June 17, 1969 C. E. H. FRÖDEN 3,450,610

PROCESS FOR REMOVING AN OXIDE LAYER FROM THE SURFACE OF HARDENED STRIP STEEL BY AN ELECTROLYTICAL METHOD

Filed Nov. 30, 1964 Sheet 1 of 3

FIG. 1

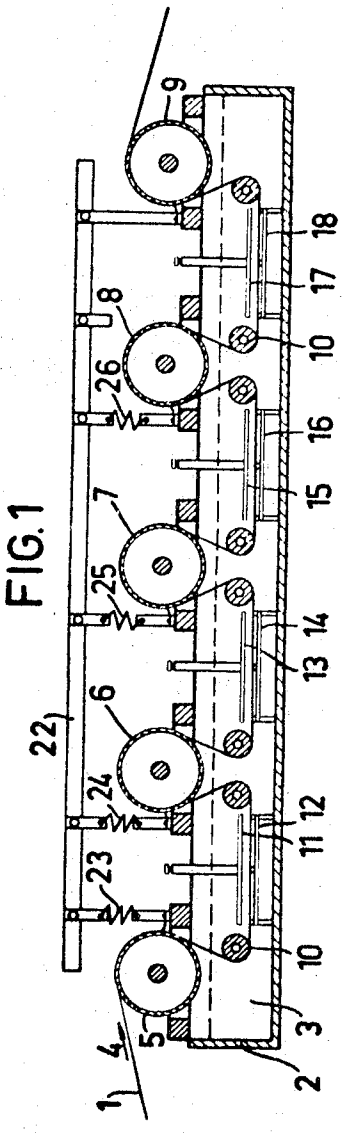
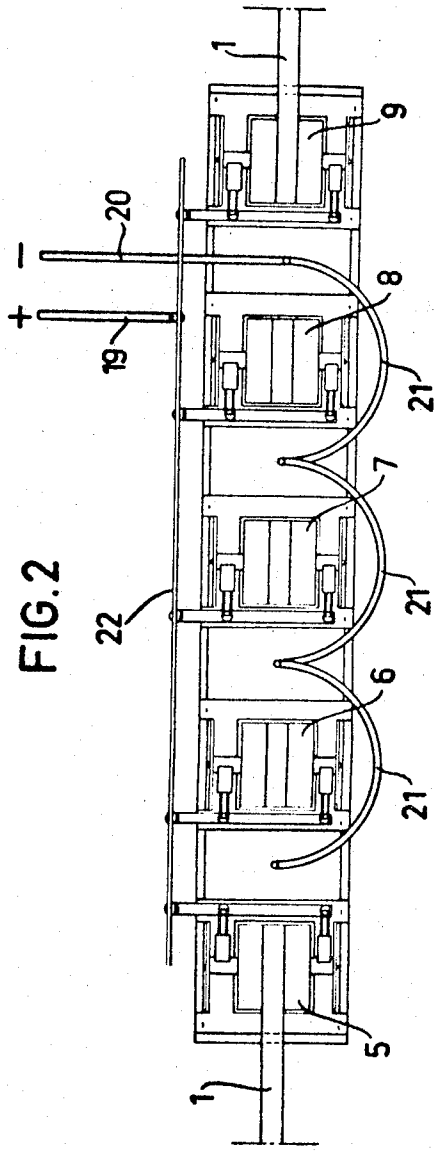


