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Leontaritis et al.

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[54] **PROCESS FOR THE PRE-TREATING OF METAL SHEETS WHICH ARE PROVIDED WITH A COATING FOLLOWING A FORMING OPERATION**

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[30] Foreign Application Priority Data

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[51] Int. Cl.**B44d 1/34, B21b 45/02**

[58] **Field of Search** 117/75, 6, 66, 49, 129, 132 R; 29/424; 72/42, 46

[56] References Cited

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[57] ABSTRACT

This invention relates to an improved process for the pretreating of metallic materials wherein the metallic material is surface-treated, covered with a removable layer comprising a water soluble, film-forming organic polymer and at least one water soluble polymer with a molecular weight of up to substantially 2,000, subsequently formed and provided with a firmly adhering protective layer.

9 Claims, No Drawings

PROCESS FOR THE PRE-TREATING OF METAL SHEETS WHICH ARE PROVIDED WITH A COATING FOLLOWING A FORMING OPERATION

The direct white enamelling of steel plate has become a very reliable process over recent years. By rationalizing the production and introducing continuous programmed manufacturing processes, it has been possible to obtain a uniform level of quality in the enamelled product accompanied by a reduction in enamelling costs. Another method of simplifying the work which has to be done in the enamelling shop is to pre-treat the band or sheet from which the semi-finished components are made before it leaves the steel mill so that it is ready for one-layer enamelling, in other words to subject it, for example, to a suitable pickling operation, followed by nickel plating. The keying surface thus obtained for one-coat white enamelling naturally has to be protected from the forming operation so that the layer applied is not damaged in any way. In conventional sheet pre-treatment techniques, protection such as this is provided by an electrolytically applied zinc layer (Belgian Pat. specification No. 557,963 and French Pat. specification No. 1,187,958).

The disadvantage of a metal protective layer such as this lies in the complicated after-treatment which makes it necessary for the enameller to set up another installation consisting of several stages (degreasing, rinsing, pickling the protective layer with acid, for example with hydrochloric acid, rinsing and neutralizing).

Similarly, it is more rational to degrease and pickle metals brought into the required form or shape by drawing, pressing, bending or other non-cutting forming techniques and subsequently provided with a firmly adhering metallic or non-metallic layer, immediately after they have been formed and then to provide them with a covering which although protecting the surface is nevertheless easy to remove. Coatings of metal whether electrodeposited or chemically deposited, stoving lacquers, dip lacquers and other plastic coatings also require as clean a substrate as possible in order to guarantee permanent protection of the surface. Accordingly, the problem of supplying metal workers with a starting material which can be used virtually directly for subsequent coating, is by no means limited to the enamelling industry.

The advantages are manifold. In addition to the saving of material, because there is now no longer any need for any additional rust removing operations or for the removal of other corrosion layers, pickling and the treatment of effluents which it involves can be carried out more economically in large installations.

A process for the pre-treatment of metallic materials which are shaped or formed and then provided with a firmly adhering protective layer after they have been surface treated and covered with a removable layer in the form of a layer of a water-soluble film-forming organic polymer, has now been found, wherein at least one water-soluble polymer with a molecular weight of up to substantially 2,000 is added to the organic film-forming polymer.

The process according to the invention is used with advantage in the enamelling industry and is particularly efficient in one-coat enamelling for which specially pretreated metal surfaces are required.

The steel plates or strips to be formed are advantageously degreased, pickled and provided with a nickel layer immediately after they have been manufactured. Surface treatment is carried out by methods known per se either purely chemically, completely electrolytically or by a combination of chemical and electrolytic stages. For example, an electrolytically degreased, electrolytically pickled and electrolytically nickel-plated sheet can be pre-cleaned by subjecting it beforehand to an alkaline coarse degreasing operation.

In this case, the sequence of pre-treatment stages would be as follows: alkaline coarse degreasing, electrolytic fine degreasing, rinsing, electrolytic pickling, rinsing, electrolytic nickel plating, rinsing and drying.

The advantage of electrolytic pre-treatment over purely chemical methods lies in a reduction of the total residence time by about 65 percent.

Thereafter, the water-soluble film-forming organic polymer is applied, for example by dip-coating or spray-coating, in admixture with the water-soluble organic polymers of low molecular weight. The complete treatment, including production of the sheet, can be carried out continuously. The sheet provided with the covering layer can then be formed by rolling, pressing, drawing or other non-cutting forming techniques. After forming, the covering can be removed or washed away with water before enamelling without any adverse effects upon the surfaces prepared for enamelling.

Surprisingly, it has been found that the coverings based on the organic polymers used in accordance with the invention act as lubricants during forming of the sheet and that there is no evidence of any deterioration in the adhesion of the enamel and the surface of the enamel even in cases where the covering is inadequately removed or is left completely intact before enamelling.

