New environment friendly pretreatment systems for Hot Dip Galvanizing industry:

- Alkaline low temperature degreasing, free of phosphates
- Acidic degreasing without phosphoric acid and with unlimited lifetime („never dump system“)
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Comparison of usual pretreatment with new developed systems which are working since about 3 years at several customers

- Environmental aspects and experience
- Future aspects:
  Additional environment saving systems for hot dip galvanizers
Phosphates are belonging to builder substances and are used to realize different effects:

In alkaline degreasing agents:

- as dispersing agent (to hold pigments in solution)
- as pH-regulator
- as softening agent for water hardness
- as inhibitor to prevent corrosion and redeposition of dirt

In (phosphoric acid based) never dump degreasing systems

- as dispersing agent (to hold pigments in solution)
- as mild acid
- as regulation aid to prevent against increasing iron concentration
- as degreasing booster
Phosphates are eutrophying (that means they will fertilise aquatic environment), therefore they have been banned as ingredients in washing agents for end users.

For industrial applications phosphates are frequently used as well today.

A lot of different alternatives are available to substitute phosphate by more environment-friendly products, so the industry did this.

For hot dip galvanizers this was only possible 3 years ago as well for acid based never dump degreasing systems.
Many installations have several heated processing solutions:

- degreasing up to 80°C
- pickling up to approx. 35°C
- preflux up to 70°C – and/or heated drying station

Energy shows as well environmental impact and increased pricing.

Recycling of energy is not often in use and not every time this will be enough to hold the temperatures shown above.
Here we are at the point to ask how energy can be saved.

Nearly no or only a bit of savings are possible for:

- **Pickling solutions:**
  up to about 35°C are partially necessary to hold pickling times short even the iron is increasing.
  With high acid concentrations and elevated temperature levels there should be used a proper additive like Leratens® AV plus to reduce emissions of HCl containing aerosols.

- **Degreasing**, only if this is used to remove paint or heavy grease.

Because this is not a typical application for hot dip galvanizers this should be done in separate smaller installations, if necessary.
Savings for energy are possible in:

- **Degreasing:**
  acid based systems are working at 25 – 30°C. The new developed phosphate-free alkaline degreaser Lerapur® 268 is working very well at typical hot dip galvanizers from about 30 – 35°C on.

- **Preflux:**
  proper additives like Leratens® Add FF are enabling to reduce the temperature of the solution even if there will not be a drying installation available.
Alkaline degreasing (conventional)

Degreasing with caustic alkali and surfactants
Temp. 50 – 85°C
Conc. 3 – 10%

For general galvanizing with high oil contaminations, spinning plants, paint stripping is possible
Alkaline degreasing conventional

**Advantages:**
- Very good degreasing performance (minimum 50°C)
- Removing paint and grease is possible
- Lower consumption vs acid cleaning systems

**Disadvantages:**
- Rinsing strongly recommended
- Limited bath life time to hold good performance
- High temperature = huge energy consumption
- High temperature leads to formation of mist / fog
- High concentration means neutralizing acid
- Drag over oil (emulsion/soap)
- Drag over phosphates
- Disposing alkali solutions in HDG not usual
Low temperature phosphate-free alkaline degreasing Lerapur® 268

Advantages:

✓ Very good degreasing performance at 30°C
✓ Low temperature means savings in energy and fog
✓ Removing paint and grease is possible at > 60°C
✓ Can be modified to emulsifying or demulsifying
✓ Free of phosphates – no contamination for acid
✓ Lower consumption vs acid cleaning systems
✓ Rinsing recommended but not necessary
✓ Reduced neutralization for acid

Disadvantages:

✓ Liquid product easy to handle
- Limited bath life time to hold good performance
- Disposing alkali solutions in HDG not usual
Phosphate-free alkaline low temperature-degreasing based on Lerapur® 268

✅ low temperature saves energy and reduces evaporation/steam

level of temperature and loss in heat:

Demand of energy for evaporation
kW each bath vs temperature

source: ABAG-itm, Pforzheim
Phosphate-free alkaline low temperature-degreasing based on Lerapur® 268

Temperature vs evaporation (Stockmeier lab 2015)

- low temperature saves energy & reduces evaporation/steam

✓
Phosphate-free alkaline low temperature-degreasing based on Lerapur® 268

- low temperature saves energy & reduces evaporation/steam

in lab (15 h) overnight =>

30°C  40°C  55°C
Phosphate-free alkaline low temperature-degreasing based on Lerapur® 268

✓ low temperature saves energy & reduces evaporation/steam

Temperature vs evaporation (Stockmeier lab 2015)

45° C

65° C
Phosphate-free alkaline low temperature-degreasing based on Lerapur® 268

✓ degreasing is possible at 30°C
check for wetting (degreasing performance)

Poor degreasing,
the water does not stay on surface

Good degreasing,
the water wets the surface
What happens with bad degreased surfaces in the acid?

