoxylite 41, which is a chromate passivating bath, containing chromium in the 6 and 3 valance states, sold by Amchem Products Inc. It has appeared, however, that the additional resistance against corrosion obtained thereby is improved considerably if this pacifying takes place on a zinc coated sheet which has been phosphated in the manner according to this invention.

This invention not only relates to the processes described, but also to the steel sheets obtained thereby. In particular this invention relates to a phosphated zinc coated steel sheet which is characterized by a phosphate layer with a mass of less than 4 g per m^2, and preferably of 2 to 3 g per m^2, and with a structure which closes the zinc layer for more than 90 percent. Normally a closing of the zinc layer of 100 percent will be obtainable.

The invention will now be explained in more detail with reference to four examples.

EXAMPLE I

For comparison reasons a steel sheet was treated in a conventional manner. Thereto a steel sheet was electrolytically zinc coated in the following manner: It was started from a sheet material with a roughness of less than 30 mils. This material was electrolytically degreased by treating it as a cathode in a degreasing bath of a usual commercial quality at about 85°C and with a current density of about 10 amps/dm^2 and thereafter rinsed with water and subsequently dried.

Thereupon the material was electrolytically zinc coated in a bath with a composition of:

200 g/l $ZnSO_4$
40 g/l $(NH_4)_2SO_4$
balance water.

At a temperature of the bath of about 48°C and a current density of about 10 amps/dm^2 a layer of zinc of about 15 g/m^2 was deposited, which corresponds to a thickness of the zinc layer of 2 microns. The sheet thus zinc coated was again rinsed in water and dried.

Thereupon samples of the sheet material were submerged during 2, 5 and 10 seconds in a phosphating bath at a temperature of 70°C. The bath consisted of a phosphating substance, commercially known as Granodine 32 of Amchem. Granodine 32 is a nickel containing nitrate activated zinc phosphate bath sold by Amchem Products Inc., Ambler P.A. Six parts of this substance were diluted to a solution with 94 parts of water. It is remarked that lower concentrations and lower temperatures of the bath retard the formation of the phosphate layer. At much higher temperatures on the contrary the phosphate layer shows discoloration. After submerging in the bath the sheet samples were rinsed by water.

The weight of the phosphate layer formed was measured and expressed in grams /m^2.

Thereupon the following experiments with these samples were made:

A = measuring of the weight of the layer formed.
B = salt spray test according to British standard BS 1224–1959
C = Lacquer bond test according to Machu.
D = microscopic estimation of the density and closing character of the phosphate layer.

The salt spray test according to BS 1224–1959 was made in the following way: During 3 minutes of each hour a fog of a solution in water of 3 percent NaCl was sprayed at room temperature in a closed box containing the samples. After four days the samples were examined visually. Thus they were judged with respect to the presence of zinc salts (white rust!) or iron oxides (red rust!).

The lacquer bond test according to Machu was made as follows: The samples were painted with an alkyd-melamine lacquer sold in the trade by the Dutch firm Sikkens as baking enamel M49/12. A lacquer layer of 25 microns was applied and thereafter it was baked at 120°C during 30 minutes.

An Erichsen test was made by pressing a depression with a diameter of 5 mm into the samples, after which in this depression a cross-scratch was made. Thereupon adhering tape (Scotch tape No. 810) was adhered to the deformed and scratched zone and thereupon this tape was drawn off from the sample to be able to judge about the bond of the lacquer of the sheet. The following gradations were used therein:

good : no loosening of lacquer (less than 1 percent).
reasonable, loosening of lacquer along the scratch up to a minimum of a width of 2 mm (1–3 percent of the lacquer is loosened).
moderate, about 10 percent of lacquer loosening in the depression.
bad, about 20 percent of lacquer loosening in the depression.

In this test the samples were, after painting, first kept submerged during 1 hour at 37°C in a bath of the following composition:

50 g/l NaCl
10 m l /l glacial acetic acid
5 g/l H_2O_2.

Below further details will be given about such tests.

EXAMPLE II

A similar steel sheet to that of Example I was zinc coated under the same circumstances. Before phosphating in a similar manner, the sheet was passed under different conditions four times between rubber rolls. In the first experiment the rolls were coated with rubber of 80° shore for the upper roll and 60° shore for the lower roll. The rolls had a diameter of 40 mm and were rotated with a peripheral speed of 500 m per hour. With roll pressures of 0.4 kg/cm and 20 kg/cm it was examined for different phosphating periods how the weight of the formed phosphate layer in g/m²changed.

