The Use of Corrosion Inhibitors in Steel Strip Production and Coating

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1. Abstract

Corrosion inhibitors are used in the steel industry in different processes for the production and plating of steel strips. For example, they are used in pickling baths for descaling after hot-rolling or in pickling baths which are located between an alkaline cleaning section and the electrolytic cells in the plating processes. Different inhibitors are required for sulphuric and hydrochloric acid pickling.

In laboratory tests performed at the research centers for surface technology of Thyssen Krupp Stahl AG (TKS) and SurTec GmbH the effect of corrosion inhibitors were studied in detail. Relatively low inhibitor concentrations protected steel surfaces from excessive pickling effects in both sulphuric acid and hydrochloric acid baths.

The use of these inhibitors in pickling solutions before zinc plating did not effect the properties of the zinc coated products or the subsequent surface treatment of them. These inhibitors increased the life time of both pickling baths and protected the steel surface during the one side plating from discoloration. By selecting the right inhibitor, hydrogen diffusion into the metal causing hydrogen embrittlement can be reduced. During descaling after hot-rolling an inhibitor in the pickling solution reduces the acid attack to the steel surface and the creation of micro flaps. To achieve a constant product quality, a regular analysis of the inhibitor concentration in the pickling bath is necessary. This can be done via HPLC-analysis or via measuring the weight losses of the test coupons during pickling.

2. Introduction

Corrosion inhibitors used in acid treatment solutions significantly reduce the overall and local pickling attack and the hydrogen absorption of steel strip. The inhibitors are extremely effective even in very small concentrations. At the same time, the lower iron dissolution leads to a considerable prolongation of the life time of the treatment solution, and the acid consumption is reduced.

For many years now in the steel industry, the use of pickling inhibitors in descaling baths after hot rolling using hydrochloric or sulphuric acid has proved to be effective. The pickling inhibitors are reducing the attack on the steel strip in the pickling line preventing the formation of micro flaps after cold rolling. On the other hand, the use of inhibitors in the acid pre-treatment of electrogalvanizing lines (EGL), which is necessary to remove oxide layers and to activate the steel surface before the electroplating process, is largely unknown.

The introduction of a pickling inhibitor into the electrogalvanizing line is intended to reduce the attack on the steel strip in the pickling area. Beside of this less corrosion active areas on the steel surface are leading to reduced iron dissolution which stabilizes the iron content in the zinc electrolyte at a lower level. A higher iron content causes a strong etching behaviour and hinders the protection of the ”cold-rolled strip side” of one-side zinc coated sheet by means of a thin zinc flash.

In cooperation with SurTec GmbH, Thyssen Krupp Stahl AG has carried out comprehensive laboratory tests to investigate the effects of a pickling inhibitor on steel strip pre-treatment in the electrogalvanizing line as well as the effects during descaling after hot rolling. Steel specimens treated in the laboratory were used to determine whether negative effects on electrolytic zinc deposition or further processability of the samples may occur when using the pickling inhibitor. Finally, operational tests were undertaken by the research department to test the feasibility in practice of the pickling inhibitor in production plants.

3. Pickling inhibitors

3.1 Functioning of inhibitors

Pickling inhibitors are interfacially active organic or inorganic substances /1, 2/. As a result of electrostatic interactions, they cover the iron surface with a monomolecular layer and thus reduce the pickling attack (Fig. 1).

