

- [54] **PRETREATMENT OF METAL SHEETS WHICH ARE COATED AFTER A FORMING OPERATION**
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[58] **Field of Search**....117/75, 6, 66, 129, 49, 132 C, 117/132 R; 72/42, 46; 29/424

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[57] **ABSTRACT**

This invention relates to an improved process for the pretreatment of metallic materials wherein the material is subjected to a surface treatment, subsequently covered with a removable layer of a water soluble, film-forming organic polymer, formed and provided with a firmly adhering protective layer.

7 Claims, No Drawings

PRETREATMENT OF METAL SHEETS WHICH ARE COATED AFTER A FORMING OPERATION

The direct white enamelling of steel sheet has in recent years become a reliable production process. By rationalizing the production and introducing continuous, programmed production methods, a consistent quality of enamelled products combined with a reduction in enamelling costs has been achieved. Further simplification of the work proceeding in the enamelling plant is provided by the fact that the strip used for producing the blanks is already pretreated for the single layer enamelling in the steel plant, i.e., a pickling process followed by nickel plating is carried out there. The surface thereby produced for obtaining a firm bond for the single layer white enamelling must, of course, then be protected before the forming operation so that no damage will occur to the applied layer. This protection can be achieved by conventional methods of pretreating the strip, involving an electrolytically applied layer of zinc (Belgian Pat. No. 557,963 and French Pat. No. 1,187,958).

The disadvantage of such a metallic protective layer lies in the complicated after-treatment which necessitates the setting up in the enamelling plant of an installation consisting of several stages (degreasing, rinsing and removing the protective layer by pickling with acid, e.g., hydrochloric acid, rinsing and neutralizing).

Similarly, it is more rational if metallic materials which are to be given the required form or shape by drawing, pressing, bending or other non-machining process and are then provided with a firmly adhering metallic or non-metallic layer are degreased and pickled immediately after their production and are then covered with a layer which protects their surfaces but which can easily be removed. Metal coatings which are deposited by electrocoating or chemical processes or stoving lacquers, dipping varnishes or other plastic coatings also require a very clean foundation for their application in order to ensure permanent protection of their surfaces. The problem of providing metal workers with a starting material which can be used practically directly for the following coating process is, therefore, not confined to the enamelling industry.

The advantages are numerous. Not only is a saving in material achieved by the elimination of additional rust removal or removal of other layers of corrosion but the pickling and the working up of waste liquor which this involves can be carried out more economically in large plants.

A process for the pretreatment of a metallic material which, after a surface treatment and covering with a removable layer, is shaped or formed and provided with a firmly bonded protective layer has now been found which is characterized in that the removable covering used is a water-soluble film-forming organic polymer.

The process is used to advantage in enamelling work and is particularly efficient for single layer enamelling which requires specially pretreated metal surfaces. The steel sheets or strips which are to be subjected to a forming operation are advantageously degreased, pickled and covered with a nickel layer immediately after they have been produced. The surface treatment is carried out by conventional methods involving either

purely chemical or purely electrolytic stages or a combination of the two. Thus, for example, an electrolytically degreased, electrolytically pickled and electrolytically nickel coated sheet could be precleaned by a rough alkaline degreasing process.

The sequence of pretreatment stages would in this case be as follows:

Rough alkaline degreasing, fine electrolytic degreasing, rinsing, electrolytic pickling, rinsing, electrolytic nickel coating, rinsing and drying.

The advantage of the electrolytic pretreatment compared with purely chemical methods is that the total time of stay is reduced by about 65 percent.

Following these stages, the water-soluble film-forming organic polymer is then applied, e.g., by the dipping or spray process. The entire treatment including the production of the sheet metal can be carried out continuously. The sheet covered with the covering layer can then be formed by rolling, pressing, drawing or other non-machining methods. After the shaping operation, the covering may be stripped off before the enamelling or washed off with water without the surfaces prepared for the enamelling process being in any way impaired.

It was unexpectedly found that the covering made of the polymers to be used according to the invention acts as a lubricant during the forming operation carried out on the metal sheet and that, even if it is incompletely removed or not removed at all before the enamelling process, neither the surface of the enamel nor the firmness of its adherence is found to be in any way impaired.

This gives rise to the interesting possibility of being able to operate the presses without using grease so that after-treatment can be completely eliminated. In practice, such a method of operation will not always be possible because it is difficult to avoid contamination by substances which are harmful to the enamelling. It is, nevertheless, very advantageous that satisfactory enamelling is ensured even if the protective layer is not completely removed.