FIG. 2



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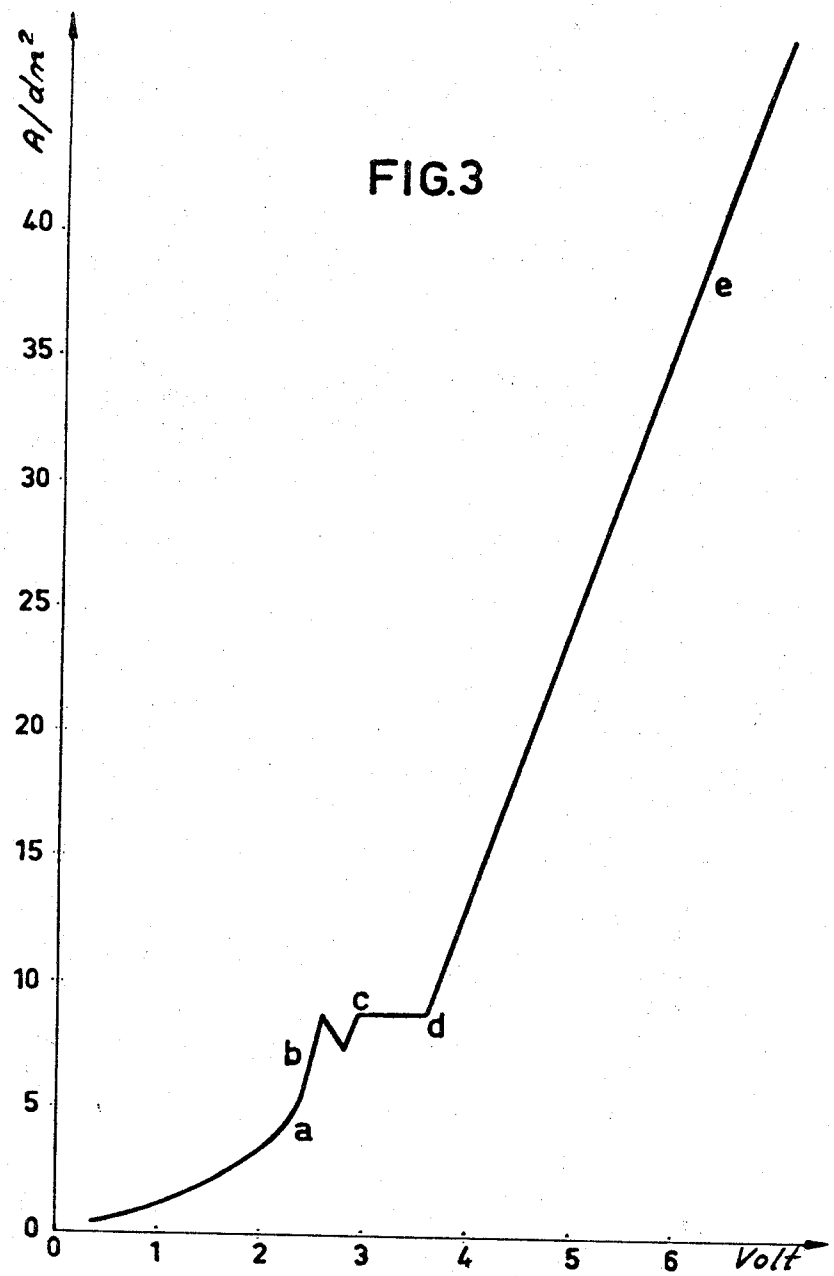
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FIG.3