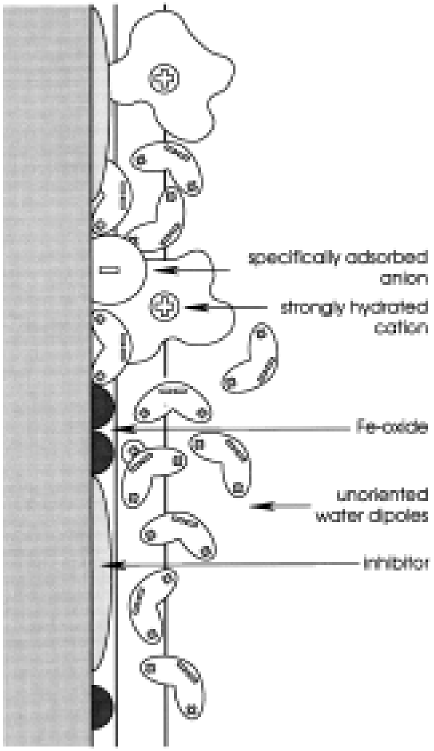

Fig. 1: Interactions of metal and inhibitor containing pickling solution

The intensity of this interaction depends on the polarity of the metal surface and the composition of the inhibitor and of the pickling medium. The polarity of the iron is different from that of the iron oxide layer, which leads to a weaker covering of the oxide layer, and thus to almost no decrease in its dissolution. Inhibitors can reduce both the metal dissolution at active centres (anodic corrosion protection) and hydrogen evolution as well as oxygen reduction (cathodic corrosion protection). This presentation is concerned only with organic inhibitors.

3.2 Chemical composition of organic inhibitors

Organic inhibitors generally feature electron-rich groups /1, 2/ that interact with the metal surface (Table 1).

Table 1: Electron-rich groups of typical organic inhibitors

Electron-rich group	Chemical formula
Alkenes	-C = C-
Alcohols	RC-OH
Amines	C-NR_2
Polymerized aromatics	Ph-X-Ph
Heteroaromatics	C_3N_3RX

4. Laboratory tests

4.1 Electrochemical measurements

Fig. 2 shows a typical current-potential curve and Fig. 3 a Tafel plot in pickling solution of 60 g/l sulphuric acid without and with inhibitor (0.1 vol% SurTec 422).

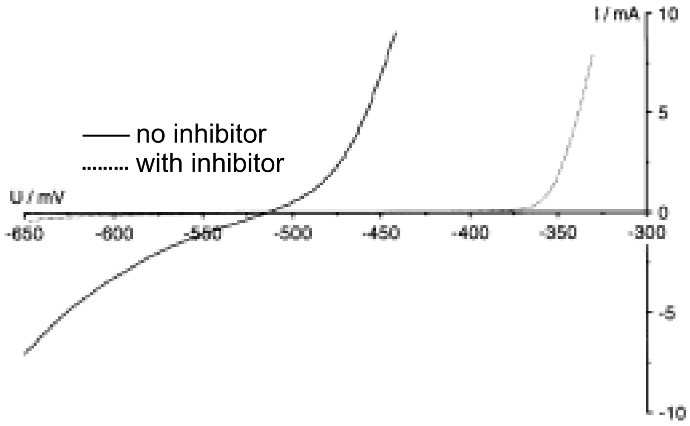

Fig. 2: Current - potential curve, 25°C, v_s = 1 mV/s, area = 1 cm^2, U = U_{SCE}

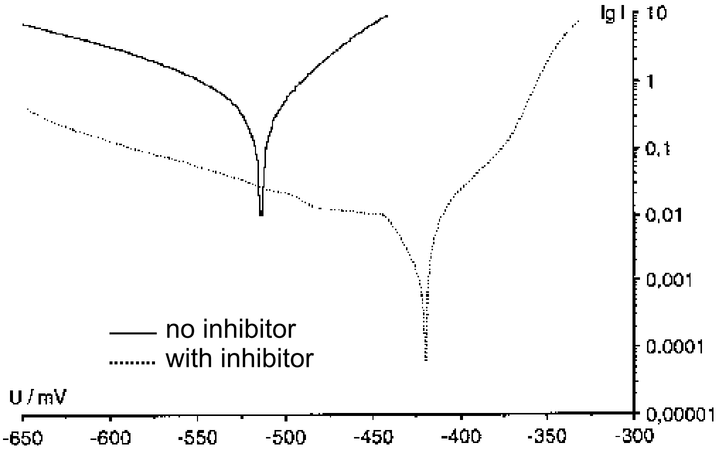

Fig. 3: Tafel plot, 25°C, v_s = 1 mV/s, area = 1 cm^2, U = U_{SCE}

It is evident that both hydrogen evolution and iron dissolution are inhibited. The corrosion current drops from 0.74 (without inhibitor) to 0.005 mA/cm^2 (with inhibitor, SurTec 422). The corrosion potential is shifted to more positive values. The considerable rise in current in the anodic area (i.e. iron dissolution) is attributable to the breakdown of the monomolecular inhibitor layer.

