The ProcessLab atline analysis system with operating unit and autosampler

Metals in dip coating baths

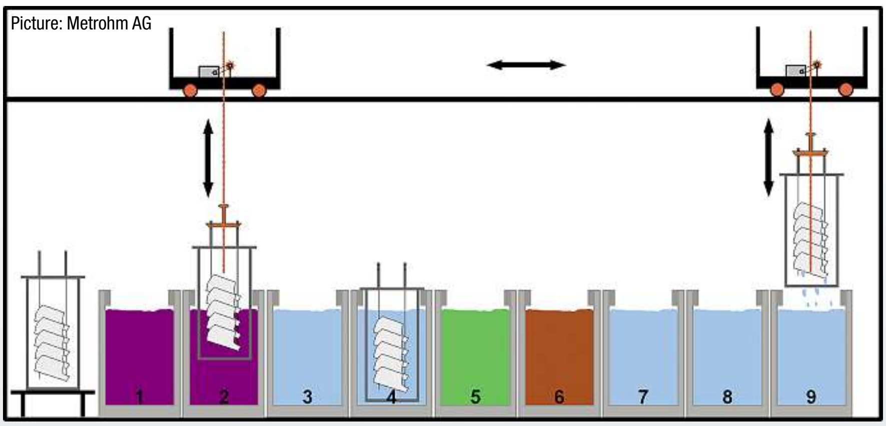
Phosphatizing of metal surfaces using an atline analysis system

With an estimated worldwide turnover of more than $ 500 million, phosphatizing is the most important metal pretreatment process. ProcessLab is a customizable modular atline analysis system that records, controls and documents all important analytical bath parameters of the entire phosphatizing process.

Frank Portala, Alfred Steinbach, Franz Müller, Michael Feige and Gerhard Kirner

The phosphatizing process produces a hard, electrically non-conducting surface coating that adheres tightly to the underlying metal. This layer protects the metal from corrosion and improves the adhesion of paints and organic finishes to be subsequently applied.

The basic phosphatizing process consists of the etching reaction and the formation of the surface coating. After thorough degreasing and rinsing of the metal workpieces, the phosphoric acid removes interfering surface-bound metal oxides and increases surface roughness. Subsequently, the alkali phosphates react with the previously generated metal ions at the surface of the workpiece, forming a layer of insoluble tertiary metal phosphates. With a coating thickness smaller than 1 µm, iron phosphate coatings provide a basic corrosion protection and are intended for interior use under controlled environments. In contrast, the addition of metal cations such as Zn^{2+}, Mn^{2+} and Ca^{2+} to the phosphatizing bath results in the formation of very resistant mixed-metal phosphates with a coating thickness between 7 and 15 µm. Due to a modified crystal structure these layers are perfectly suited for outdoor use or rough interior environments. Both iron and zinc phosphatizing occur by the same mechanism. However, the latter process is characterized by the preferential incorporation of zinc cations. The iron cations at the metal surface hardly contribute to the metal phosphate formation. A first-class corrosion protection is achieved by the supplementary addition of further cations (e.g. Ni^{2+}) to the phosphatizing bath, resulting in even better surface properties.



Operating sequence of the phosphatizing process

Degreasing baths (1, 2):	removal of oil, grease and wax residues from the metal surface
Rinsing baths (3, 4):	elimination of degreasing chemicals with water
Activation bath (5):	activation of the metal surface
Phosphatizing bath (6):	formation of a surface layer of insoluble heavy metal tertiary phosphates
Rinsing baths (7, 8, 9):	removal of acid residues, soluble salts and all nonadherent particles present on the metal

Phosphatizing of metal surfaces

The work pieces and car bodies to be phosphatized run through different baths where they are sequentially degreased, rinsed, activated, phosphatized and again cleaned. A single analysis system — ProcessLab — specially adapted to the par-

F. Portala is Manager Competence Center ProcessLab and A. Steinbach Scientific Writer for Metrohm AG, Herisau/Switzerland. F. Müller and M. Feige are Managing Directors of Deutsche Metrohm Prozessanalytik GmbH & Co. KG, G. Kirner is staff member in the Project Planning section.

