Journal of Korean Institute of surface Engineering
Vol. 32, No. 3, Jun., 1999

Ferrous Chloride Pickling Bath
A new process for pre-treatment of metals

U. H. Ericson*, H. A. H. Ericson**

** Korrosionsforskning AB, Sweden, ** Corrint Svenska KB, Sweden*

Abstract

A new additive for semi-brightness finish in nickel electroplating, having a quarternary ammonium salt structure, has been developed in this study. The effectiveness of the new additive was tested in laboratory-scale eletroplating tests as well as in a full-scale factory plating line. An examination of the plated surface showed that the new additive is as good as the one produced by the most commonly used additive in the nickel plating industry. The plated surface was examined by SEM, EPMA, and Reflectance Spectroscopy, and was found to be compatible to the one obtained with commercial additives. The new additive has a shelf life comparable with those of other commercially available additives. The additive developed in this study has an excellent potential to be used commercially.

Key words : *Nickel electroplating, Semi-brightness finish, Satin effect, Plating additives, Quarternary ammonium salt*

1. Background

This process system relates to methods for pickling iron or steel objects, before a subsequent surface treatment or a mechanical processing.

Before the mechanical processing of objects of iron or steel, e.g. by drawing, milling or pressing, or before application of any anti-corrosive film, the surface coating usually must be removed. This coating can comprise various oxides, e.g. rust, being formed by chemical corrosion. Other coatings can consist of scale from a preliminary heat treatment or rolling skin from a preliminary rolling. These different coatings are normally removed by pickling in acid baths.

Normally, either sulphuric acid or hydrochloric acid is used for pickling carbon steel or cast iron. The former is less expensive to buy, but the hydrochloric acid presents several technical advantages, often making the total economy for this acid the most profitable.

A pickling bath intended for pickling with hydrochloric acid normally comprise about 200 g HCl per liter. During pickling, normally performed at a temperature of about 20℃, iron is solved as Fe^{2+}. The proportion of iron in the pickling bath rises gradually until it, after some use, reaches about 80~85 g per liter pickling solution. The proportion of acid in the pickling bath is now about 80-100 g per liter pickling solution. The pickling continues very slowly during these circumstances making it necessary to exchange the pickling solution for regenerating or dumping. In total, 10-12 kg of hydrochloric acid is used per kg of dissolved iron.

2. Regeneration of pickling baths

The depositing or regenerating of used pickling solution is vary important from various points of view. Partly because these pickling baths constitute a dangerous waste, which has to be destructed before deposition. Partly because the pickling bath has a significant value with respect to the content of remaining free acid, solved iron and a corresponding amount of negative ions.

The hydrochloric solution can be regenerated through a roasting process within an oil-burning oven. Thereby the solved iron forms iron oxide and hydrogen chlorine. The later is absorbed while the pickling acid is recovered. One disadvantage with this process is that a certain amount of hydrogen chlorine is lost because also the remaining free acid goes into the oven.

It is also possible to regenerate the pickling solution through electrolysis. The iron in the solution will be deposited at the cathode of the electrolytic cell. The electrolyte (the pickling solution) must form an almost neutral solution of ferrous chloride in order to enable the electrolysis. Since the pickling solution, however, contains a comparatively large proportion of remaining acid, there will mainly be development of hydro gen gas at the cathode, i.e. the deposition of metal will be small in relation to used electric energy.

The solution can be neutralised by evaporation and crystallisation of iron chloride and separation of remaining surplus acid, which can be returned to the pickling process.

Because of the solubility of iron chloride, the evaporation of the bath must be complete to enable crystallisation. Further more, the subsequent electrolysis will consume a lot of electric energy, since a great deal of the chloride is used up by the development of gas, while oxidation of ferrous chloride to ferric chloride takes place at the anode. The gradual increase of Fe III changes the polarity leading to the forming of basic salts while the electrolytic efficiency declines steeply.

From this, an electrolytic cell for recovery of pickling acid must have a ion-exchange membranes as a partition between anode and cathode, so that the acid formed at the anode will not prevent the deposition of metal at the cathode.

By using a pickling bath with a high concentration of iron and a low concentration of acid, electrolytical regeneration can be performed without ion-exchange membranes. However it can be favourable to separate the flow through the anode chamber from the flow through the cathode chamber. This can be done with simple diffusion membranes. A high current efficiency can be obtained with high circulation flow over the regenerating unit, with small differences in concentration in the incoming and outgoing bath solution.

3. Pickling bath compositions

A useful pickling solution may comprise between 100-200 g free hydrochloric acid per liter solution with between 0-80 g Fe^{2+} and usually attacks the base metal furiously. When objects of iron or steel with scales, normally comprising Fe_2

$O_3 \times FeO$-oxides, are pickled, pittings occur. This happens because the surface of the base metal usually is rather small compared to the oxide surface, i.e. the cathode, wherein the oxide has high electric potential in relation to the iron within said solution and is cathodic in relation to the base metal, which becomes the dissolving electrode, because of its anodic potential. Therefore, the scales are not dissolved in the acid, but rather " explodes" away from the surface, because the acid penetrates below the scale and lifts it away. The consequence is severe pittings on the base metal, because of the anodic current density (corrosive current) is very high. While the proportion of acid in the solution declines, the difference of potential also declines and thereby the pickling effect of the solution. The Fe_3O_4- oxide is deposited as sludge on the bottom of the pickling bath. The proportion of iron rises during conventional pickling, while the proportion of acid declines. At the beginning of the process the difference of potential between the iron oxides is at least 1000 mV. The base metal Fe then acts as anode, meaning that the iron oxides form $Fe^0 \rightarrow Fe^{2+}$. The surface of the metal is therefore pitted when it is exposed by fractures and pores in the oxide coating. It is normal to use an inhibitor or restrainer in the pickling bath to reduce the pitting damage on the base metal.