Acid will need contact with iron! There will not be a reaction of acid at not wetted spots. There is time necessary to penetrate oil films.

Result:
The etched surface will not be even. Additional contaminations are dragged into the pickling acid.
Emulsifying or demulsifying can be adjusted depending onto the chosen surfactant mixture & the characteristics of removed oils, the Lerapur® 268 – System can be adjusted either emulsifying or demulsifying.
A conventional degreasing system without flooding and without oil separator will be only usable for emulsifying degreasing system. In demulsifying system this will lead to re-contaminate the surfaces by floating oil.
Degreasing with overflowing and oil separator

Water, if possible from alk. rinsing to hold volume in degreasing bath

pumping skimmed solution into oil separator

continuously flooding by pump (to move flotations out of treating area)
solution without oil back to degreasing free flow (or with pump via buffering tank)

replenishment of degreasing agent

wasting / recycling

This technology can be used as well for pickling and rinsing bathes to separate floating substances
Acid degreasing based on phosphoric acid

Basing on phosphoric acid (mixture)
Temperature: 20 – 35°C
rinsing after degreasing will not be necessary
unlimited lifetime of degreasing solution
sludge removing frequently necessary
heating elements can be damaged by incrustations

For general galvanizing with low to medium oil contaminations,
more needs in pickling quality
Paint stripping is not possible
Why to use phosphoric acid?
Iron in course of time for different acids (simplified)
Acid degreasing on base of hydrochloric acid has to be changed at ca. 150 -180 g/l iron completely or partionally (lifecircle of customer) iron ($\text{Fe}^{2+}$) in course of time at our customer using pickling degreaser Leraclen® BEF
phosphoric acid based degreasing is limiting iron by precipitation therefore it has never to be dumped (Life circle at customers)

course of time of phosphoric based degreaser at customer A: make up and approx. 3 years use

course of time of phosphoric based degreaser at customer B: approx. 7 years after make up and following 6 years of use
Heating elements in phosphoric based degreasing solutions can be incrustated by sludge.
Conventional acidic degreasing (based on phosphoric acid)

**Advantages:**
- Rinsing isn’t necessary => 1 more acid bath
- Bath life time: **Never Dump**
- Good degreasing performance
- Not neutralizing pickling bath
- Less disposal once a year: sludge
- No or very low energy usage

**Disadvantages:**
- Degreasing performance a bit less vs alkaline degreasers
- Demand for chemicals higher than alkaline degreasers
- Possible contamination of acid by phosphates
- Possible incrustation of heating elements
New acidic degreasing without phosphoric acid Leraclen® PF 10.1

Advantages:
✔ Rinsing isn’t necessary => 1 more acid bath
✔ Phosphate free – low contamination for pickling
✔ Very good degreasing performance
✔ Not neutralizing pickling bath
✔ Less disposal once a year: sludge
✔ No incrustation on heating elements
✔ No or low energy usage
✔ Bath life time: Never Dump

Disadvantages:
- More consumption vs alkaline
- Less degreasing power vs hot alkaline
New acidic degreasing without phosphoric acid Leraclen® PF 10.1

- **customer A (completely new made up)**
- **customer B (coming from phosphoric acid based System)**
New acidic degreasing without phosphoric acid Leraclen® PF 10.1

Sludge behaviour and cleaning in phosphate-free cleaning systems

Cleaning customer A
settlement on heating,
easy to remove by water spray

Cleaning after 1 year
customer B – heating
without incrustations

cleaning after 1 year
customer B – sludge easy
to remove by pump
Pickling acid:

Minimizing emissions by adding Leratens® AV plus

- improves lifetime of acid
- reduces formation of aerosols
- minimizes and avoids floating substances