The use of an inhibitor in the pickling bath also has a positive effect on corrosion behaviour in the electrolyte (Table 2). Determination of the iron content in the electrolyte with the same immersion time shows that it is somewhat less in the case of pickling treatment with an inhibitor. This is attributable to the reduced attack on the steel surface and grain boundaries in the pickling bath.

The use of an inhibitor in the electrolyte is shown to be particularly advantageous. In this case, however, it is necessary to be sure beforehand that the inhibitor will neither attack any DSA anodes that may be present, nor impair crystallization and the adhesion of the zinc coating.

Table 2: Behaviour of steel in a sulphuric acid electrolyte with 20 g/l H_2SO_4;

(v_S = 1 mV/s, U_{SCE} = -650 - 400 mV, 25°C, N_2-rinsing, area = 40 cm^2)

Inhibitor	c [vol.-%]	Corr. current [mA/cm^2]	Rd [mOhm]	Fe [mg]
Without	0	0.075	208	0.17
SurTec 422	0.1	0.051	282	0.16
SurTec MS 3/96	1.0	0.043	-	0.12
SurTec MS 3/96	0.02 1)	-	-	0.10

1) No inhibitor in the pickling solution, but in the electrolyte

4.2. Influence of different pickling parameters on metal attack

Iron dissolution shows an exponential increase in accordance with temperature (Fig. 4). With 0.1 vol% inhibitor the rise is comparable, though lower by a factor of 100. In addition, the iron content, especially Fe(III), has a marked influence on the pickling attack (Table 3).

4.3 Tests with cold-rolled sheet

Cold-rolled steel sheet from mild unalloyed steel was exposed to the different treatment solutions in an immersion pre-treatment line in the laboratory comparable with the EGL-process (Table 4). In addition the samples were either only alkaline cleaned and pickled or also exposed to the zinc electrolyte without current.

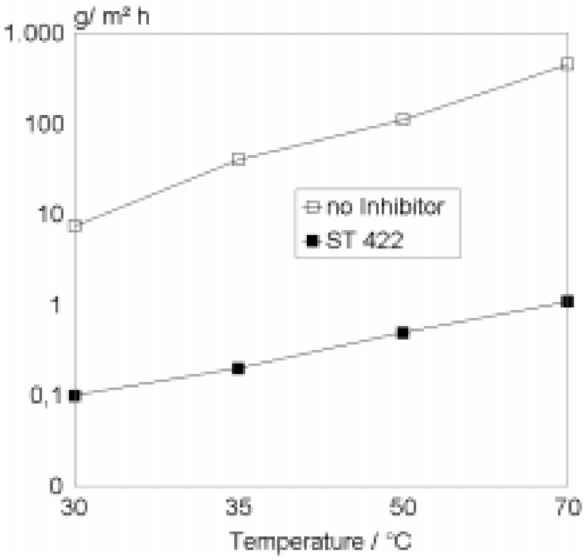

Fig. 4: Fe-dissolution vs. temperature, 10 % sulphuric acid, immersion time = 1 h

Table 3: Influence of Fe(II)- and Fe(III)-content on iron dissolution in a pickling bath

Test	Inhibitor	Fe(II) [g/l]	Fe(III) [g/l]	Fe dissolution [g/h m^2]
1	0	34	3.2	53
2	0.1	34	3.2	4
3	0.1	17	1.6	2
4	0.1	54	3.2	4
5	0.1	54	4.2	7

