

Monitoring of a complete process line for the phosphatizing of metal surfaces using an at-line analysis system

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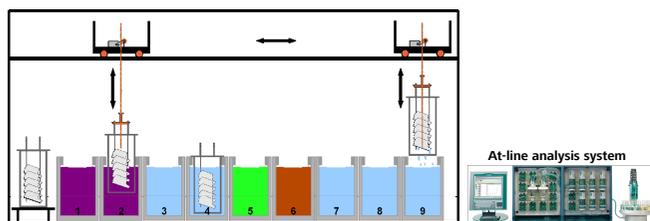
Introduction

With an estimated worldwide turnover of more than 500 million US dollars, phosphatizing is the most important metal pretreatment process. 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 the thorough degreasing and rinsing of the metal workpieces, the phosphoric acid removes interfering surface-bound metal oxides and increases the 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 Zn²⁺, Mn²⁺, and Ca²⁺ to the phosphatizing bath results in the formation of very resistant zinc phosphates with a coating thickness between 7 and 15 µm. Due to a modified crystal structure these layers are perfectly suited for outdoor use under hostile 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. Ni²⁺) to the phosphatizing bath, resulting in even better surface properties.

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 particular requirements of the phosphatizing process, controls all bath-relevant parameters.



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

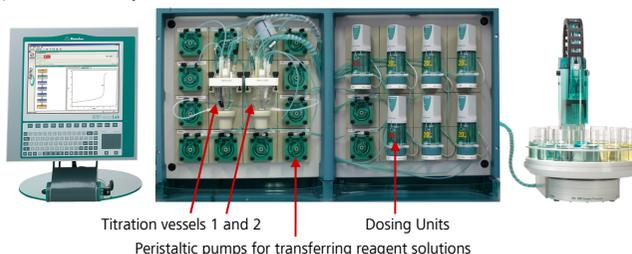
Phosphatizing bath (6): formation of a surface layer of insoluble heavy metal tertiary phosphates

Rinsing baths (7, 8): removal of acid residues, soluble salts and all non-adherent particles present on the metal

Final rinsing bath (9):

At-line analysis system

In an at-line system the analytical unit is positioned directly at the process line allowing for an on-site determination of parameters required. Manual sampling occurs at various 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 an efficient process control through the determination of all bath-relevant parameters. The user-friendly integrated operation software and the TFT screen offer straightforward and easy handling. 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 at-line 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.



Titration vessels 1 and 2
Peristaltic pumps for transferring reagent solutions
Dosing Units

Analytical parameters

The at-line analysis system controls and documents the important bath-relevant parameters.

	Degreasing 1	Degreasing 2	Rinsing 1	Rinsing 2	Activation	Phosphatizing	Rinsing 3	Rinsing 4	Final rinsing
(a) Conductivity	✓	✓	✓	✓	✓	✓	✓	✓	✓
(b) pH value	✓	✓	✓	✓	✓	✓	✓	✓	✓
(c) Free alkalinity	✓	✓	✓	✓	✓	✓	✓	✓	✓
(d) Total alkalinity	✓	✓	✓	✓	✓	✓	✓	✓	✓
(e) Free acid						✓			
(f) Total acid						✓	✓	✓	
(g) Nitrite or H ₂ O ₂						✓			
(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 EP (pH ≈ 8.7...9.0) corresponds to the free and the second EP (pH ≈ 3.7...4.0) to the total alkalinity, respectively

(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) Nitrite or hydrogen peroxide as accelerators (bath 6)

- accelerate the process of phosphatizing and thus increase sample throughput
- are determined by redox titration

(h) Zinc (bath 6)

- is crucial for the formation of metal phosphates (phosphophyllite, Zn₂Fe(PO₄)₂ · 4H₂O; hopeite, Zn₃(PO₄)₂ · 4H₂O) on the surface
- is quantified by titration with EDTA using an ion sensitive indicator electrode

(i) Fluoride (bath 6)

- increases the reactivity of the phosphatizing process and masks interfering aluminum ions by forming [AlF₆]³⁻ complexes
- is determined in a separate reaction vessel to increase sample throughput

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 extent 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, nitrite or hydrogen peroxide, zinc and fluoride. The described ProcessLab at-line analysis system controls, records and documents the important analytical parameters of the entire phosphatizing process. The combination of the analytical methods involved as well as the intuitive handling via the well-arranged user interface allow for complete process control. The analytical functions are supplemented by the integrated operation software that offers numerous possibilities for data processing and documentation of the measured values.

The at-line analysis system described meets all requirements regarding process monitoring and documentation.

Literature

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