The drawing shows the curve for this weight and the result of such a measurement for the sheet according to Example I (experiment A).

It appears clearly therefrom that the phosphate layer behaves quite differently depending upon the pretreatment between rubber rolls.

For the "rolled" sheet the phosphate layer builds up very rapidly, but the weight thereof soon reaches a certain limit. For the sheet not pretreated the phosphate layer builds up very slowly, but only at very much thicker layers a deceleration in the formation thereof was found.

When looking through the microscope (experiment D) it appeared that the non-pretreated sheet had a phosphate layer with a coarse structure, which layer moreover only started to close after a phosphating time of 5 seconds and was only fully closed after about 30 seconds. The "rolled" sheets showed a very fine structure of the phosphate layer and this layer was already entirely continuous and closed within 2 to 3 seconds.

EXAMPLE III

As it appears from the enclosed graph that there is a small influence of the pressure of the elastic rolls, even for such considerable differences in roll pressure, it was now tried to vary other conditions during this rolling.

It appeared that the hardness of the rolls could be varied between rather wide limits without giving a significant influence on the product obtained. Variations between 60° and 80° shore do not show a clear difference.

A roll pressure of 15 kg/cm gave substantially the same results as the results given in the enclosed drawing for 20 kg/cm.

Also for considerable variations in the roll speed and the roll diameters the new phenomenon which the invention uses appears to be rather considerably insensitive. On the other hand it appeared to be favorable not to choose the number of passages between the elastic rolls too low and preferably it should be 3 or 4.

EXAMPLE IV

A zinc coated sheet was passed four times between rubber rolls before being phosphated. The pressure of the rolls was 20 kg/cm, the roll speed was 500 m/hour and the roll diameter was 40 mm. The rolls had a shore hardness of 70°. For this sheet the results of the salt spray test (experiment B) and of the Machu-lacquer bond test (experiment C) were determined in a similar way as for the sheet of example I. The following table gives the results:

phosphating time seconds	salt spray test B		lacquer bond test C	
	pretreated		pretreated	
	no	yes	no	yes
	Ex.1	Ex.4	Ex. 1	Ex.4
2	very bad	good	bad	good
5	very bad	good	moderate	good
10	bad	good	good	good

It appears therefrom convincingly that the resistance against corrosion (salt spray test) as a result of the new process becomes better than was obtainable with the known processes, even after long phosphating times. The lacquer bonding after 2 seconds of phosphating is already at a level which previously required 10 seconds of phosphating. As a phosphating liquid Granodine 32 may be used as specified.

We claim:

1. An improved process for manufacturing phosphated zinc coated steel sheet, which process comprises the step of

a. effecting phosphating of the zinc coated steel sheet by submerging the same in a phosphating solution,

wherein the improvement comprises

b. passing the zinc coated steel sheet, before subjecting it to step (a), between at least one pair of rolls with surfaces of rubbery material having a shore hardness of 40° to 90°, and
c. causing the said rolls during step (b) to exert on the sheet a force of at least 0.4 Kg/cm of roll length.

2. An improved process as claimed in claim **1**, wherein:

e. in step (a) the submergence of the rolled sheet is maintained only about 3 seconds and at a temperature of about 70°C.

3. An improved process as claimed in claim **1**, in which:

e. step (b) is practiced by passing the zinc coated sheet between such rolls 3 or 4 times before it is subjected to step (a).

4. An improved process as claimed in claim **1**, wherein:

e. step (c) is practiced by causing the rolls to exert on the sheet a force of about 20 Kg/cm of roll length.

5. An improved process as claimed in claim **1**, wherein:

e. step (b) is practiced with rolls with rubbery surfaces having a shore hardness of 60° to 80°.

6. A phosphated zinc coated steel sheet produced by the process of claim **1**, said sheet having a phosphate layer with a mass of less than 4 g/m^2 and a structure which is over 90 percent closed over the zinc layer.

7. A phosphated zinc coated steel sheet as claimed in claim **6**, in which the phosphate layer has a mass in the range of 2 to 3 g/m^2.

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