# New Pretreatment in Plating Lines

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Recently, many industrial part cleaning lines have been transformed from solvent cleaning (CHC, chlorinated hydrocarbons) to aqueous systems in order to comply with environmental and ecological mandates. This led to the evolution of new, high-quality aqueous cleaning concepts. At the same time, the need for reduced chemical waste further motivated the industry to develop reliable recycling systems. This presentation shows how these two technologies were incorporated to produce highly efficient, innovative aqueous cleaning systems in preplate cycles. Markedly improved cleaning, more stable processes and lower chemical consumption are achieved. An overview of the chemistry of demulsifying cleaners is discussed, as well as their use in practice, analytical controls and recycling techniques. Case studies illustrating applications in zinc and nickel plating lines are presented.

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## Introduction

Earlier works show that minimizing cleaners consumption through using oil separators, centrifuge and micro- or ultrafiltration is limited to cleaners which combine builder substances and surfactants into one product ("coventional cleaner").

In the new modular cleaning systems, the builder component and the surfactants are formulated as individual components. This allows the optimization of builder to surfactant ratios to meet various cleaning needs. In order to achieve high quality cleaning, effective recycling and ease of handling and dosing, the new cleaning components are formulated in highly concentrated liquid form, along with demulsifying type surfactants.

## Cleaning Systems

A common problem encountered in conventional emulsifying cleaners, is the increase of builders concentration in the bath due to the higher consumption of surfactants compared to builder substances (salt effect). When recycling is used with this type of system using oil separator, centrifuge or cross flow filtration, where most of the builder substances are returned to the bath, the salt effect becomes more pronounced, necessitating frequent bath replacement. To realize longer, more stable, cleaner life requires minimizing the above mentioned salt effect. This is accomplished with a new strategy: Modular cleaning systems. The problems when a conventional cleaner is used with recycling equipment are shown in **Figures 1 a, b**.

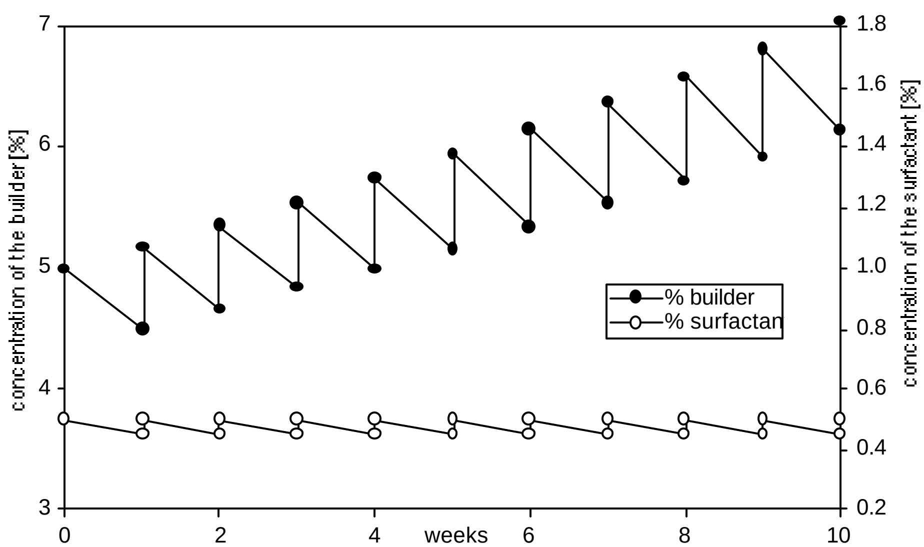



**Fig. 1a:** Increase of builder substances by dosing a conventional cleaner. To maintain the cleaning capability of the bath, the dosing of a conventional cleaner causes an increase of builder components in the cleaning bath.