HCl 160g/l + 23 g/l Fe + ironchips 10 Minuten covered with paper

Splashes of HCl coloured by Methylorange

Without addition

0,5% Leratens® AV plus
More environmental aspects

**flux**

Minimizing emissions by Leratens® Flux Additiv FF

- reduced demand for flux salt and less formation of zinc-ash
- minimizes drying times and temperatures
- reduces emissions of ammonia during galvanizing
## Vergleich alkalischer Entfettungssysteme in Feuerverzinkereien

<table>
<thead>
<tr>
<th></th>
<th>alkalische Entfettung konventionell</th>
<th>alkalische Entfettung Tieftemperatur phosphatfrei Lerapur® 268</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ansatzkonzentration</td>
<td>4 – 10% Pulver oder 2 – 12Vol% flüssig + Tensid 0 – 2Vol%</td>
<td>3Vol% Lerapur® 268 + 0,3Vol% Leratens® 1006</td>
</tr>
<tr>
<td>Lieferform</td>
<td>meist Pulver</td>
<td>flüssig</td>
</tr>
<tr>
<td>Temperatur</td>
<td>50-80°C</td>
<td>ab 30°C</td>
</tr>
<tr>
<td>Spüle</td>
<td>dringend empfohlen</td>
<td>empfohlen</td>
</tr>
<tr>
<td>Entfettungsleistung</td>
<td>gut – sehr gut</td>
<td>gut – sehr gut</td>
</tr>
<tr>
<td>Standzeit</td>
<td>Monate – Jahre</td>
<td>Monate – Jahre</td>
</tr>
<tr>
<td>Schlammbildung</td>
<td>wenig bis mittel</td>
<td>gering</td>
</tr>
<tr>
<td>Alkali-Gefährdung</td>
<td>mittel – sehr hoch</td>
<td>mittel</td>
</tr>
<tr>
<td>Phosphat</td>
<td>oft (bis über 20%)</td>
<td>phosphatfrei</td>
</tr>
</tbody>
</table>
### Comparison of Alkaline Degreasing Systems for Galvanizers

<table>
<thead>
<tr>
<th></th>
<th>Conventional Alkaline Degreasing</th>
<th>Low Temperature Alkaline Degreasing Without Phosphates (Lerapur® 268)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Make Up Concentration</strong></td>
<td>4 – 10% powder or 2 – 12Vol% liquid + surfactant 0 – 2Vol%</td>
<td>3Vol% Lerapur® 268 + 0,3Vol% Leratens® 1006</td>
</tr>
<tr>
<td><strong>Form</strong></td>
<td>Most important powder</td>
<td>Liquid</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>50-80°C</td>
<td>Above 30°C</td>
</tr>
<tr>
<td><strong>Rinsing</strong></td>
<td>Strongly recommended</td>
<td>Recommended</td>
</tr>
<tr>
<td><strong>Degr. Performance</strong></td>
<td>Good – Very Good</td>
<td>Good – Very Good</td>
</tr>
<tr>
<td><strong>Lifetime</strong></td>
<td>Months - Years</td>
<td>Months – Years</td>
</tr>
<tr>
<td><strong>Sludge Formation</strong></td>
<td>Low to Medium</td>
<td>Low</td>
</tr>
<tr>
<td><strong>Danger from Alkali</strong></td>
<td>Medium – Very Dangerous</td>
<td>Medium</td>
</tr>
<tr>
<td><strong>Phosphates</strong></td>
<td>Often (up to more than 20%)</td>
<td>Free of phosphates</td>
</tr>
</tbody>
</table>
# Vergleich saurer Entfettungssysteme in Feuerverzinkereien