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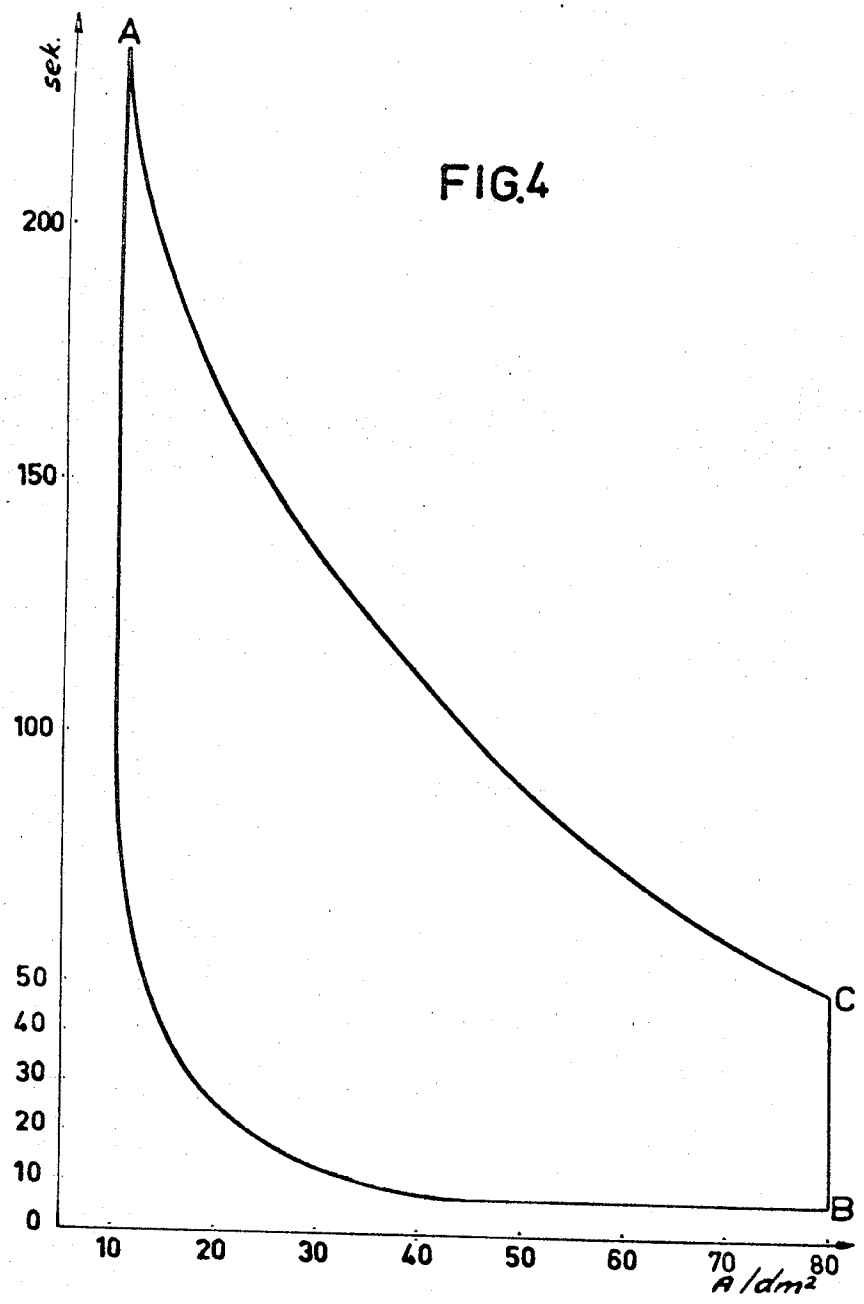


FIG.4

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3,450,610

PROCESS FOR REMOVING AN OXIDE LAYER FROM THE SURFACE OF HARDENED STRIP STEEL BY AN ELECTROLYTICAL METHOD

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Int. Cl. C23b 1/06
U.S. Cl. 204—145 3 Claims

ABSTRACT OF THE DISCLOSURE

Surface oxide electrolytically removed from hardened and tempered strip steel whilst latter moves as anode through electrolyte past a cathode. After oxide is removed, resulting oxide-free surface is passivated. Electrolyte contains in excess of 20% by weight of chromium oxide and in excess of 60% by weight of phosphoric acid.

This invention relates to a process for removing by an electrolytical method an oxide layer from the surface of hardened and tempered strip steel that is continually conveyed through an electrolyte, with the strip steel acting as the anode, and with one or several cathodes disposed in the electrolyte in such a way that the oxide layer is removed when the strip steel passes the cathode or cathodes.

