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(I) Phosphating from Steel and Zinc

(1) Introduction

Most metals react in their components with air so that a thin film of reactant product covers the surface of a tool/instrument. These formed salts adhere only moderately and are therefore an unsuitable base for a paint layer.

To stabilize this effect, a deposit of amorphous or crystalline structure on the metal surface, create an excellent base-coat for the following coat of paint.

When a metallic surface, for example iron or zinc, is dipped into phosphoric acid (H_3PO_4) the metal dissolves and forms corrosion product salts. If these are only moderately soluble, then they form on the upper surface a non sticturing flaky coating. The acid continues to react until all the free acids are need up or the metals has dissolved.

If the corrosion products are insoluble, then a film forms on the surface until it is completely covered. The deposit works like an insulator and protects the metal from further acid corrosion.

If one prepares such metal phosphates carefully, observing particular parameters (bath conc., temp., pH-value, exposure time, spray pressure) then one achieves firm adhesive crystal structure.

For a trouble free chemical tension, to form a non-conducting crystal structure, the metal surface must be free from oxides, drawing agents and processing oils for which our alkaline EKASIT and SURFACLEAN degreasing agents, are more than suitable.

The chemistry of a phosphating process can be described in simple steps:

metal + phosphate acid → soluble phosphate → insoluble phosphate
(intermediate stage) (firmly formed on the metal surface)

Chemically generated phosphate crystals form a bulky film that looks like coarse felt under a microscope. The following layer of paint then has every advantage to anchor itself on the rough connecting phosphate coat, because the crystal structure is approx. 5 times bigger than the underlying metal surface.

With a first class zinc phosphate coating a penetrating voltage of 25 - 30 V/ μm has been measured, meeting it an ideal insulator.

The phosphate coating now covers the metal surface with a poor conductor, the insoluble metal phosphate deposit. This works as an insulating layer and slows down the electro chemical processes that are responsible for the corrosion of the metal.

(1.1) Phosphating procedure

Most common phosphating processes are the following:

- (1) Iron phosphate (non-layering),
- (2) Zinc phosphate (layering) and
- (3) Manganese phosphate (layering).

In literature the term "non-layering" is used more often, however, this is a little misleading, because a precipitation is always formed on the goods, even with an iron phosphate. However the coatings are much thinner, than the, so called, "layering" zinc or manganese phosphates.

The process differs not only in name but also in regard to the chemical reaction in the build-up of the phosphate coating (see chapter II).

A phosphate bath contains either

- (a) just the anion (phosphate), meaning the Cation Fe^{++} steams from the base metal to be covered or
- (b) all significant components i.e. the metal-cation (Zn^{++} , Ca^{++} , Mn^{++} , Ni^{2+}) and the phosphate-anion.

Iron phosphating: Suitable to treat steel, zinc and, under certain circumstances, aluminium. There is a build-up of iron or zinc phosphate, however, aluminium deoxidises and is passivated.

An iron phosphate bath works at a pH-level of 4 – 6 and a temp. of 25 – 65 °C.

Zinc phosphating: This process can be used to treat parts made of steel and zinc. A zinc phosphate deposit forms on the base material by a pH = 2.2 – 3.2 and a temp. of 50 – 85 °C.

Manganese phosphating: This phosphate coating is suitable for steel surfaces only; the process itself works at a pH = 2.2 – 2.4 and 90 – 95 °C.

Manganese phosphate coatings are used to protect transmission and engine parts such as cam shafts, gears etc. as a lubricant during break in periods.

Manganese phosphate coatings are not suitable to be painted or powder coated.

(1.2) Coating thickness

Measuring the coating thickness in µm (1/1000 mm) will result only in average values because of the rough crystalline surface. Therefore it is more recommendable to measure the weight of the coating using g/m² as described in DIN 50942.

Phosphate coatings may be applied by immersion or spray process, the achievable coating weights are shown in the following table:

	<u>Application</u>	<u>Coating weight</u>	<u>Metal phosphate</u>
(A) <u>Iron</u>			
SURFASIT D 1	immersion / spray	0.4 – 0.6 g/m ²	Fe
SURFASIT D 2	spray	0.2 – 0.4 g/m ²	Fe
SURFASIT D 3	immersion / spray	0.2 – 0.6 g/m ²	Fe
SURFASIT D 6	immersion / spray	0.2 – 0.6 g/m ²	Fe
SURFASIT D 10	immersion / spray	0.2 – 0.6 g/m ²	Fe
SURFASIT D 11	spray	0.2 – 0.6 g/m ²	Fe
SURFASIT D 33	spray	0.2 – 0.4 g/m ²	Fe
SURFASIT IP 6	spray	0.2 – 0.6 g/m ²	Fe
SURFASIT D 38	spray	0.4 – 0.8 g/m ²	Fe
(B) <u>Zinc</u>			
SURFACOTE 125	immersion spray	2.0 – 6.5 g/m ² 1.5 – 4.0 g/m ²	Zn/Ni
SURFACOTE 222/223	immersion spray	2.0 – 3.5 g/m ² 1.5 – 3.0 g/m ²	Zn/Mn
SURFACOTE 240	immersion spray	3.8 – 4.8 g/m ² 1.7 – 2.5 g/m ²	Zn/Mn
SURFACOTE 270	immersion	2.0 – 5.0 g/m ²	Zn/Fe
SURFACOTE 333/334	immersion spray	2.5 – 5.5 g/m ² 1.5 – 3.0 g/m ²	Zn/Ni/Mn
SURFACOTE 480	immersion	15.0 – 30.0 g/m ²	Zn
SURFACOTE 775	immersion	1.5 – 3.5 g/m ²	Zn/Ca/Ni
SURFACOTE 780	immersion	1.5 – 3.5 g/m ²	Zn/Ca
(C) <u>Manganese</u>			
SURFACOTE MN/2	immersion	10.0 – 40.0 g/m ²	Mn
SURFACOTE MN/3	immersion	10.0 – 20.0 g/m ²	Mn