The process according to the invention is not restricted to enamelling processes but can be applied to similar technical processes in which the metal articles are provided with a protective layer after they have been formed; however, a carefully cleaned surface and in some cases also a specially pretreated surface is necessary to ensure firm adherence of the protective layers. As already mentioned above, the process is also advantageous, for example, in the production of metal articles which, after they have been formed, are metalized by electrocoating or chemical treatments or covered with plastic coatings.

The following are suitable for use as water-soluble film-forming polymers: polyethylene oxide; polyvinyl alcohol or partially saponified polyvinyl acetates; polyvinyl pyrrolidone, polyacrylamides and copolymers which contain acrylamide, e.g., copolymers of this type with acrylic acid esters or acrylic acids, optionally in the form of their salts; polyacrylic acid or polymethacrylic acid and their copolymers, optionally in the form of their salts; water-soluble cellulose derivatives such as methyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose; alginates and pectins; water-soluble

copolymers which have been formed by reacting maleic acid anhydride copolymers e.g., with styrene, isobutylene or ethylene with decomposition of the anhydride group, these compounds being understood to mean acids, amides or amide ammonium salts; polymers which form films of exceptionally high strength and elasticity, e.g., polyethylene oxides, polyvinyl alcohols, carboxymethyl cellulose (sodium salt) and hydroxyethyl cellulose are especially suitable.

The coatings according to the invention may be applied by conventional methods, e.g., fusible polymers can be applied in the form of their melts, e.g., by spraying, immersion or brush coating or in the form of a foil. To apply very thin films, it is advantageous to spray an aqueous or organic solution on the support or to dip the support into the solution and evaporate off the solvent. Powder application followed by sintering may also be carried out.

The process of the invention is described in the following examples.

EXAMPLE 1

A cold rolled steel sheet having the following approximate analytical composition:

C	= 0.004 percent
Mn	= 0.320 percent
S	= 0.035 percent
P	= 0.040 percent
Si	= 0.020 percent
Cu	= 0.027 percent

was degreased by an alkaline treatment, rinsed warm and cold, pickled for 6 minutes in 9% H_2SO_4 at 75° C, nickel coated for 6 minutes in a 1.2% $NiSO_4 \cdot 7 H_2O$ solution at 70° C. at pH 3, rinsed and finally neutralized. This pretreated sheet was then coated with a 2 percent aqueous solution of a polyvinyl alcohol by spraying. The polyvinyl alcohol used had a K value of 70 (K value according to Fikentscher, *Zellulose Chem.* 13, 1932, pages 58 and 71). The metal sheet was then formed, using a grease-free tool, and finally enamelled by direct enamelling with a B-Ti white enamel of the following composition:

38	% SiO_2
0.5	% Al_2O_3
21	% B_2O_3
15	% alkali metal oxide
2	% fluorine
19	% TiO_2
0.5	% Mg
3	% P_2O_5

without previous removal of the polyvinyl alcohol layer.

After the usual stoving at 820° C., the enamelling showed very good adherence of the enamel and enamel surface.

EXAMPLE 2

A steel sheet having the analytical composition indicated in Example 1 was roughly degreased with alkali and then completely degreased electrolytically, rinsed, electrolytically pickled in a solution of 150 g of $Na_2SO_4 \cdot H_2O$ /l and 5 ml of H_2SO_4 conc./l for 1 minute at a current intensity of 10 A/dm², rinsed and finally nickel coated in a solution of 80 g of $NiSO_4 \cdot 7 H_2O$ per liter, 10 g of NH_4Cl /l, 20 g of $MgSO_4 \cdot 7 H_2O$ /l

and 5 g of H_3BO_3 /l at a current density of 0.5 A/dm² for 1 minute.

After rinsing, the sheet was dip-coated with a 1 percent solution of a carboxymethyl cellulose (in the form of its sodium salt, viscosity of the solution 300 centipoises) and, after drying, it was formed by a forming process conventionally employed in enamelling works using a hydraulic press. After the forming operation, the protective layer was cleaned off with water and the piece was dried and then enamelled by direct white enamelling with a B-Ti white enamel of the composition described in Example 1. Both the adherence and the enamel surface were excellent.