In the process of the hardening and tempering of strip steel an oxide layer is normally formed upon the surface of the strip, which results in a stain on the strip. In such cases as a bright surface is desired this oxide layer has to be removed. Formerly, such a removal of the oxide layer was performed mechanically, e.g. by means of a brushing operation. When dealing with thin strips, about 0.30 mm. or less, the mechanical removal of the oxide layer may cause certain disadvantages. Thus, the strip may turn out uneven owing to the heat of friction, and in the case of very thin material (about 0.07 mm. or less) further difficulties may arise in the shape of fractures, fissures, or the like of the strip steel.

By the mechanical removal of the oxide, a surface with a specific appearance is achieved, e.g. a brushed surface, which is not always desirable. If, for instance, the cold-rolling which has preceded the hardening and tempering process has been performed in such a way that a very bright and scratch-free surface or a specific dullrolled surface has been obtained, this surface will be altered in an undesirable way owing to the mechanical removal of the oxide layer.

At times it may be difficult to remove the oxide layer by mechanical means, and on account of this the mechanical removal of the oxide layer may take a considerable length of time and may be expensive.

In the chemical or electrolytical process of the pickling, polishing or finishing of steel and metals the oxide layer is removed at the same time as a certain corrosion of the underlying metal takes place. The said corrosion causes great disadvantages especially in respect of thin strips when even an insignificant pickling effect may imply a serious drawback. Furthermore, in the process of the pickling and polishing of hardened steel it has not so far been possible to avoid subjecting the material to considerable embrittlement owing to the absorption of hydrogen.

From e.g. the German patent specification No. 763,900 it is known that a pickling and/or polishing effect appears after a long time (10–30 minutes) if low concentrations of CrO_3 mixed with phosphoric acid are used. The German

patent specification relates solely to batch treatment and not to a continual process.

The effect of the chromic acid in this connection is not commented upon in the abovementioned specification. A British patent specification No. 526,854, which also deals with electrolytic polishing but according to which an electrolyte consisting of phosphoric acid, sulphuric acid and chromic acid is used, indicates that the chromic acid has been added in order to increase the brightness of the steel surface.

The process according to the present invention serves the purpose of eliminating the inconveniences encountered in previously employed methods, and it is mainly characterized in that, after the oxide layer alone has been removed, when the strip steel passes the cathode or cathodes the surface of the underlying strip steel is passivated by means of a CrO_3-content of at least 10% by weight in an electrolyte which, in addition to CrO_3 and water, consists of at least 50% by weight of phosphoric acid.

Although the theory of passivation has not been explained in every detail it is at present considered that the mechanism consists in the creation of a multi-atomic but very thin, (about 50 A) dense oxide or hydroxide layer which prevents diffusion.

It is already known that such layers of passivation in non-alloyed C-steel can be produced by strong oxidizing agents alone, e.g. nitric acid or chromic acid, normally in high concentrations.

The passivation depends upon several factors. Thus, it was previously considered that normally no passivation of steel is met with in strong acids.

An elevated temperature and an increased current density in the electrolytical process also render the passivation of the anode more difficult in the presence of strong acids.

Phosphoric acid was proved suitable for the removal of the oxide layer. In order to increase the speed of the process, the strip steel is connected as the anode in a circuit. When only phosphoric acid is used, however, the steel lying under the oxide is also corroded with or without the use of current.

It has now unexpectedly been found that an addition of chromic acid of at least 10% by weight to a solution which, after this addition, contains at least 50% H_3PO_4 (sp. gr. 1.75) in water, effectively retards the corrosion upon the surface of the steel from which the oxide has been removed, both with and without the use of current. The following composition of the bath is suitable, the percentages being by weight:

H_3PO_4—50–68%, preferably above 60%
CrO_3—10–28%, preferably above 20%
H_2O—4–10%, preferably below 20%

The most suitable composition has proved to be:

	Percent
H_3PO_4	65
CrO_3	25
H_2O—4–40%, preferably below 20%	

Thus, the chromic acid would seem to have two functions, viz. almost completely to neutralize the corrosion upon the surface of the steel from which the oxide has been removed in the course of the electrolytic treatment and to prevent the electrolyte from the chemical corrosion of the steel before the electrolyte has been removed by rinsing.

The amount of chromic acid required for the passivation depends upon the concentration of phosphoric acid in such a way that a higher CrO_3-content is required at a higher H_3PO_4-content.

It has been found that a good effect is achieved at a temperature of not more than 35° C. and not less than 15° C. The most suitable temperature is 25° C.

The method may be employed for hardened and tempered strip steel of the following composition, the percentages being by weight:

	Percent
Carbon	0.60–1.35
Silicon	0.10–2.00
Manganese	0.20–1.50
Chromium	0.00–0.40
Nickel	0.00–2.25

and iron and impurities in amounts which are normal for such steel.

It has been found that contents higher than those indicated above as the maximum limits, render it difficult or impossible to restore the initial surface. The lower limits are fixed with due regard to the normal minimum limits for the respective material contained in hardened C-steel. A C-content below 0.60% may easily be considered per se but since the method relates to the removal of an oxide layer from hardened strip steel, a lower limit is of little interest. Example.

An example of the application of the present invention is shown in the following:

The material which consists of hardened and tempered strip steel having the dimensions 12.7 x 0.04 and a composition of:

	percent by weight
C	1.20
Si	0.23
Mn	0.35
Cr	0.13

the remainder consisting of iron and the usual impurities and which is covered by a thin oxide layer, is continually passed through an electrolyte of the composition shown below, and in which the steel is connected as the anode.

The equipment for the electrolytical removal of the oxide is shown in the attached drawing.

Temperature of the bath: 25° C.
Total length of time in the bath: 30 seconds
Composition of the bath: 65% H_3PO_4, 25% CrO_3 and the remainder H_2O.
Cell voltage: 6.0 volts
Anodic current density: 30 A/dm.^{2}
Distance between anode and cathode: 10 mm.
Relation anode : cathode surface=1:5

After such a treatment a surface completely free from oxide is obtained without the slightest visible corrosion upon the surface of the steel itself.

The current density, composition of the bath, temperature of the bath, length of time in the bath, may be varied within certain limits, and they may be adapted in such a way that only the oxide layer is removed and the underlying surface is not corroded at all or only very slightly. Thus, on the whole by this treatment the surface finish and the surface appearance of the unhardened steel will be restored. Consequently, there is no electrolytical polishing of the strip steel material.

The relation between current density and voltage is shown in the attached FIGURE 3. For cell voltages between 0–2.6 volts the current density increases considerably in the area *a–b*. Between *b* and *c* there is an area where both voltage and current density are very unstable. Between *c* and *d* the current density remains constant, while it increases very much between *d* and *e*.

If voltages to the left of *a* are applied the oxide layer upon the anode is not dissolved. Between *a* and *b* the oxide begins dissolving but in this area an etching effect is obtained. Also between *b* and *c*, a certain etching of the surface of the anode is obtained. Between *c* and *d*, a smooth dissolution of the oxide is obtained without any

trace of etching effect on the surface of the anode. Thus, point *c* on the curve represents the lowest voltage (2.9 volts) that can be applied. On the *d–e* sector of the curve the same results are obtained as on the *c–d* sector but, since here the current density greatly increases for the higher cell voltage, the dissolution of the oxide is more rapid. The current density limits cannot be determined without taking the length of time into account. It has been found that, for the *d–e* sector of the curve, which is the sector of the current density/voltage curve used in practice, the relation between current density and length of time is the one which is shown in FIG. 4 at a temperature of 25° C. Times below A–B do not result in a complete dissolution of the oxide, while times above A–C produce an incipent etching effect. With the present power supply methods current densities above 80 A/dm.^{2} seem to be very difficult to use in a continuous line owing to the risk of flash-over between the strip steel and the power supply rolls.

The values indicated in FIGURES 3 and 4 are not generally applicable to every type of bath composition and to all temperatures; they are given merely as examples of the possible variations of thes factors.

An appliance for the carrying out of the process of the present invention may be arranged in such a way that strip steel is conveyed through one or several vessels containing an electrolyte, the strip steel acting as the anode. One or several cathodes are arranged in the electrolyte.

The present invention is described in the accompanying drawing which illustrates a practical embodiment of the electrolytical treatment described above.

FIG. 1 shows in a schematized manner a section of an appliance seen from the side, and

FIG. 2 shows the same appliance seen from above.

FIGS. 3 and 4 have been referred to above.

Strip steel **1** comes from a coiling not shown here and is conveyed in the direction of arrow **4** through an existing electrolyte **3** in a vessel **2** of suitable type. On its passage through the electrolyte the strip steel passes a number of conductive rolls, so-called current rolls. In the example shown these are five in number and they are designated **5**, **6**, **7**, **8** and **9**. From the last current roll **9** the strip steel is conveyed to a rinsing and drying appliance, not shown in the example. The current rolls are arranged above the upper surface of the electrolyte. In order to lead the strip steel into the electrolyte breaking rolls **10** are arranged in the bath. Two such breaking rolls are placed between each adjacent pair of current rolls. Between each pair of the breaking rolls two starting sheets **11** and **18** are arranged, one on each side of the strip steel.

The current is fed via bars **19** and **20** directly to the current roll **9** and the cathodes **17** and **18**. The other cathodes **11–16** are connected to the cathodes **17** and **18** by means of busbars **21**. Busbar **19** is connected to the distribution bar **22**. The current rolls **5–8** are connected to the distribution bar **22** via the series resistances **23–26**.

The current rolls are preferably made of stainless steel but they could of course be made of any other suitable material. The current is conducted to the strip steel **1** through the current rolls, and the material in these shall consequently be conductive.

The cathodes **11–18** consist of stainless steel plates having a greater width than that of the strip steel and they are placed on each side of strip steel **1** at a distance of 10–30 mm., preferably 20 mm. from each other. The cathodes could of course also be made of any other resistant conductive material.

The current density is mainly controlled by means of the applied voltage.

The speed of the strip steel depends upon the current density and the length of the appliance. With an effective length of the bath of about 2.5 metres the speed can suitably be between 3 and 6 metres per minute. The speed depends of course upon the thickness of the oxide layer.

According to the process of the present invention it is possible e.g. continually to remove the oxide layer from hardened and tempered thin feeler gauge teel having a thickness of 0.02 mm. while maintaining the extremely narrow tolerances required for this type of steel. Consequently it is already possible to give the material its correct and final thickness during the cold-rolling process.

What I claim is:

1. A process for removing an oxide layer by an electrolytical method from the surface of hardened and tempered strip steel that is continually conveyed through an electrolyte, the strip steel acting as the anode, and with one or several cathodes disposed in the electrolyte in such a way that the oxide layer is removed when the strip steel passes the cathode or cathodes, in which process, after the oxide layer alone has been removed, the surface of the underlying strip steel in passing the cathode or cathodes is passivated by a CrO_3-content of 20 to 28% by weight in an electrolyte which, in addition to CRO_3 and water, consists of more than 60%, but not more than 68% by weight of phosphoric acid.

2. A process according to claim **1** wherein the strip steel has the following composition:

	Percent by weight
C	0.60–1.35
Si	0.10–2.00
Mn	0.20–1.50
Cr	0.00–0.40
Ni	0.00–2.25

and impurities in amounts which are normal for such steel, the balance being iron.

3. A process according to claim **1**, wherein the temperature of the electrolyte is below 35 centigrades.

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U.S. Cl. X.R.

204—34, 140.5