The analytical parameters of the phosphatizing process at a glance

Process	Degreasing		Rinsing		Activation	Phosphatizing	Rinsing		Final rinsing
Bath number	1	2	3	4	5	6	7	8	9
a) Conductivity	•	•	•	•	•		•	•	•
b) pH value	•	•	•	•	•		•	•	•
c) Free alkalinity	•	•							
d) Total alkalinity	•	•	•	•	•				
e) Free acid						•			
f) Total acid						•	•	•	
g) Accelerators						•			
h) Zinc						•			
i) Fluoride						•			

(a) Conductivity (baths 1, 2, 3, 4, 5, 7, 8 and 9)
■ allows to draw important conclusions regarding the ionic strength in the activation bath and the extent of contamination in the rinsing baths;
■ monitors the cleaning process in the rinsing baths;
■ is determined directly in the sample vessel immediately after sampling.

(b) pH value (baths 1, 2, 3, 4, 5, 7, 8 and 9)
■ is a crucial parameter in the degreasing, rinsing and activation baths;
■ is determined in the sample vessel prior to the determination of other analysis parameters.

(c, d) Free and total alkalinity (baths 1, 2, 3, 4 and 5)
■ are determined by titration with hydrochloric acid; the first end point (EP; pH 8.7...9.0) corresponds to the free and the second EP (pH 3.7...4.0) to the total alkalinity.

(e, f) Free and total acid (baths 6, 7 and 8)
■ provide information concerning the progress of the phosphatizing process and the total amount of metal phosphate formed on the surface;
■ are determined by titration with NaOH. The first EP (pH 4.5...4.7) corresponds to the free acid and the second EP (pH 8.7...9.0) to the total acid content.

(g) Accelerators (bath 6)
■ accelerate the phosphatizing process and thus increase sample throughput;
■ are determined by redox titration.

(h) Zinc (bath 6)
■ is crucial for the formation of metal phosphates (phosphophyllite, $Zn_2Fe(PO_4)_2 \cdot 4H_2O$; hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$ on the surface);
■ is quantified by titration with EDTA using an ion-selective indicator electrode.

(i) Fluoride (bath 6)
■ increases the reactivity of the phosphatizing process and masks interfering aluminum ions by forming $[AlF_6]^{3-}$ complexes;
■ is determined in a separate reaction vessel to increase sample throughput.

ticular requirements of the phophatizing process, controls all bath-relevant parameters.

Atline analysis system

In an atline system the analytical unit is positioned directly at the process line allowing for on-site determination of the parameters required. Manual sampling occurs at different sampling points of the production line. This proximity combined with the modular concept — all analytical modules are accommodated in a single housing impervious to dust and splashes — allows efficient process control through the determination of all bath-relevant parameters. The user-friendly software and the TFT screen provide straightforward and easy operation. Additionally, a barcode reader guarantees unambiguous sample identification and makes laborious manual data entering obsolete. Automation of analytical tasks allows to easily manage high sample throughputs, at the same time enhancing repeatability. The presented ProcessLab atline analysis system records, controls and documents the important process parameters. The analytical data set is stored in a database and can be processed internally or transferred to a process control system.

Conclusions

The metal surfaces are treated using strictly defined process steps in different degreasing, cleaning, rinsing, activation and phosphatizing baths. The various bath parameters have to be closely monitored as they determine to a large extend the quality of the coating produced. The parameters determined in the cleaning, degreasing and rinsing baths are pH value, conductivity plus free and total alkalinity, while the phosphatizing bath is analyzed for free and total acids, accelerators, zinc and fluoride. The described ProcessLab atline analysis system monitors, records and documents the important analytical parameters of the entire phosphatizing process. The combination of the analytical methods involved as well as the intuitive operation via the user-friendly interface allow for complete process control. The analytical functions are supplemented by the integrated software that offers numerous possibilities for data processing and documentation of the measured values.

The atline analysis system described meets all requirements regarding process monitoring and documentation. ■

References
[1] Sankara Narayanan T.S.N., Surface pretreatment by phosphate conversion coatings – a review, Rev. Adv. Mater. Sci 9 (2005) 130-177.
[2] Rausch W., The phosphating of metals, Finishing Publications Ltd., London (1990) 418.
[3] Paul S., Surface coatings: science and technology, John Wiley & Sons (1996) 950.
[4] Uhlig H.H. and Revie R.W., Corrosion and corrosion control, Wiley-Interscience (1985) 464.
[5] Zhang X.G., Corrosion and electrochemistry of zinc, Plenum Press (1996) 475.