<table>
<thead>
<tr>
<th>Vergleichsstufe</th>
<th>phosphorsaure Entfettung konventionell</th>
<th>saure Entfettung phosphatfrei Leraclen® PF10.1</th>
<th>Beizentfetter (Entfettung in Salzsäure)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ansatzkonzentration</td>
<td>2 – 10 Vol% flüssig</td>
<td>3 Vol% Leraclen® PF10.1</td>
<td>0,5 – 2% Beizentfetter + 10 – 200 g/l HCl</td>
</tr>
<tr>
<td>Lieferform</td>
<td>flüssig</td>
<td>flüssig</td>
<td>flüssig</td>
</tr>
<tr>
<td>Temperatur</td>
<td>20 – 35°C</td>
<td>20 – 40°C (max. 50°C)</td>
<td>20 – 40°C</td>
</tr>
<tr>
<td>Spüle</td>
<td>nicht erforderlich</td>
<td>nicht erforderlich</td>
<td>nicht erforderlich</td>
</tr>
<tr>
<td>Entfettungsleistung</td>
<td>mittel – gut</td>
<td>gut</td>
<td>mittel</td>
</tr>
<tr>
<td>Standzeit</td>
<td>meist unbegrenzt</td>
<td>meist unbegrenzt</td>
<td>bis 160 g/l Eisen</td>
</tr>
<tr>
<td>Schlammbildung</td>
<td>ja, pumpfähig</td>
<td>ja, pumpfähig</td>
<td>wenig</td>
</tr>
<tr>
<td>Säure-Gefährdung</td>
<td>wenig – mittel</td>
<td>wenig – mittel</td>
<td>mittel – hoch</td>
</tr>
<tr>
<td>Phosphatgehalt</td>
<td>bis zu 100 g/l</td>
<td>phosphatfrei</td>
<td>phosphatfrei</td>
</tr>
<tr>
<td>Verkrustungen</td>
<td>Heizung gefährdet</td>
<td>keine</td>
<td>keine</td>
</tr>
<tr>
<td>Entsorgung</td>
<td>nur Schlamm</td>
<td>nur Schlamm</td>
<td>komplette Lösung</td>
</tr>
</tbody>
</table>
### Comparison of Acid Based Degreasing Systems for Galvanizers

<table>
<thead>
<tr>
<th></th>
<th>Conventional Phosphoric Based Acid Degreasing</th>
<th>Degreasing Without Phosphoric Acid Leraclen® PF 10.1</th>
<th>Pickling Degreaser (Degreasing in Hydrochloric Acid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Make up concentration</td>
<td>2 – 10 Vol% liquid</td>
<td>3 Vol% Leraclen® PF 10.1</td>
<td>0.5 – 2% Beizentfetter + 10 – 200 g/l HCl</td>
</tr>
<tr>
<td>Form</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
</tr>
<tr>
<td>Temperature</td>
<td>20 – 35°C</td>
<td>20 – 40°C (max. 50°C)</td>
<td>20 – 40°C</td>
</tr>
<tr>
<td>Rinsing</td>
<td>Not necessary</td>
<td>Not necessary</td>
<td>Not necessary</td>
</tr>
<tr>
<td>Degr. performance</td>
<td>Medium – Good</td>
<td>Good</td>
<td>Medium</td>
</tr>
<tr>
<td>Lifetime</td>
<td>Never dump</td>
<td>Never dump</td>
<td>Max. 160 g/l iron</td>
</tr>
<tr>
<td>Sludge formation</td>
<td>Yes, pump able</td>
<td>Yes, pump able</td>
<td>Low</td>
</tr>
<tr>
<td>Danger from acid</td>
<td>Low – Medium</td>
<td>Low – Medium</td>
<td>Medium – High</td>
</tr>
<tr>
<td>Phosphates</td>
<td>Up to 100 g/l</td>
<td>Free of phosphates</td>
<td>Free of phosphates</td>
</tr>
<tr>
<td>Incrustation</td>
<td>Danger for heating</td>
<td>No incrustation</td>
<td>No incrustation</td>
</tr>
<tr>
<td>Waste</td>
<td>Only sludge</td>
<td>Only sludge</td>
<td>Complete solution</td>
</tr>
</tbody>
</table>

**Notes:**
- Leraclen® PF 10.1 is a pickling degreaser (degreasing in hydrochloric acid).
- Make up concentration includes the concentration of the degreaser solution in liquid.
- Rinsing is not necessary for degreasing systems without phosphoric acid.
- Temperature ranges are provided for each system, with max. 50°C for phosphoric-based systems.
- Lifetime considerations include the maximum iron content that the system can handle before dumping is necessary.
- Sludge formation is considered, with options for pumping ability.
- Danger from acid levels range from low to medium, with phosphates also noted.
- Incrustation danger is noted for heating, with no incrustation for systems without phosphoric acid.
- Waste management includes only sludge or a complete solution.
Vielen Dank von Jürgen Kader
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