(1.3) Corrosion Protection

The corrosion resistance of phosphated metal surfaces can be increased with a subsequent conversion coating. Also because of the chemical reaction, the ability for a layer to serve as a gas-coat (under-coat) is remarkably increased.

This additional treatment is often called “chromating”, because most of the conversion coating solutions contain chromium components, however, we can offer a chromium-free passivation which greatly eases the problem with waste water treatment. Painted or powder coated deposits of our SURFASIT iron phosphate (coating weight of 0.2 – 0.8 g/m²) will resist between 144 – 168 h in a salt spray test. The corresponding SURFACOTE zinc phosphate deposits (in thin layers) of 2 – 4 g/m² have established more than 240 h salt spray test resistance.

If the zinc phosphate parts are not to be painted or (powder coated) directly, then they could be sealed using our SURFASEAL corrosion protection oil, or using our ULTRA Tec 500 process prior to any painting or powder coating.

(1.4) Quality Control

A phosphated and painted or powder coated metal surface must pass the following quality controls, that have been developed over the past years:

	<u>DIN</u>
(a) Cross hatch test	53151
(b) Salt spray test	EN ISO 9227 NSS
(c) Condense water (Humidity test)	DIN EN ISO 6270-0
(d) Bending test	DIN EN ISO 1519
(e) Erichsen test	DIN EN ISO 1520

The choice of an iron or zinc phosphate deposit depends on the quality required for the coated parts.

To summarise the benefits of the phosphating of metals one can say that:

- (1) Phosphating neutralise residues of alkali that could harm the adherence of paint or powder coatings, thereby accelerating the corrosion process.
- (2) Phosphating possess a relative symmetrical crystal structure and therefore form an excellent base for paints/powders. Parts with shape-edges and corners are evenly covered, preventing the paint or powder from running off during the burn-in period.
- (3) Phosphating increase the surface of the parts so the adherence of the following coating is improved remarkably.

- (4) Phosphating also form capillaries and micro cavities, which
 - (a) promote the bonding of the layer on the metal surface,
 - (b) improve the adhesion of drawing lubricants (used in cold forming, tube and wire drawing). The absorbance of oil and anti-corrosives is improved.
- (5) They cushion the base material against scratching and isolate it from electrochemical corrosion.
- (6) They prevent the reaction between certain components of the paint or powder and the sensitive base material of the part.
- (7) They reduce the speed of corrosion from a damaged surface to an intact area of the part caused by several substances and the atmosphere itself.

(2) Spray or Dipping Installation

When constructing a phosphating equipment several elements must be taken into consideration.

- (I) When placing the work pieces on racks or conveyors, they must be
 - (a) prevented from being scooping which could contaminate all following treatment steps,
 - (b) free from capillaries, cracks and splits, also
 - (c) sharp edges.
- (II) The conveyor times between the single stages must be kept short, so that a minimum amount of water evaporates. Do not allow any drying of the parts between the single stages!
- (III) To remove surface swimming oil and grease, an suitable bath overflow should be installed.
- (IV) Flat jet nozzles are proved to be the most suitable to assemble.

It is very important to rinse the parts thoroughly between each stage of the process. Water with a hardness of 20 °dH or more is not suitable.

It is recommended to exchange approx. 20 % of the rinsing bath volume by fresh water every hour. In a spray installation the amount of rinsing water should be at least 5 l/m² of surface of the parts. Even on flat surfaces approx. 150 ml/m² of water adhere on the part and will be carried into the next station of the installation. To prevent the parts carrying excesses from degreasing agents or phosphates, we recommend to use approx. 10 – 15 l of rinsing water per m² surface part.

As a final step the parts should be rinsed with deionized water from a spray nozzle ring that feeds approx. 2 l water per m² object surface to completely remove any water-soluble residues. Degreasing agents or chemical residues from the phosphates may cause problems later on by producing unwanted osmotic effects. Formed during the drying cycle, these residues may be the reason for the dreaded "bubbles" in the paint coating.

A spray installation is the more preferred method. Through kinetic energy, a spray jet from a SURFASIT Iron Phosphate solution increases the cleaning effect of a part in order to obtain a more uniform phosphate coating with improved adherence properties.

With a SURFACOTE Zinc Phosphate the common spray installation produce a fine-grained crystal structure, which is an important advantage for the following paint layer (see diagram).