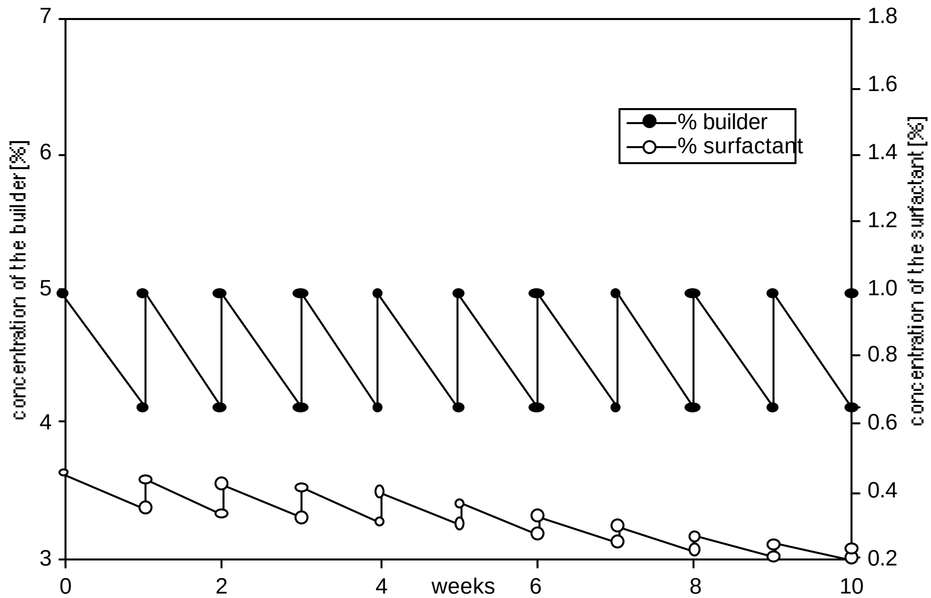



**Fig. 1b:** If the builder concentration is held constant, the surfactant concentration and therefore the cleaning capability decreases.

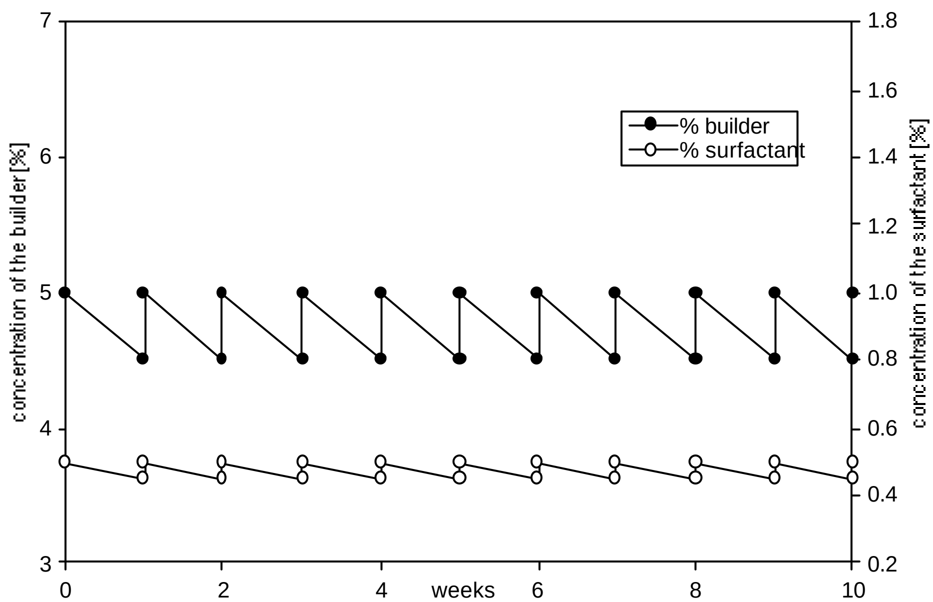



**Fig. 1c:** Dosing of a modular cleaning system - concentration of builder and surfactant remains constant.

The irregular consumption of the single additive cleaner can be explained by the varying amount of oil binding with corresponding levels of surfactant. On a macroscopic scale, the concentration of surfactant decreases quicker than the concentration of builder substances. **Fig. 1c** shows how the concentration of builder and surfactants are maintained at a constant level in a modular cleaning system. The ideal ratio of builder and surfactant concentration can be maintained by dosing one builder component, which is adjusted to the material to be cleaned, and one surfactant component according to the results of the bath analysis. The basic composition of builder and surfactant components is described below.

## The Raw Material

Important criteria in selecting the raw materials used for the builder and surfactants are:

- cleaning capability
- environmental toxicity and
- permeability on several commercial micro- and ultrafiltration membranes

**Builder module:** Sodium hydroxide, phosphates, borates and soft complexing agents like organic acids, comprise the building blocks for the formulation of builder modules suitable for the different basis metals. . For example, a neutral builder module (pH 7) for aluminium and brass, and a highly alkaline module (pH 14) for ferrous metals. The modules are silicate free because silicates can block the micro- or ultrafiltration membrane (Possible formation of gelatinous silicic acid at certain pH values). All builder modules show a recycling rate of their components of about 80 % to 90 %.