With a continuing pickling operation the concentration of iron will increase. At the same time a corresponding amount of acid is consumed. When the concentration of iron will pass 90-100 g per liter the process reaction will go down and the corrosion on the base metal will be very low. The chemistry of the bath has totally changed. The iron in the bath has gone over from a cathoinic Fe^{2+} -form to a complex $(FeCl_4)^{2-}$ anion. Since the pickling is carried out at a high concentration of iron and therefore a low proportion of free acid, the oxides are dissolved without any or very little pitting of the base metal. The favourable pickling effect, in spite of high concentration of iron in the pickling solution, is a result of the ability of chloride to form large complexes. At an iron concentration of 200 g per liter the concentration of free acid is very low and the solution will be easy to maintain either by chemical regeneration or a partly electrolytic treatment.

3. Ferrous chloride pickling advantages

First of all it is a much more resource lean process than the conventional pickling process. The acid consumption is much lower, the volume of spent pickling bath is much lower, the dissolving of the base metal is also less. The cost for neutralising and destruction is reduced in the same degree. This sums up to a process that is not just more environmental friendly but also more economical.

The more even surface after the pickling prolongs tool and die life in a eventual following mechanical processing. We have also observed that the smaller surface area and the decline of product rejects saves, for example zinc in hot dip galvanising.

The risk for hydrogen embritlement is much less due to that less hydrogen gas will be formed.

Several positive side effects can also be observed, for example the acid fumes from the bath, even at a higher bath temperature are considerable less. This gives a much better work environment. The need for ventilation is reduced.

The process is a continuous process with fixed bath composition, giving a more uniform quality.

Provided that the pickling bath is free from other heavy metals the spent bath can be used for the control of phosphates in sewage treatment plants. Simultaneous precipitation in an activated biochemical bed is used.

Due to the high concentration of metal and the low concentration of free acid the conditions for several different regenerating systems are favourable.

4. Case stories

The most interest for this pickling system has been from industries that use large quantities of pickling solutions, for example steel wire and band forming and hot dip galvanising industry.

In the electro plating industry the interest has focused on the advantage of less risk for hydrogen embritlement and the more uniform quality.

Example 1.

A wire drawing industry, producing 13,000 tons per year of low carbon steel wire. Wire diameter (mean value) 6 mm.

Operation disposition.

1.	Corrint ferrous chloride pickling	24,000 liters
	Fe^{2+}	185 g per liter
	HCl	35 g per liter
	Additive Corrint 110	1 ml per liter
	Additive Corrint 115 LF	3 ml per liter
	Temperature	35℃
2.-3.	Counter flowing rinses.	3 m^3 per hour
4.	Borax bath	8,000 liters
	Borax 10 aq	75 g per liter
	Temperature	70℃
5.	Hot air drying	

To ferrous chloride pickling bath, about 1 m^3 of HCl 30% is transferred every day (300 ton per year). At the same time the same volume of pickling bath is pumped over to a storage tank for later transportation to the local sewer plant for phosphorous control (400 ton per year).

	Conventional Hydro chloric pickling Cost per year US $	Corrint Ferrous chlorid pickling Cost per year US $
HCl 30 %	75,000	37,500
Spent pickling bath	100,000	-12,500
Additives	7,000	25,000
	182,000	50,000

The concentration of acid could be lower and at the same time the concentration of iron higher. This is not possible today due to poor bath agitation. If a good bath agitation could be installed the cost for acid could be reduced further.

Example 2.

A hot dip galvanising industry, producing 12,000 tons per year of galvanised products. Mostly big constructions.

Operation disposition.

1.	Alkaline degreasing	55,000 liters
	pH	10
	Temperature	30 ℃
2.	Corrint ferrous chloride pickling	110,000 liters
	Fe^{2+}	195g per liter
	HCl	25g per liter
	Additive Corrint 110	2ml per liter
	Additive Corrint 115 LF	2ml per liter
	Temperature	35℃
3.-4.	Counter flowing rinses.	0.1 m^3 per hour

5. Preflux 55,000 liters
   Zinc ammonium chloride 400g per liter
   Temperature 70℃
6. Hot air drying
7. Hot dip zinc

To ferrous chloride pickling bath, about 0,5 m^3 of HCl 30% is transferred every day (120 ton per year). At the same time the same volume of pickling bath is pumped over to a storage tank for later transportation to the local sewer plant for phosphorous control and unfortunately to destruction due to contamination of zinc (160 ton per year).

	Conventional Hydro chloric pickling Cost per year US $	Corrint Ferrous chloride pickling Cost per year US $
HCl 30 %	45.000	15,000
Spent pickling bath	50,000	10,000
Additives	2,000	10,000
	97,000	35,000

The company is at this moment building a new plant. This plant will be totally automated and prepared for an electrolytic regenerating unit. The amount of waste leaving the new plant will be extremely low.

5. Summary

1) Using a continuous "feed & bleed" process gives a more unified quality. This is important when working under a certified quality system. It will also save process chemicals and produce less waste.

2) Pickling in a ferrous chloride bath will give a more even surface structure, this benefits the after following processes. Ferrous chloride pickling saves process chemicals and produce less waste. The produced waste is also more economical to take care of.

3) A ferrous chloride bath is suitable to regenerate. When using electrolytic regenaration an high current efficiency can be obtained under the right circumstances.

4) The spent pickling bath can be used for alternative processes.