EXAMPLE 3

A cold rolled metal sheet of the analytical composition indicated in Example 1 was pretreated by the method described in Example 1, but it was nickel coated by the reduction process using sodium phosphite as the reducing agent for 3 minutes at 30° C. The pretreated sheet was brush-coated with a 1 percent aqueous hydroxypropyl cellulose solution. When this layer was dry, the sheet was pressed in the enamelling works to form the cover plate of an electric stove available on the market. The layer of hydroxypropyl cellulose was then removed by spraying it with water. The formed sheet was then directly white enamelled with a B-Ti white enamel of the composition described in Example 1. Both adherence and enamel surface were excellent. (The viscosity of the 1 percent solution of hydroxypropyl cellulose was 100 centipoises).

EXAMPLE 4

A steel sheet of the analytical composition indicated in Example 1 was pretreated as in Example 1. The pretreated sheet was coated with a 1 percent aqueous polyethylene oxide solution by spraying, and, when dry, it was subjected to a forming operation of the type conventionally used in enamelling works. The polyethylene oxide layer was then removed by dipping the formed sheet into a bath of warm water. The subsequent enamelling with a B-Ti white enamel of the above composition gave excellent results as regards adherence and enamel surface (the viscosity of the 1 percent polyethylene oxide solution was 100 centipoises).

EXAMPLE 5

A thin sheet having the analytical composition indicated in Example 1 was pretreated as described in Example 1 and coated by spraying with a 2 percent polyvinyl alcohol solution. The quantity of the polymer thereby applied to the sheet was about 2.2 g of pure polyvinyl alcohol per m² of sheet surface. After drying, the coated sheet was subjected to a shaping operation conventionally carried out in enamelling works. The layer of polyvinyl alcohol was then removed by brushing it under running water. Direct white enamelling with a B-Ti white enamel of the above composition was then carried out. Both adherence and enamel surface were excellent. (The polyvinyl alcohol used had the same molecular weight as in Example 1.)

EXAMPLE 6

Three metal sheets A,B and C of the analytical composition indicated above were pretreated as described in Example 1. Sheet A was formed in the enamelling works to produce a cover plate for an electric stove. The formed sheet was then directly white enamelled with a B-Ti white enamel of the above composition. Both adherence and enamel surface were very poor. Sheet B was formed and then sprayed with water. Direct enamelling with the B-Ti enamel of the above composition yielded very poor results as regards adherence and enamel surface. Sheet C was coated with a 2 percent aqueous polyvinyl alcohol solution by spraying after the pretreatment and then formed in the same way as sheets A and B. The polyvinyl alcohol layer was then removed by spraying with water. The formed sheet was thereafter directly white enamelled with the B-Ti enamel of the above composition. Both adherence and enamel surface were excellent, in contrast to sheets A and B. (The K value of the polyvinyl alcohol used was 50.)

A steel sheet of the analytical composition described in Example 1 was pretreated as in Example 1. The pretreated sheet was coated by spraying with a 1 percent aqueous polyethylene oxide solution and then subjected to the conventional forming operation carried out in the enamelling works without first being dried. The polyethylene oxide layer was then removed by dipping the formed sheet into a bath of warm water. Subsequent enamelling with a B-Ti white enamel of the composition indicated in Example 1 yielded excellent results as regards adherence and enamel surface. (The

viscosity of the 1 percent polyethylene oxide solution was 100 centipoises.)

What is claimed is:

1. In the process for the treatment of a metallic material, wherein the material is subjected to a pickling surface-treatment, covered with a removable layer, shaped, the removable layer removed and the material provided with a firmly adhering protective layer, the improvement wherein the removable layer consists essentially of a water-soluble film forming organic polymer.

2. A process as claimed in claim 1, wherein the metallic material is steel.

3. A process as claimed in claim 1, wherein the firmly adhering protective layer is a layer of enamel.

4. A process as claimed in claim 1, wherein the shaping operation is a non-machining shaping operation.

5. A process as claimed in claim 1, wherein the water-soluble film forming organic polymer is a member selected from the group consisting of polyethylene oxide, polyvinyl alcohol, hydroxymethyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose and mixtures thereof.

6. A process as claimed in claim 5, wherein the polymer is applied to the metallic material from dilute aqueous solution, the water being removed to leave a solid film, and the film being removed by water after shaping.

7. A process as claimed in claim 6, wherein the metallic material is a steel sheet which is shaped in a press, the film being removed with water and the sheet thereafter being enamelled.

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