**Surfactant module:** The surfactant modules are nonionic surfactants with a low oil binding capacity. Due to their demulsifying property, they do not hold the oil in the cleaning bath like an emulsifying cleaner. This type of surfactant module can be adjusted for either immersion or spray cleaning operations. The recycling rate of the surfactant module depends on the kind of oil (e.g. mineral oil, lubricant etc.) which has to be removed and the cleaning technique used. The recycling rate of immersion surfactants ranges between 50 % and 80 %, the rate of spray surfactants from 30 % to 50 % (turbidity point).

## Recycling Equipment

**Oil Separator:** Oil, fat and grease which are not emulsified are removed from the cleaning bath. The demulsifying surfactant module supports the phase separation by specific weight. The lighter oil phase accumulates at the top of the oil separator and the oil-free aqueous phase, which contains builder and surfactant components, is fed back into the cleaning bath.

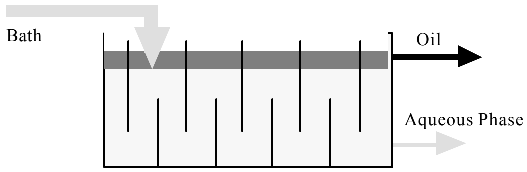



**Fig. 2:** Oil separator

**Cross Flow Filtration:** Microfiltration membranes with pore sizes from 12 µm to 0.2 µm and ultrafiltration membranes with pore sizes from 100 nm to 4 nm are used to separate oil from the cleaning baths. Builder components and demulsifying surfactants with low oil binding capacity can pass through the membrane and are fed back into the cleaning bath (permeate). The oil phase remains in the retentate and can be concentrated for waste disposal or oil reclamation.

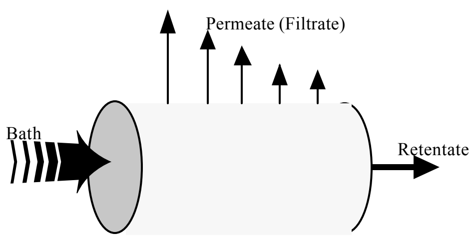


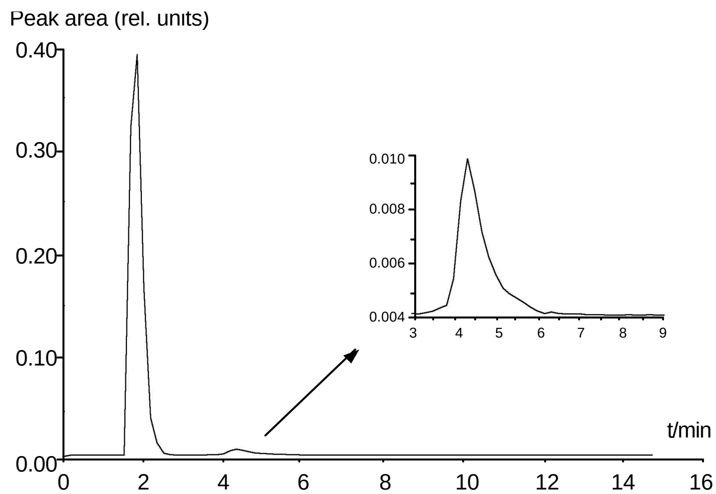

**Fig. 3:** Cross Flow Filtration

**Process control**

Control of the bath components, builder and surfactant, are essential to maintain satisfactory recycling.

**Analysis of the builder module:** The concentration of the builder module can be obtained easily by volumetric analysis (titration), by conductivity measurement or photometric determination of the phosphate concentration.

**Analysis of the surfactants:** In the starting phase the surfactant concentration in the cleaning bath and the aqueous phase of an oil separator or in the permeate of a micro- or ultrafiltration can be determined by HPLC (HPLC = **H**igh **P**erformance **L**iquid **C**hromatography) to determine the optimum recycling ratio and fix the dosing matrix. The analytical parameters are given below (**Fig. 4**).




| | |
|---|---|
| column: | 250 mm x 4 mm ID |
| filling: | reversed phase column 7 $C_{18}$ |
| mobile phase: | methanol/water 85/15 |
| flow: | 1 ml/min |
| pressure: | 150 bar |
| temperature: | room temperature |
| detection: | refraction index (RI) |

**Fig. 4:** Chromatogram (HPLC) of an aqueous surfactant blend (left) and isolated surfactant peak (right)

## Case Studies

### 1 - Cleaning Plant for Immersion Cleaning (5 Tanks)

Small parts made of brass and steel are placed in boxes to be cleaned in a plant consisting of five tanks. After each cleaning step the boxes are forwarded to the following bath. The cleaning process takes place in the first two tanks followed by three rinses. All tanks are connected in cascade from bath 5 to bath 1 (**Fig. 5**).