Table 4: Description of the treatment solutions used in the laboratory tests

Treatment solution	Composition	pH value	Temp. [°C]	Immersion time [s]
Alkaline cleaner	30 g/l concentrate	13	65	60
Pickling solution	34.1 g/l H_2SO_4 4.4 g/l Fe_{total} 0.2 Vol.% Inhibitor	< 1.0	50	10
Zinc electrolyte	79.8 g/l Zn 17.1 g/l H_2SO_4 62.5 g/l Na_2SO_4 1.9 g/l Fe_{total}	1.2	55	10

A scanning electron microscope (SEM) was used to evaluate the change in the surface formation caused by contact with the process solutions, and to monitor the effect of adding the inhibitor.

In the initial state the cold-rolled (CR) steel surface shows only the topography resulting from cold-rolling, batch-annealing and temper rolling, and appears altogether uniformly dark grey (Fig. 5a).

Fig. 5a: Initial state of the CR-sample

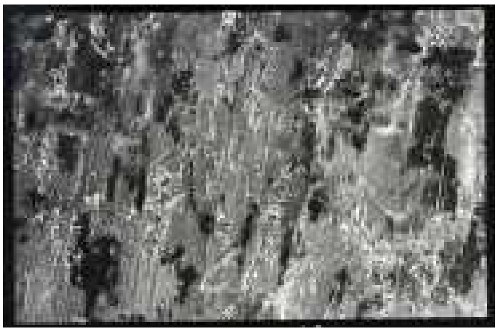

Fig. 5b: CR-sample pickled without inhibitor

Fig. 5c: CR-sample pickled with inhibitor

On the other hand, after alkaline electrolytic cleaning and pickling in sulphuric acid without or with inhibitor, light-grey areas are apparent on the CR-strip surfaces, and are attributable to an intensified corrosive attack of the pickling solution with local etching of the steel surface. Samples pickled without inhibitor (Fig. 5b) show an overall attack on up to 80 % of the CR-strip surface, which can be reduced to about 10 to 20 % by addition of inhibitor (Fig. 5c).

The combined action of alkaline cleaner, pickling solution and zinc electrolyte (currentless) results without pickling inhibitor, as anticipated, in a wide-coverage corrosive attack, which can be detected as a light-grey surface area in the SEM image (Fig. 6a). If an inhibited pickling solution is used the protective effect on the steel surface is also obtained with the subsequent electrolyte contact (Fig. 6b). Then, however, the light-grey areas are subject to a stronger local pickling attack.

Fig. 6a: CR-sample after pickling <u>without</u> inhibitor and electrolyte contact

Fig. 6b: CR-sample after pickling <u>with</u> inhibitor and electrolyte contact

The sheet samples pickled with or without inhibitor were treated in the laboratory phosphating devices (immersion or spray phosphating), in order to test the phosphatability of the cold-rolled steel surface. The coating weight of the phosphate layer was determined and crystallization was checked by SEM for form, size and uniformity. No significant differences from the usual phosphate layer structure on cold-rolled steel were observed.

4.4. Testing electrogalvanized laboratory samples

In order to evaluate the influence of a pickling inhibitor on the further processability of electrolgalvanized sheet, slit steel strip (width 100 mm, thickness 0.8 mm) was galvanized on one side in a electrogalvanizing pilot line (Fig. 7).

The specimens, with a zinc coating thickness of approx. 7 µm, were tested with regard to coating adhesion and zinc crystallization shape.