This affords the interesting advantage that pressing can be carried out in the absence of lubricants, thus completely eliminating the need for any after-treatment. In practice, a procedure such as this will not always be possible because it is almost impossible to avoid contamination by substances which interfere with enamelling. Nevertheless, it is of considerable advantage that enamelling can be satisfactorily carried out even in cases where the protective layer is not completely removed.

The coatings according to the present invention show extremely high elasticity and resilience so that reliable surface protection is guaranteed even in the event of extreme mechanical forming (for example deep drawing). In comparison with coatings based on unmixed film-forming polymers, it is possible to obtain an adequate protective effect with considerably reduced layer thicknesses. Another advantage is that after the sheet has been formed the coatings can be removed much more quickly with water because the rate of dissolution is considerably increased by virtue of the addition of low-molecular weight polymers.

The process according to the invention is by no means limited to enamelling processes, and can also be applied in similar technical fields in which formed metal objects are subsequently provided with a protective layer, for which purpose a carefully cleaned substrate and in some cases a specially pretreated substrate is required to ensure satisfactory adhesion of the pro-

protective layers. As already mentioned, the process affords advantages, for example also in the production of metal objects which after forming are galvanically or chemically metallized or provided with plastic coatings.

Suitable water-soluble film-forming polymers include polyethylene oxide; polyvinyl alcohol and partially hydrolyzed polyvinylacetate; polyvinyl pyrrolidones; polyacrylamides and copolymers containing acrylamides with, for example, acrylic esters or acrylic acids optionally in the form of their salts; polyacrylic acid and 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 obtained by reacting maleic acid anhydride copolymers with, for example, styrene, isobutylene, or ethylene, accompanied by elimination of the anhydride group, including salts, amides and amide ammonium salts. Polymers of the kind which show particularly outstanding film strength and film elasticity, for example, polyethylene oxides, polyvinyl alcohols, carboxymethyl celluloses (sodium salt), hydroxyethyl cellulose, are particularly suitable.

The following substances may be used as the water-soluble polymers of low molecular weight: polyethylene oxide and polyethylene glycol, polypropylene glycols and polyvinyl ethers with molecular weights below 2,000 also reaction products of phenols or alcohols with from 3 to 30 mols of ethylene oxide.

The water-soluble polymers of low molecular weight are used either individually or in admixture in quantities of from 1 to 75 percent, based on the film-forming polymer.

It was surprising that such favorable coatings should be obtained with mixtures of this kind especially since corresponding polymers with molecular weights of for example from 10,000 to 50,000 give protective layers which are not nearly so elastic and effective as those obtained, for example, from blends of film-formers of high molecular weight and polymers with molecular weights in the range from for example 200 to 1,000.

The coatings according to the invention can be applied by conventional methods, for example fusible polymers can be applied in the form of their melts for example by spraying, dipping, brush-coating or in the form of a film. To apply particularly thin films, an aqueous or an organic solution is preferably sprayed on to the substrate, or alternatively the substrate is dipped into the solution and the solvent evaporated off.

The process according to the invention is illustrated by the following Examples:

EXAMPLE 1

A cold-rolled steel sheet with the approximate analysis:

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 subjected to alkaline degreasing, rinsed with hot and cold water, pickled for 6 minutes at 75° C. in 9%

H₂SO₄, rinsed, nickel-plated for 6 minutes at 7° C./pH 3 in 1.2% NiSO₄·7H₂O solution, rinsed and finally neutralized. Thereafter, the pretreated sheet was coated by spraying with an aqueous solution containing 1 percent of polyvinyl alcohol and 1 percent of polyethylene glycol, molecular weight 400. The polyvinyl alcohol used had a K-value of 70 (K-value according to Fikentscher, *Zellulose Chem.* 13, 1932, pages 58 and 71). The sheet thus coated was then formed using a grease-free tool. The lubricating effect of the polymer layer during drawing of the sheet sections was extremely good. The tools did not show any signs of damage even after prolonged periods of grease-free pressing.

The formed sheets were subjected to direct white enamelling with a B-Ti-white enamel of the following composition:

38 % of SiO₂
0.5% of Al₂O₃
21 % of B₂O₃
15 % of alkali metal oxide
2 % of fluorine
19 % of TiO₂
0.5% of Mg
3 % of P₂O₅

with the polymer layer still intact. After stoving in the usual way at 820° C., the enamel showed excellent adhesion and an outstanding surface.

EXAMPLE 2

A steel plate with the same analysis as in Example 1 was subjected to alkaline pre-degreasing and then to electrolytic fine degreasing, rinsed, electrolytically pickled for 1 minute in a solution of 150 g. of Na₂SO₄·10 H₂O/liter and 5 ml. of concentrated H₂SO₄/liter at a current density of A/dm², rinsed and then nickel plated for 1 minute in a solution of

80 g. of NiSO₄·8 H₂O/l
10 g. of NH₄Cl/l
20 g. of MgSO₄·7 H₂O/l
5 g. of H₃BO₃/l

at current densities of 0.5 A/dm².