If a large surface, bulky parts or complete bundles must be prepared for painting, a dipping installation or immersion phosphate bath should be the preferred choice. In order to get a fine crystalline structure of the zinc phosphate coating, we recommend a conditioning stage with our SURFA-rins process or to choose one of our zinc/calcium type phosphates.

Immersion zinc phosphating is also preferred, when a certain thick phosphate coating is required (i.e. pipe or wire drawing, or when an anti-corrosive oil is to be used later).

The choice of a suitable phosphate installation is just as important as the decision for the correct process. SURFASIT iron phosphates only require a mild steel tank (DIN 17 100-2); for the more acidic SURFACOTE zinc and manganese phosphates an adequate rubber lining or stainless steel tanks must be used. A stainless steel quality meeting the material specification no. 1.4571/V4A is sufficient in most cases.

In order to get a maximum of heat distribution and a minimum of sludge, we recommend to heat phosphating tanks with large surface heaters only. Indirect heating should be preferred.

The advantages and disadvantages of a phosphating system are summarised in the following table:

	<u>Spray</u>	<u>Dipping</u>
Cost of plant	high	low
Production capacity	high	medium
Degreasing	ideal	medium
Chemical costs	low	low to medium
Fixed costs for maintenance	high	low
Phosphate coating	fine-grained crystals	middle to coarse crystals

(3) Iron Phosphate

(3.1) Sequence of events

Deposits of SURFASIT Iron Phosphates are usually formed in 3 stages:

- (1) Degreasing (cleaning) and phosphating simultaneously, e.g. in the same stage.
- (2) Rinse with water.
- (3) Rinse with completely deionized water.

Any metal or steel supplier should be asked not to use animal or natural drawing aid products. Steel coils should also have no more than 1 – 3 g/m² of mineral oil on the surface in order to ensure best cleaning and phosphating success.

In order to achieve best results, normally each gram of oil requires approx. the same amount of the corresponding SURFASIT product to be removed. A rule of the thumb is: With a working time of 8 hours a day and 1 – 3 g/m² of oil on the parts, the iron phosphate bath must be replenished with approx. 10 % of the amount of product needed for a new bath make-up daily. A complete new make-up of the phosphate solution should be made if the total amount of oil in the phosphate solution exceeds 5 ml/l as a maximum.

If the parts to be treated are heavily oiled or dirty, then it is more recommendable to use a five-stage process using an alkaline EKASIT or SURFACECLEAN spray or immersion cleaner in the first stage as e.g. in zinc phosphating installations.

(3.2) Quality Characteristics

Our SURFASIT Iron Phosphates are suitable for steel, zinc and aluminium surfaces, available as free flowing salt mixtures or as high concentrated liquids.

Depending on the composition of the SURFASIT Iron Phosphate bath the colour of the phosphate coating varies from light and dark grey to dark blue. Because of its amorphous structure this phosphate type is called a non-coating phosphate.

In order to ensure degreasing and phosphating properties in a single stage our SURFASIT Iron Phosphates contain beside the inorganic components also emulsifier and biodegradable wetting agents for both spray and immersion application. The effects of the surfactants can be intensified using a mixture of SURFACECLEAN Special Wetting Agents.

If hot galvanised parts and pieces made of aluminium alloys are treated with a SURFASIT Phosphate the adherence of the following coating is improved remarkably.

(3.3) Iron Phosphating and Painting

A SURFASIT Iron Phosphate deposit can act as a temporary corrosion protection film, e.g. if the treated parts have to be stored for a while prior to further painting or powder coating.

Iron phosphate is normally used as a basis for powder coatings on indoor articles only.

Iron phosphate coatings are suitable for optimised paint or powder coating adherence.

(3.4) Conversion Coatings

Although iron phosphate deposits normally provide excellent adherence for the following lacquer or powder coating, these attributes can be widely increased using a passivation from our SURFASEAL-line.

(4) Zinc Phosphate

(4.1) Working Sequence

SURFACOTE Zinc Phosphate is made up in 5 – 6 stages.

- (1) Degreasing
- (2) Rinse with water (2 x)
- (3) Pickling, if necessary
- (4) Rinse with water (2 x)
- (5) Pre-dip in SURFA-rins if not already been done in step (1).
- (6) Phosphating
- (7) Rinse with water.
- (8) Final rinse with deionized water.

(4.2) Quality Properties

Our SURFACOTE Zinc Phosphates can be used on steel as well as zinc surfaces. They are supplied as liquid concentrates, for fine to middle crystalline zinc or zinc/calcium layers depending on the formulation. Because zinc phosphate processes do not allow a single stage cleaning and phosphating procedure, a separate cleaner (spray or immersion) must be used in the first stage.

Our SURFACOTE Zinc Phosphates are most suitable for galvanised and hot galvanised work pieces.

Already at 3 mg/l aluminium is toxic for every zinc phosphate. Therefore, this metal can be treated only when the bath was adjusted individually to the needs of each production. For this you can use our SURFACOTE Additiv Nr. 6 which masks the aluminium ions (Al^{++}) and makes them harmless.

(4.3) Zinc Phosphate Coating and Painting

Although iron phosphates provide a good basement for painting or powder coating, zinc phosphates are much more suitable, especially if the parts are exposed to outdoor climate, from e.g. weather, store strikes or rock salt.