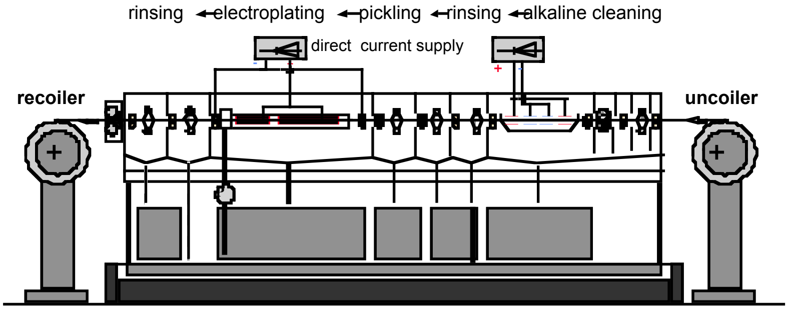

Fig. 7. Laboratory Electrogalvanizing Line of the Thyssen Krupp Stahl AG

The adhesion of the zinc coating was tested at ambient temperature and after heat treatment at 300 °C. To assess adhesion at ambient temperature, the specimens were stretched by approx. 20 % in a tensile testing machine, and finally the surface was inspected microscopically for any detachments of the zinc coating. In addition, the adhesion of the zinc coating after heat treatment (300 °C/30 min) was checked by means of a Tesa tape test. The specimens tested exhibited a good adhesion of the zinc coating both with and without the addition of inhibitor to the pickling solution.

It was possible to exclude an influence of zinc crystallization on the basis of the laboratory tests. The SEM-tested zinc structure of the coating was in accordance with the known forms of crystallization, i.e. oblique or base-oriented zinc crystals, depending on the plating current density (Fig. 8 a-b).

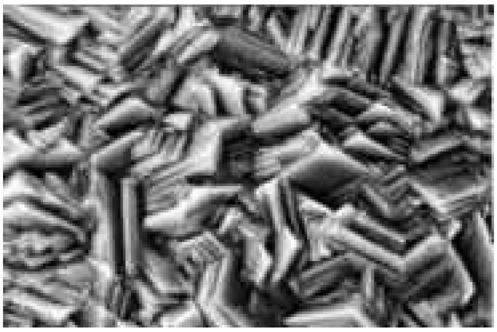

Fig. 8a: Zinc coating with oblique crystals

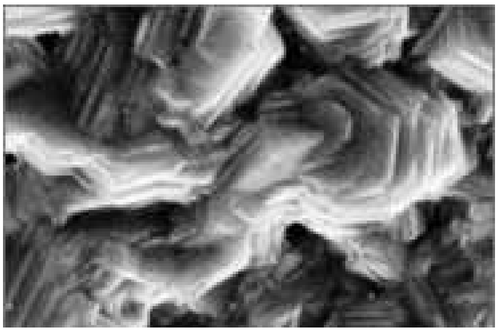

Fig. 8b: Zinc coating with base oriented crystals (magn. 3000:1)

The results with respect to adhesion and crystallization of the zinc coating allow the conclusion that the inhibitor applied with the pickling solution is no longer present on the cold-rolled strip surface before entry into the electrolytic cells of the EGL.

4.5 Hydrogen diffusion

The hydrogen permeation in a pickling solution with approx. 50 g/l H_2SO_4 and 3 g/l Fe_{total} was measured on cold-rolled sheet specimens of a soft unalloyed steel. Tests with and without inhibitor in the pickling solution showed that hydrogen permeation, and consequently the absorption of active hydrogen, can be considerably reduced by the addition of inhibitor. Fig. 9 offers a graphic representation of the results of permeation measurement with an inhibitor concentration of 0.10 vol%.

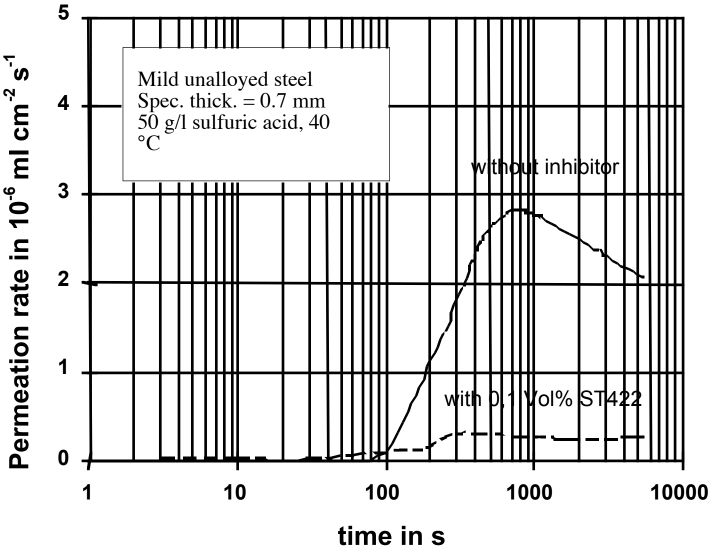

Fig. 9: Hydrogen permeation in pickle using an inhibitor

Table 5: Behaviour of different rinsing techniques on the surface using an inhibitor

Test No.	Pickle *)	Rinse	Red rust [%]
1	30 s, no inhibitor	pH 1.8	100
2	30 s, 0.1 vol% SurTec 422	pH 1.8	100
3	30 s, no inhibitor	neutral	5 -10
4	30 s, 0.1 vol% SurTec 422	neutral	1 – 5
5	as # 4	neutral + brushing	10-20

*) 70.8 g/l H_2SO_4; 4 g/l Fe_{total}; 40°C

4.6 Rinsing technique

An acid rinse after pickling removes an inhibitor film completely like a mechanical brushing, as it was shown by laboratory corrosion tests (Table 5). In this case, steel specimens are pickled with or without inhibitor, variously rinsed, and finally dried in the air. There is a lower proportion of red rust if inhibitor remained on the cold-rolled steel surface.

5. Results of the TKS production trials

5.1 Production trial EGL # 2, Duisburg

The first application of the findings of the laboratory tests was the experimental use of the inhibitor in the sulphuric acid pickling zone of the EGL # 2, Duisburg. A inhibitor concentration of 0.1 vol% was maintained by addition of 3 l inhibitor concentrate per shift to the pickling bath. The two-stage spray pickling zone was applied with a specific overflow to ensure an Fe_{total} content of < 5 g/l.

The specific concentration of pickling inhibitor and of the other main elements was determined at regular intervals by chemical analysis of the pickling solution and of the zinc electrolyte. The inhibitor concentration was determined in accordance with the supplier's specification, initially with a UV spectral photometer, and later by means of High Performance Liquid Chromatography
(HPLC).
The principal findings of the production trial are:

- Discontinuous addition of the inhibitor concentrate or continuous addition by means of a controlled volume pump does not guarantee the adjustment of a constant inhibitor content. Consequently the controlled addition of inhibitor should be supplemented by the addition of fresh water.
- No carry-over of inhibitor into the zinc electrolyte was observed during check analyses. It was possible to stabilize the iron content in the zinc electrolyte in a range of < 2 g/l Fe_{total} with the existing bath parameters.
- The utilization properties of the electrogalvanized sheet, i.e. adhesion, phosphating behaviour etc., are not impaired.

5.2 Production trial EGL # 1, Bochum

An inhibitor was used experimentally in EGL # 1, Bochum on the basis of the positive results in Duisburg's EGL # 2. The spray pickling section is used without overflow, which leads to a constant iron enrichment in the sulphuric pickling solution. The pickling solution is renewed when it reaches 25 g/l Fe_{total}. The entrainment losses associated with the throughput of the steel strip are compensated by the addition of acid and fully demineralized water.

The chronological course of the concentration of the pickling inhibitor, of the sulphuric acid and of the iron content was determined analogously to the procedure in EGL # 2, Duisburg by analysis of the pickling solution and of the zinc electrolyte. It was possible to slow down the iron increase in the pickle significantly by adding inhibitor, so that the Fe_{total} -content reached 25 g/l only after about three months (Fig. 10).

The principal findings of the production trial are:

- The life time of the pickling solution is extended by the addition of inhibitor from 1 to more than 3 months.
- Discontinuous addition of the inhibitor concentrate (always 1 l per shift) does not lead to the adjustment of a constant inhibitor content.

- No carry-over of inhibitor to the zinc electrolyte was observed in check analyses.
- The properties of the electrogalvanized steel sheet, i.e. adhesion, phosphating behaviour etc., are not impaired.

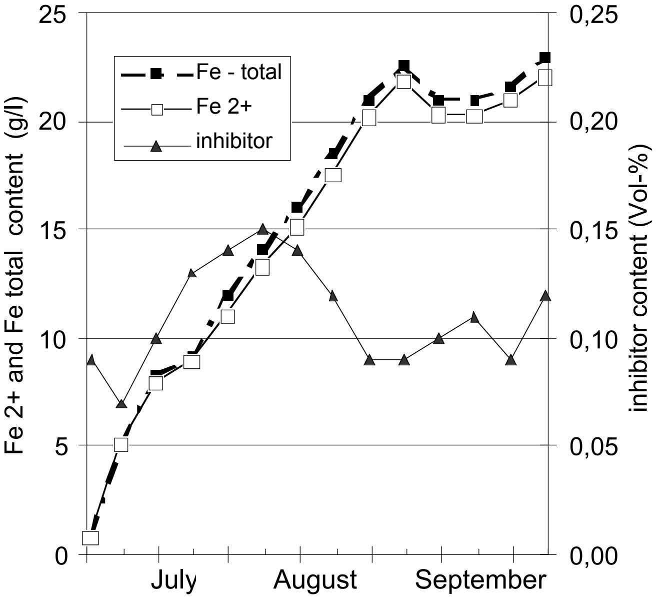

Fig. 10: Fe-content vs. time, 5% sulphuric acid, temperature 45 °C

5.3 Production trial EGL, Neuwied (Rasselstein AG)

Before its coating section, the electrogalvanizing line of Rasselstein AG (RaAG) in Neuwied includes an immersion pickle stage operated with hydrochloric acid without overflow. Finally, there is a cascade rinsing section.

Until now, fresh pickling solution was applied before the start of a one-side strip coating production campaign, to ensure a visually faultless „cold-rolled strip side” of the one-side coated sheet. A variably strong etching attack of the pickling solution and ZnNi electrolyte on the steel surface can result in optical roping on the uncoated steel side, which is attributable to a locally limited, increased pickling attack and associated slight differences in roughness.

It was possible to reduce the iron increase in the pickling solution by more than 60 % by adding 2 vol% of an inhibitor appropriate to hydrochloric acid (Fig. 11).

The principal findings of the production trial are:

- The inhibitor leads to a threefold prolongation of the life-time of the pickling solution.
- There is a parallel 50 % reduction in acid consumption.
- A positive effect on the macroscopic appearance of the ”cold-rolled strip side”, especially with one-sided coating, is observable as a result of the reduced pickling attack.

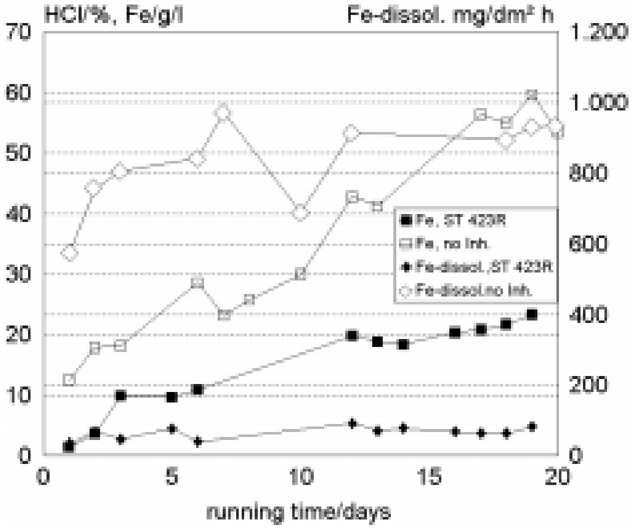

Fig. 11: Fe-content and Fe dissoloution rate vs. time 2 vol% SurTec 423 R, approx. 20 % hydrochloric acid, 25°C

6. Inhibitors used for descaling after hot roll mill

Pickling solutions for descaling after hot rolling are much more agressiv compared to the pickling before electroplating. Usually the acid concentration (hydrochloric acid, sulfuric acid >150 g/l), temperature (60-95 °C) and immersion time (>15 s) are high. Due to cracks in the oxide layer the removal is not homogeneous (especially when sulfuric acid is used) leading to a local attack of the base metal as shown in principal in figure 12.

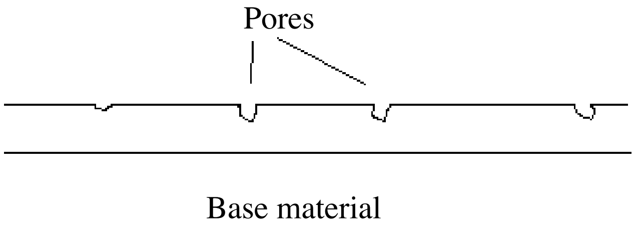

Fig. 12: Attack of the base material during descaling

During cold rolling some of these pores are closed leading to micro flaps, see figure 13.

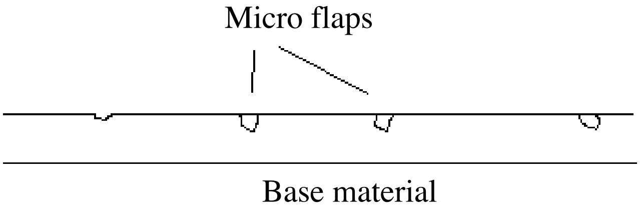

Fig. 13: Creation of micro flaps during cold rolling

After zinc plating, followed by laquer and heat treatment some of these flaps are opened creating pine holes as shown in figure 14.

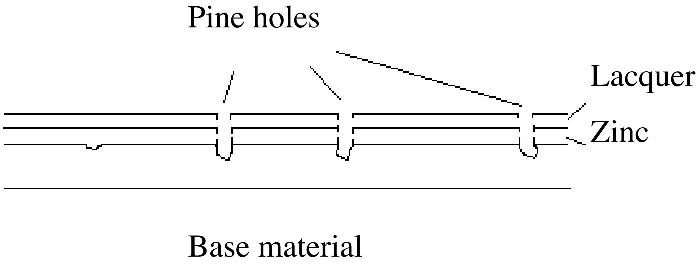

Figure 14. Creation of pine hols after heat treatment

As discussed in detail before an inhibitor reduces the attack of the base material with more or less no influence on the descaling. This reduces the creation of micro flaps strongly.

7. Analysis

A regular analytical inspection of the inhibitor concentration, ideally within the range of +/-30 % of the recommended concentration, is required for the following reasons:

- The inhibition is considerably reduced if the concentration is too low.
- Two- or three-fold overdosing is also disadvantageous.
  - The inhibition does not increase any further.
  - Costs rise without any additional benefit.
  - A drastic overdose can lead to reduced activation of the steel surface and to adhesion problems, which are especially critical in the case of ZnNi-coatings.
  - There is a danger of carry-over into subsequent areas.

The following methods were used to determine the concentration:

7.1 UV analysis

If the inhibitor is UV-active, the inhibitor content can be rapidly and inexpensively determined at the very start in a clear pickling solution. With a long service life, however, the pickling solution becomes discoloured and UV determination leads to imprecise results.

7.2 HPLC

High Perfomance Liquid Chromatography is certainly the best process, since it produces exact, reproducible results irrespective of any bath contamination. The analysis, however, is expensive and time-consuming.

7.3. Indirect determination by means of iron decrease

Since an inhibitor leads to a marked reduction in weight loss, its effectiveness can be ascertained by determining the decrease. Since only a balance is needed, the process is simple and can be carried out on site. Overdosing, however, cannot be ascertained in this way.

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