After pre-rinsing, the plate was dip-coated with a solution containing 1 percent of carboxymethyl cellulose (sodium salt, viscosity of the solution 300 centipoises) and 0.5 percent of polyethylene glycol, molecular weight 400, and after drying was subjected to forming in a hydraulic press of the kind commonly used in enamelling shops. After forming, the protective layer was removed by spraying with water, the section was dried and then subjected to direct white enamelling with a B-Ti enamel of the above composition. The adhesion and also the surface of the enamel were both excellent.

EXAMPLE 3

Cold-rolled thin sheet with the same analysis as above was pre-treated in the same way as described in Example 1, except that after reduction with sodium hypophosphite as the reducing agent it was nickel plated for 3 minutes at 30° C. The pre-treated sheet was brush coated with an aqueous solution containing 1 percent of polyvinyl alcohol and 0.5 percent of a reaction product of 1 mol of nonyl phenol with 12 mols of ethylene oxide. After the layer thus applied had been dried, the sheet was pressed in an enamelling shop to

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form the cover plate of a standard electric cooker. The polymer layer was then removed by spraying with water. Thereafter, the formed sheet was subjected to direct white enamelling with a B-Ti white enamel of the above composition. The adhesion and also the surface of the enamel were both excellent.

EXAMPLE 4

A steel sheet of the above analysis was pre-treated as described in Example 1. The pre-treated sheet was spray coated with an aqueous solution containing 1 percent of polyethylene oxide and 0.6 percent of a reaction product of 1 mol of butanol and 10 mols of ethylene oxide (viscosity of the solution being 100 centipoises) and, after drying, was subjected to forming by a method commonly used in enamelling shops. Thereafter, the polymer layer was removed by dipping the formed sheet in a warm water bath. Subsequent enamelling with a B-Ti white enamel of the above composition gave excellent results with regard to adhesion and surface finish.

EXAMPLE 5

A thin sheet with the same analysis as above was pre-treated in the same way as described in Example 1 and then spray coated with an aqueous solution containing 2 percent of polyvinyl alcohol with a molecular weight as specified in Example 1 and 1.2 percent of polyethylene glycol, molecular weight 600. After drying, the sheet thus coated was subjected to forming by a method commonly used in enamelling shops. The polymer layer was then removed by brushing in running water. This was followed by direct white enamelling with a B-Ti white enamel of the above composition. Both the adhesion and the surface of the enamel were excellent.

EXAMPLE 6

Three thin sheets A, B and C with the same analysis as above were pre-treated in the manner described in Example 1. Sheet A was formed in an enamelling shop into a cover plate for an electric cooker. The formed sheet was then subjected to direct white enamelling with a B-Ti white enamel of the above composition. The adhesion and also the surface of the enamel were both poor. Sheet B was formed and then sprayed with water. Direct enamelling with a B-Ti enamel of the above composition gave poor results in regard to adhesion and surface finish. After pre-treatment, sheet C was spray coated with an aqueous solution containing 1 percent of polyvinyl alcohol (with a K-value of 50) and 1 percent of polyethylene glycol, molecular weight 400, and then formed in the same way as sheets A and B. The polymer layer was then removed by spraying with water. Thereafter, the formed sheet was subjected

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to direct white enamelling with a B-Ti enamel of the above composition. In contrast to sheets A and B, the adhesion and also the surface of the enamel were both excellent.

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 and at least one water-soluble organic polymer with a molecular weight of up to substantially 2,000 and is applied to said metallic material as an aqueous solution.

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 a polyethylene oxide, polyvinyl alcohol, hydroxymethyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose and mixtures thereof.

6. A process as claimed in claim 5, wherein the water-soluble polymer of molecular weight up to substantially 2,000 is added to the film-forming polymer in a quantity of 1 to 75 percent of the film-forming polymer and is a member selected from the group consisting of polyethylene glycol, polypropylene glycol, polyvinyl ether, a reaction product of a phenol with ethylene oxide, a reaction product of an alcohol with ethylene oxide and mixtures thereof, the polymers being 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.

8. A process as claimed in claim 1, wherein the water-soluble polymer of molecular weight up to substantially 2,000 is added to the film-forming polymer in a quantity of 1 to 75 percent by weight of the film-forming polymer.

9. A process as claimed in claim 1, wherein the water-soluble polymer with a molecular weight of up to substantially 2,000 is a member selected from the group consisting of polyethylene glycol, polypropylene glycol, polyvinyl ether, a reaction product of a phenol with ethylene oxide, a reaction product of an alcohol with ethylene oxide and mixtures thereof.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,706,124 Dated December 19, 1972

Inventor(s) Lambis Leontaritis et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 22, delete "b" and insert -- by -- .

Column 6, line 32, after "percent" insert -- by weight -- .

Signed and sealed this 29th day of May 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents