Application Bulletin

Of interest to:	General analytical chemistry, metals / electroplating, iron, etching bath, Fe^{2+}, Fe^{3+}, steel	P 1, 10

Determination of Fe^{2+}, Fe^{3+}, total and free acid in an etching bath (steel industry)

Summary

Acid etching baths are used for oxide removal and cleaning of the surface of different types of steel. To keep the bath in an optimum condition the Fe^{2+}/Fe^{3+} and free acid/total acid ratios must be maintained within certain limits. Auxiliary substances like hydrogen peroxide are added to influence the Fe^{2+}/Fe^{3+} ratio, which is responsible for a constant activity of the bath.

The quality of the end products depends directly on the correct composition of the etching bath. Keeping these parameters in an optimum range results in a permanently higher quality and at the same time lowers costs due to lower reagent consumptions.

This bulletin describes the monitoring of an etching bath in the steel industry. ProcessLab offers a solution that automatically evaluates the desired bath parameters (free acid, total acid, Fe^{2+} and Fe^{3+}). Due to the flexibility offered by ProcessLab the determination of hydrogen peroxide can be integrated very easily.

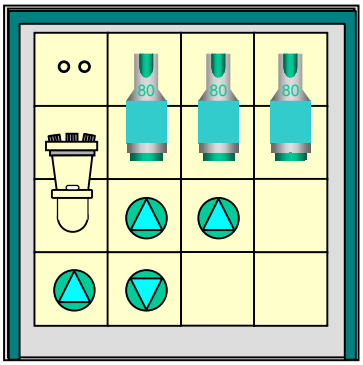
Features/general information

- All 4 parameters in one system
- OneButton analysis
- Easy to operate for semi-skilled staff
- Direct feedback of the measured results to the process control system
- Can be used for different baths without additional costs
- Additional parameters can be measured at minimum costs (e.g. H_2O_2)
- The method can be used in the lab as well

Accessories used

- 1 x 2.875.0010; 875 ProcessLab Base Unit L, 1 Metrohm Dosing & Measuring Controller (incl. IPC, I/O controller and TFT/Keyboard terminal)
- 2 x 6.7201.000; Measuring amplifier
- 3 x 2.800.0010; 800 Dosino
- 2 x 6.3032.220; Buret 20 mL
- 1 x 6.3032.210; Buret 10 mL
- 2 x 6.7205.020; Peristaltic pump 320 mL/min
- 2 x 6.7205.030; Peristaltic pump 120 mL/min
- 1 x 6.0259.100; Unitrode
- 1 x 6.0451.100; Comb. Pt ring electrode
- 1 x 6.7202.100; Digital input 4 DI 24V DC
- 2 x 6.7202.200; Digital output 4 DO 24V DC
- 1 x 6.7202.400; Analog output 2 AO 4-20 mA

Wet part layout



System view

Reagents

- c(NaOH) = 0.1 mol/L (Dosino 2)
- c(KF) = 3 mol/L (Peristaltic pump; 120 mL /min)
- $c(Ce(SO_4)_2)$ = 0.1 mol/L (Dosino 3)
- Demineralized water (Peristaltic pump; 320 mL/min)

Calibration and storage of the sensors

- Electrodes have to be checked regularly for correct function
- When not used the Unitrode is stored in 3 mol/L KCl (250 mL; 6.2308.020)
- The redox electrode (Pt ring) can be stored in demin. water if not in use

Theory

General information

A freshly prepared bath will have nearly the same content of free and total acid. During a lifecycle the amount of free acid decreases. These analyses described here allow to decide whether a bath needs to be replenished or not.

There are mainly 2 types of baths which are used for the etching of steel.

Classical bath

The classical bath contains 10-28% HNO_3 (50%), 3-8% HF and 0.1% detergents. Nitric acid is a strong oxidant and prepares the surface for being passivated in the air.

Nitrate-free bath

To reduce environmental hazards (evolution of nitrous gases) nitrate-free baths are often used. These consist of 3-5% HF, 10-25% H_2SO_4/H_3PO_4 and 1-5% H_2O_2. Due to the additional oxidant H_2O_2 it is necessary to analyze this parameter as well and substitute the reagent if needed.

Parameters

Sampling

Sampling is done via the so-called Dosino loop (Dosino 1), but instead of a 150 cm tubing a normal Metrohm tubing has been used. A sample size of 1 mL requires a minimum volume of 2 mL, which corresponds to a tubing length of appr. 60 cm.

Free acid

The free acid is needed to remove tinder layers and coloring of the steel due to welding treatments. Additionally a stable passivation layer is formed which prevents the material from oxidizing further. The analyzed parameter corresponds to the content of acid which is available for the etching process. The type or mixture of acid may vary as the requirements of the process differ from plant to plant. An end-point at pH 4.2 is often used for determining the free acid.

Total acid

During the lifetime of an etching bath the content of metal ions constantly increases. The metal salts formed have slightly acidic properties and react in this analysis as well. In most cases an endpoint at pH 8.6 is set and used for the calculation of the total acid content.

Fe^{2+}/Fe^{3+}

The Fe^{3+} is calculated from the difference of total acid and Fe^{2+}. The ratio of Fe^{2+}/Fe^{3+} gives a measure of the oxidative properties. If needed this can be corrected by addition of an oxidant like H_2O_2. The overall content of iron increases as well and allows a conclusion about the actual condition of the bath.

Analysis

Free acid

After sampling the sample is transferred into the vessel and diluted with water. Then the addition of KF is necessary to mask the iron, otherwise it will react as well in the titration. The titration is done to the endpoint of pH 4.2, which refers to the content of free acid.

Total acid

A proper amount of sample is taken and pipetted into the vessel. After diluting the sample with demin. water the titration is performed using 0.1 mol/L NaOH. The first inflection point at pH 4.2 corresponds to the free acid, the second one at pH 8.6 is equivalent to the total acid.

Fe^{2+}

The sample is measured into the titration vessel and then diluted with demin. water. The resulting endpoint using the Pt electrode and Ce^{4+} as titrant corresponds to the Fe^{2+} content.

Fe^{3+}

The Fe^{3+} content is calculated from the difference between total acid and Fe^{2+}.