The colour of a zinc phosphate varies from light to dark grey, the corrosion protection is very good, and with a layer weight of up to 4 g/m², provides excellent basement for painting or powder coating.

For a following paint or powder coating the finest possible zinc phosphate coating is recommended. Fine, dense packed crystals reduce porosity of the phosphate layer and thereby considerably avoid corrosion.

The size of the crystals depends highly upon pre-treatment, bath parameters (bath make-up), working temperature and the spray pressure of the zinc phosphate.

Smaller crystals are formed in a free floating phosphate bath, better than in a stirred solution. Normally zinc phosphate coatings produced in spray installations are much more refined due to the kinetic energy exposed to the surface during the phosphating process.

Our mild alkaline EKASIT / SURFACELEAN Cleaner will help to achieve dense, refined phosphate coatings.

For extremely fine crystal requirements our zinc / calcium phosphates SURFACOTE 775 produces a micro-crystal line deposit in an immersion process. 1.5 – 3.5 g/m² of zinc / calcium phosphates can be achieved without problems. This phosphate coating guarantees a good contact for paint and also has excellent corrosion protection. The calcium in a SURFACOTE zinc phosphate bath has the effect that singular crystals are only 1/20 the size of those produced in a pure zinc phosphate. These micro-crystalline layers come into effect when the phosphated goods are to be shaped or lacquered in an electro-dipping installation.

(4.4) Conversion Coatings

A SURFASEAL passivation seals the zinc phosphated surface and greatly increases its corrosion protection. Compared in salt spray test following DIN EN ISO 9227 it was shown that the passivation of phosphated surfaces increased the corrosion protection to a value twice as much as before.

(4.5) **Corrosion Protective**

Our special oils of the SURFASEAL series can be emulsified with water. They can conserve the persistent zinc- and manganese phosphate coatings (see capital 5). Our recommendation and preference is a coarse zinc- or manganese phosphate coating because they can absorb much more oil.

(4.6) **ULTRA Tec 500**

With ULTRA Tec 500 we offer a process that gives a sealed, protective inorganic coating to the SURFACOTE zinc phosphate layer.

This combination increases the corrosive resistance up to 200 h (DIN EN ISO 9227 NSS) or 350 – 400 h if the goods are dipped in an extra bath of SURFASEAL corrosion protection oil.

ULTRA Tec 500, applied to a SURFACOTE zinc phosphate coating, gives lubricant properties, comparable to a manganese phosphate, this results in the favourable friction required for treated parts / pieces.

(5) **Manganese Phosphates**

With our manganese phosphate SURFACOTE MN/2 we produce a black manganese phosphate coating on steel parts. To achieve a uniform but thick coat, the parts must be activated in a separate bath prior to the phosphating process. There are 2 activators to choose from.

We recommend the following method:

- (1) Cleaning in a strong alkaline degreaser (e.g. SURFACELEAN 900)
- (2) Rinse
- (3) Pickling, if necessary
- (4) Rinse
- (5) (a) Activate in SURFACOTE Pre MN (coarse to medium crystal size) or
(b) SURFACOTE Activator Part 1 or 2 (medium to fine crystal size).
- (6) Phosphating in SURFACOTE MN/2 or SURFACOTE MN/3
- (7) Rinse
- (8) Post-dip in a SURFASEAL oil emulsion

(II) The Chemistry of Phosphating

(1) Balance and pH-levels

The basis for every phosphatizing solution is the tri-basical ortho phosphoric acid and its salts. This acid may form different stages, namely

- (1) $\text{H}_3\text{PO}_4 \leftrightarrow \text{H}^+ + \text{H}_2\text{PO}_4^-$ (primary phosphate)
- (2) $\text{H}_2\text{PO}_4^- \leftrightarrow \text{H}^+ + \text{HPO}_4^{2-}$ (secondary phosphate)
- (3) $\text{HPO}_4^{2-} \leftrightarrow \text{H}^+ + \text{PO}_4^{3-}$ (tertiary phosphate)

The equilibrium of the shown formulas depend on the pH value. At pH 2 there are phosphoric acid molecules (H_3PO_4) as well as primary phosphate (H_2PO_4^-) ions while HPO_4^{2-} and PO_4^{3-} ions are absent. In case of an increase of the pH value (e.g. adding some alkali) the equilibrium shown in (1) will move to the right until there are H_2PO_4^- ions only left at a pH of 4.5. If addition of alkali is continued, formula (2) comes into play forming now HPO_4^{2-} ions (beside of H_2PO_4^- ions) which will remain at a pH value of 9.5. Further increase of the pH value will form tertiary phosphates as the one and only form to be left at pH 14.

Beside of phosphoric acid there are some other substances in our phosphating solutions like accelerators, coating foaming cathions, activators, detergents etc.

(2) Nomenclature

Especially for the documentation of important parameters of a phosphating solution some special expressions were agreed in the past:

- (a) Total acid (TA) which is the sum of free hydrogen ions (H^+), zinc ions (Zn^{2+}) as well as the primary phosphate.
- (b) Free acid (FA) which corresponds to the content of free acid represented by the free hydrogen ion (H^+).
- (c) Primary phosphate (PP) which is the content of H_2PO_4^- .
- (d) The acid ratio (AR) which is a quotient of total acid divided by the free acid.

The most important parameters (a) and (b) can be determined by simple titrations using 0,1 N sodium hydroxide (NaOH) where the used ml correspond to "Points total acid" or "Points free acid".

Concentration of Zn^{2+} (also called zinc level) is simply determine as a formula $\text{TA} = \text{FA} + \text{PP} + \text{Zn}^{2+}$ namely with $\text{Zn}^{2+} = \text{TA} - \text{FA} - \text{PP}$. Under normal circumstances it is not necessary to control zinc or primary phosphate because these additives will be adjusted by the addition of SURFACOTE concentrates automatically.

It must be pointed out that the pH value of a phosphatizing bath has nothing to do with the determined amount of points!

(3) The chemical reaction in the build up of a phosphate coating

Phosphating of metals represent a couple of different chemical reactions which, for better understanding, must be divided up in single steps as follows:

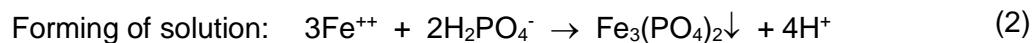
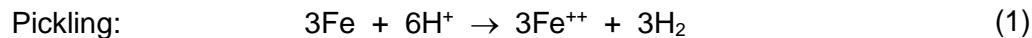
- (a) Pickling reaction forming of a phosphate coating and
- (b) forming of solution
- (c) sludge formation.

Reaction (a) consumes acid which results in a raising pH value. Due to this reason more water insoluble metal phosphates can be formed which will be responsible for the phosphate layer until the surface is completely covered with phosphate crystals meaning that further acid no contact longer attacks uncovered base material.

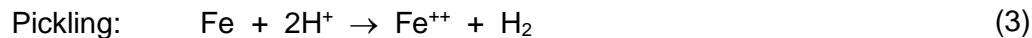
Coating forming phosphating processes (zinc or manganese phosphate) will continue to build up a coating but in a different way. In addition unwanted sludge is formed which can be removed by sludge thickener systems or special filtering equipment in order to avoid any “dusty deposit”.

To visualise the chemical properties, following formulas should give at least a very simplified overview to the reactions which go along with phosphating of metal surfaces:

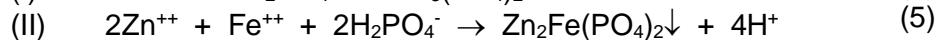
(a) Iron phosphating



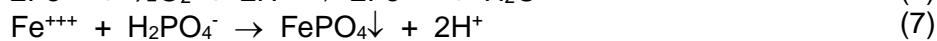
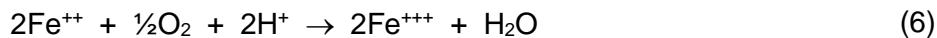
(b) Zinc phosphating



Forming of solution:



Forming of sludge

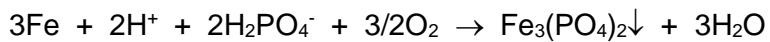


(c) Manganese phosphating

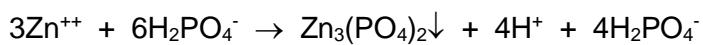
Very similar to both reactions from zinc phosphating

Simplified different reactions of phosphating look as follows:

Iron



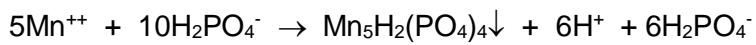
Zinc



Zinc/Calcium



Manganese



(III) Disposal of phosphates

Spent solutions of phosphatizing installations contain substances which may harm our environment so a suitable waste water treatment of both rinsing and phosphating solutions is of great importance prior to any disposal.

The following information does not claim to be a step by step guide how to handle a special phosphating solution but may be helpful in order to find out the best fitting procedure for a special given situation.

In any case any action should be checked with the local authorities for waste and waste water treatment.

For all described methods we use lime or chalk which can be made up easily by dispersing approx. 20 kg of calcium hydroxide $\text{Ca}(\text{OH})_2 \times \text{H}_2\text{O}$ for chemical purposes in approx. 100 l of cold water.

Do not use any calcinated chalk which contains also carbonates and sulphates as well as other chemicals not suitable for waste water treatment. Furthermore these products start to get very hot when dispersed in water.

(A) Iron Phosphates

Iron phosphates are used for both cleaning and phosphating in a single stage so a spent solutions contain usually oil, fatty residues as well as phosphates and other inorganic chemicals and wetting agents.

(a) Waste water with only a few oil residues

- (1) Add 1 kg/m³ of our AW Sorb.
- (2) Stir for 5 – 10 minutes.
- (3) Add very slowly and under further stirring small portions of lime carefully watching that the final pH value of pH 8.5 does not exceed. Avoid any overdosage.
- (4) Allow the precipitated metal hydroxides to settle down. This sequence which can be accelerated by adding 1 – 10 g/m³ of our flocculant SEDAC 705. SEDAC 705 should be added as given in the corresponding technical bulletin only.
- (5) Allow the mixture to settle down and to be cleared.
- (6) Filter the clear solution over a filter press and check whether the heavy metal values of the filtrate correspond with the local authorities regulations.

In any case a pressed sludge must be dumped in a special place according with the local regulations.

(b) Waste water with higher content of oil as well as spent iron phosphating concentrates

- (1) Adjust the solution to be treated to pH 2 – 3 using diluted sulphuric acid (H_2SO_4). The addition of trivalent iron salts may improve the precipitation of the heavy metals in iron phosphate solutions; furthermore they crack emulsions more easily, so the addition of iron(III)-chloride or iron(III)-sulphate is highly commended.

$FeCl_3$: For each m^3 add approx. 750 g of iron(III)-chloride ($FeCl_3$) or 1 200 g $FeCl_3 \cdot 6H_2O$.

$Fe_2(SO_4)_3$: For each m^3 add approx. 900 g iron(III)-sulphate ($Fe_2(SO_4)_3$) or 1 250 g $Fe_2(SO_4)_3 \cdot 9H_2O$.

- (2) Oil or grease which separates during this process can be removed from the bath surface easily.
- (3) Add 1 kg/ m^3 of our separating agent SORBAN.
- (4) Stir for 5 – 10 minutes.
- (5) Add small amounts of lime under permanent stirring until the final pH-value reaches 8.5 as a maximum. Avoid any overdosage!
- (6) Add flocculent SEDAC 705 according to our technical bulletin.
- (7) Allow to settle down until the upper part of the solution gets clear.
- (8) Analyse the clear solution for proper heavy metal values according to the local waste water restrictions.

Pressed sludge must be dumped in a special waste disposal area.

(B) Zinc- and Manganese Phosphatings

This type of phosphating solutions do normally not contain any oil or fatty residues because a separate cleaning stage is switched in the first stage prior to the phosphating stage, however, higher concentrations of heavy metal ions like Zn^{++} , Ni^{++} and Mn^{++} can be observed when compared with iron phosphate processes.

(a) Waste water

- (1) The type of zinc phosphating processes do often contain nitrit (NO_2^-) as a kind of accelerator which can be easily analysed by corresponding test kids available at most companies for analytical chemicals.

There are two different ranges of concentration, namely

- (I) $0.1 - 0.3 - 0.6 - 1 - 2 - 3 \text{ mg/l } NO_2^-$
- (II) $1 - 5 - 10 - 20 - 40 - 80 \text{ mg/l } NO_2^-$

To get a first overview about the nitrite concentration test kid II should be used.

The decomposition of 1 g sodium nitrite ($NaNO_2$) requires approx. 1,4 g sulfamine acid (SO_2NH_2OH). Since the chemical reaction of the decomposition of the nitrite runs spontaneously the corresponding amount of sulfamine acid can be added to the waste water directly prior to any further treatment.

To ensure complete NO_2^- free waste water check with test kid I.

Nitrite may be determined also by a photometer. However, this method is far more expensive and requires more time hence gives no advantages.

- (2) Continue as described under (A)/(b) 1 – 8.

(b) Zinc-/Manganese Phosphate

Under normal circumstances a new bath make up of zinc or manganese phosphating solution is very seldom. However, a spent bath should be collected in a separate tank from where small portions can be added to the running waste water treatment. This procedure avoids excess amounts of sludge which could badly interfere the function of the waste water treatment system.

(IV) Costs

The financial calculation of phosphatizing of metals will be influence by the type of phosphating equipment as well as the costs of the required chemicals. Therefore, this calculation may varied from case to case remarkably.

In any case following type of costs must be taken into account:

- (1) Fixed overheads
- (2) Deduction
- (3) Interest rate
- (4) Maintenance of installation
- (5) Operation costs for heating system (cleaner/phosphate bath)
- (6) Operation costs for drying oven
- (7) Costs for chemicals (cleaner, rinse conditioner, phosphate concentrates, conversion coatings)
- (8) Costs for water
- (9) Costs for waste disposal

(V) Paint and Powders

Commercial liquid paint or powder is available for spray or dip processes for almost any kind of painting of phosphated work pieces.

Powder coating: This type of coating is based on a powdered paint particles (made of resins and synthetic material) which will be applied by spray pistols containing a negative loaded electrode so that the (negative loaded) powder will precipitate on the (positive loaded) work piece in an electro statically field of 50 000 – 100 000 V. This powdered coating remains on the goods and will be backed to the final paint film of 40 – 120 µm in the oven at 170 – 220 °C.

Electro dip painting: A mixture of 90 % of water and approx. 10 % of water soluble resins and other organics ingredients represent the electro dip paint which is stored in a special tank which is switched as cathode while the goods to be painted are switched as anode when dipped into this paint.

The painting process itself takes place at voltages of 50 – 400 V and 25 – 40 °C for 1.5 – 3 minutes. The resulting paint film is burned in for 15 – 30 minutes at 160 – 190 °C.

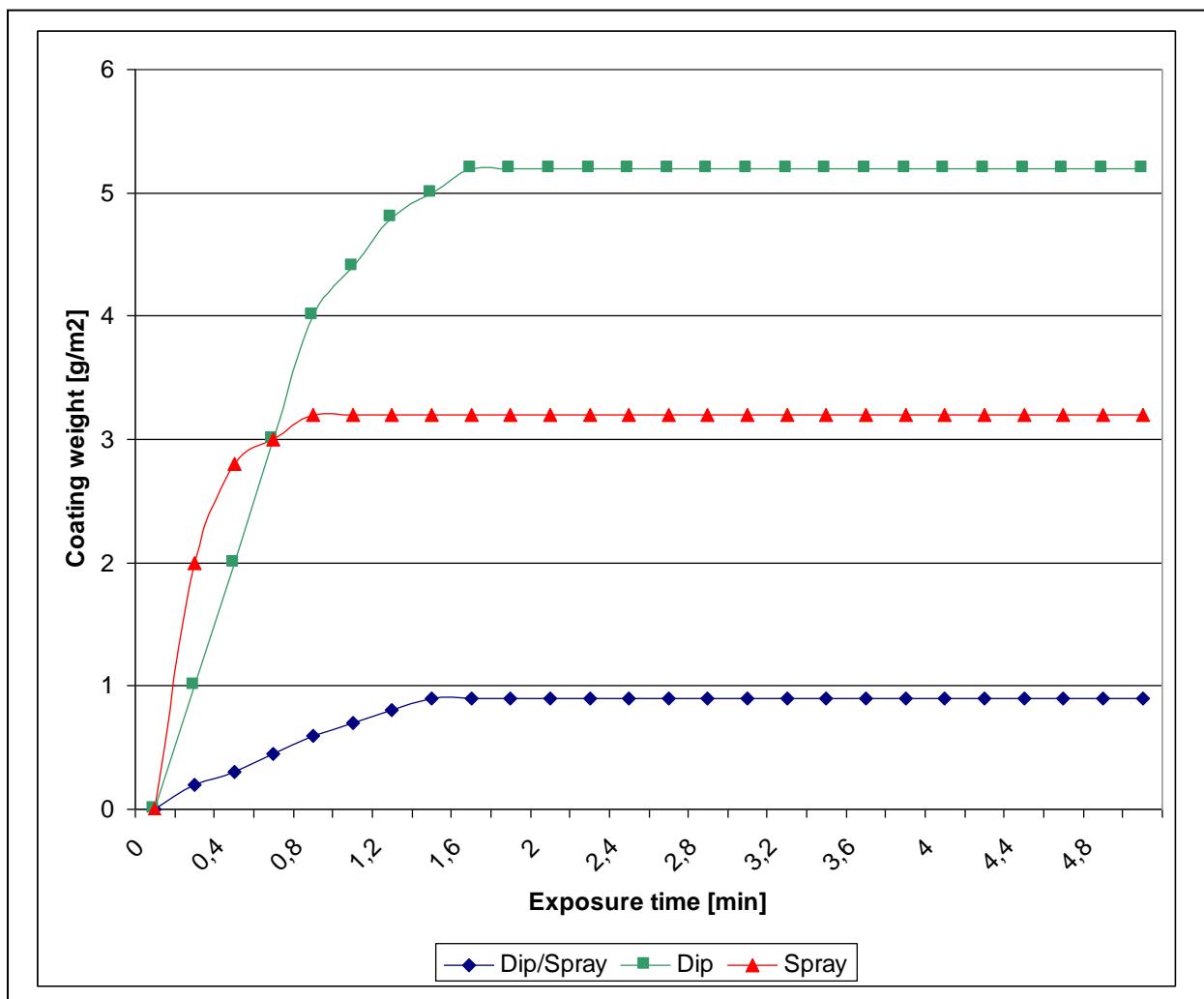
The diagram shows the build-up of phosphate coatings on steel as a function of treatment time and coating weight using an iron or nitrite accelerated zinc phosphating solution.

Curve (1): Iron phosphate (spray / immersion system)

Curve (2): Zinc phosphate, nitrite accelerated (immersion system)

Curve (3): Zinc phosphate, nitrite accelerated (spray system).

The curves (2) and (3) of the diagram show zinc phosphate coatings which will be representative as a basement prior to the painting of work pieces. By changing the bath parameters thicker coatings may be achievable anyway.



(VI) Our Product Range

Various products of our product line for pre-treatment and phosphating have been protected by international registered trade names.

We supply our cleaners under the trade name EKASIT, while our phosphates are named as SURFASIT for iron phosphating processes and SURFACOTE for zinc- and manganese phosphating processes.

Our crystal refiners are called SURFA-rins and SURFACOTE Pre MN while our conversion coating products and corrosion protectives carry the trade name SURFASEAL.

We frequently improve our processes while listening to our customers' demands; taylor-made products may available upon special requirements.

At the present time we can supply following standard products:

Phosphating processes

(A) Iron

(a) Spray and immersion processes:

- SURFASIT D 1: Liquid, single component process. This mild acidic concentrate shows remarkable cleaning power. A special pH-adjustment is not required.
- SURFASIT D 2: Iron phosphating without combination of wetting agents for the use in spray processes. Is used in systems with separate degreasing step or in combination with a suitable wetting agent such as SURFACEAN N 970, SURFACEAN N 971, SURFACEAN N 1000 or Netzmittel 229.
- SURFASIT D 3: Liquid concentrate; properties similar to SURFASIT IP 6 which is mentioned further below in this chapter.
- SURFASIT D 6: As SURFASIT D 3 but designed mainly for steel surfaces.
- SURFASIT D 10: Fluoride-free version of SURFASIT D 1. A pH adjustment is not necessary.
- SURFASIT D 33: Liquid acidic concentrate with remarkable high amount of powerful surfactants. Produces a very fine and dense phosphate coating which is an excellent base prior to lacquering/coating.
- SURFASIT IP 6: Free flowing salt mixture for a combined degreasing and phosphating of iron. For the treatment of zinc and aluminium SURFACOTE Additiv Nr. 6 must be added.

Ready-to-use process after make-up.

(b) Spray processes:

- SURFASIT D 11: SURFASIT D 11 is an acidic liquid concentrate and is used in high pressure spray systems. This product is a combination of cleaner and iron phosphate.
- SURFASIT D 38: For the use in spray processes. Produces extremely thick iron phosphate coatings on steel surfaces.

Cleaning aids

Following products may be added to the ready-to-use phosphate bath in order to improve the cleaning effect upon requirement.

- (1) SURFACELEAN N 971: Liquid additive.
- (2) SURFACELEAN N 1000: Liquid surfactant for the use with neutral cleaners and phosphating solutions. SURFACELEAN N 1000 removes even resined oil and grease.

All our surfactants are biodegradable according to the worldwide environmental restrictions.

(B) Zinc

- SURFACOTE 125: Liquid concentrate, suitable for spray and immersion application. Forms fine crystalline layers. The bath is accelerated by nitrite (NO_2^-), which is added separately.
- SURFACOTE 222/223: Zinc phosphating based on zinc and manganese (nickel-free). Suitable for spray and immersion application at temperatures of 55 to 70 °C. Forms fine crystalline layers. The bath is accelerated by nitrite (NO_2^-), which is added separately.
- SURFACOTE 240: Low temperature zinc phosphating based on zinc and manganese (nickel-free). Works in immersion processes at temperatures from 27 to 45 °C and in spray systems from 35 to 45 °C.

Forms very fine, thin phosphate layers and provides very good protection against corrosion and infiltration in subsequent coatings. The bath is accelerated by nitrite (NO_2^-), which is added separately.
- SURFACOTE 270: Liquid concentrate, for immersion application. This process produces very fine crystals and is specially designed to be used prior to electro painting and/or tube drawing.
Internal chlorate-based accelerator.
- SURFACOTE 333/334: Trications phosphating. Very good corrosion and infiltration protection in combination with subsequent coating. Our process is used in spray or immersion applications.

SURFACOTE 480: Liquid concentrate, suitable for soak and barrel equipment. Depending on the concentration, fine to middle crystalline structures (low concentration) or coarse crystalline structures (high concentration) of the zinc phosphate coating can be obtained.

SURFACOTE 775: Liquid concentrate, for immersion application. Zinc-Calcium-Type process featuring extremely fine, dense crystals. Highly recommendable as basement for electro paints.

(C) Manganese

SURFACOTE MN/2, SURFACOTE MN/3: Liquid manganese phosphate processes for immersion application. Coarse to fine crystal size according to the used crystal refiner. Suitable for steel qualities up to approx. 3% of Chromium. Low sludge processes.

(D) Special additives

SURFA-rins: Crystal refiner for SURFACOTE zinc phosphate processes

SURFACOTE Pre MN: Crystal refiner for SURFACOTE manganese phosphate.

SURFACOTE Activator MN Part 1 and Part 2: These both salts can be used only combined. Our rinse activates steel surfaces in order to achieve more uniform coatings and accelerates the build up of fine crystalline coating.

(E) SURFACOTE Additive Nr. 6

Masks aluminium-ions which normally act as a poison in zinc phosphating solutions.

This product is NOT suitable for SURFACOTE 775!

(F) Passivations

All products are liquid concentrates, suitable for spray and immersion processes.

SURFASEAL 4: Chromate-free conversion coating for all types of phosphate deposits.

SURFASEAL 30: Passivation of iron and zinc phosphate coatings prior to lacquering. In order to improving lacquer adhesion.

SURFASEAL 440: Phosphate and chromium free alternative for the pre-treatment of steel, aluminum and zinc surfaces. SURFASEAL 440 forms a conversion coating, which provides a very good base for subsequent lacquer or powder coatings. The GSB and Qualicoat approval for the alternative pre-treatment of aluminum was achieved.

The bath operates at low temperatures. During operation, the formation of sludge is largely avoided. Also in the wastewater disposal sludge is noticeably less than in phosphate-containing products.

(G) Corrosion protection oils

SURFASEAL: Emulsifying oils of different types; fitted for the respective usage.

(H) ULTRA Tec 500

Our process provides SURFACOTE zinc phosphate coatings which have a special texture, not only with a protective, inorganic deposit, but it also seals them.

(I) Waste water treatment

- (1) White chalk for chemical purposes
- (2) AW Sorb
- (3) SEDAC 705
- (4) Testing chopstick "Merckoquant Nitrit Test"

Detmold, 11.11.2016
Pde-ca