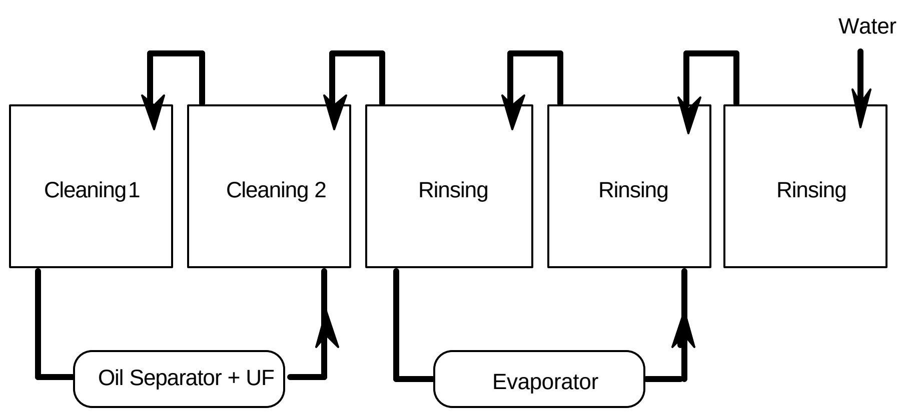



**Fig. 5:** Scheme of a Cleaning Plant for Immersion Cleaning (5 Tanks)

Prior situation using conventional cleaning:

- Contamination level: 30-130 mg/kg parts
- Desired cleaning quality (residual contamination): 10 mg/kg parts
- Different cleaners were used
- Cleaner life limited to 2 weeks
- Desired quality could only be achieved with an additional external cleaning step.

An ultrafiltration (ceramic membrane; pore size 0.2 µm) for the bathes 1 and 2 was installed and a demulsifying cleaning system was used (concentration: 3 % builder module; 0.3 % of the surfactant module)

New set up

- Concentration of builder (3,8 %) und surfactant modules (0,25 %) remained constant
- Most of the oil is removed in bath 1 (oil content (200-3000 mg/l))
- Oil content in bath 2 was reduced (50 mg/l)
- Residual contamination of 10 mg/kg parts was diminished to approx. 3 mg/kg parts
- Cleaner life increased to more than 3 months

**2 - Cleaning Plant for Spray Cleaning (3 Tanks)**

Parts made of steel are cleaned in a 3 stage spray cleaning plant. The cleaning process takes place in stations 1 and 2. Station 3 is used for passivation. All tanks are joined in cascade from bath 3 to bath 1.

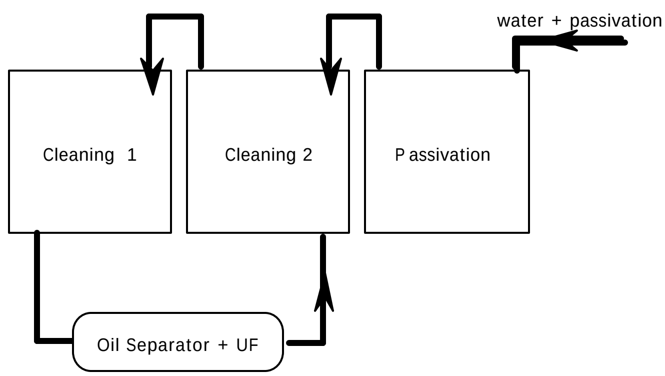



**Fig. 6:** Scheme of a Cleaning Plant for Spray Cleaning (3 Tanks)

Prior situation:

- High oil content build up in the cleaning stations resulting in low cleaning quality
- foam problems
- short bath life time of 3-4 weeks

The cleaning plant was equipped with a mobile ultrafiltration which is used 5 days a month. The cleaner system consists of a demulsifying neutral cleaner (concentration 1-2 %) and a spray surfactant module.

New set up:

- High cleaning quality, low oil content
- Foam problems eliminated
- Increase of cleaner life to more than 22 weeks

### 3 - Nickel Plating Line

The hot degreasing in a nickel plating line was switched over to a demulsifying system with an alkaline builder system and a demulsifying surfactant blend. The same surfactant blend was also used as an additive in the HCl pickling tank. In the electrolytic cleaner, a soft complexing agent was used as an additive to sodium hydroxide.

The only additional equipment was an oil separator, which was already installed but was ineffective for emulsifying cleaners. The emulsifying hot degreasing baths (5000 l) were dumped each month. After changing to demulsifying modular cleaners the cleaner solution life was increased up to 1 year.

### 4 - Barrel Zinc Plating

The hot degreasing in a barrel zinc plating line for fasteners is operated as shown in **Fig. 7**.

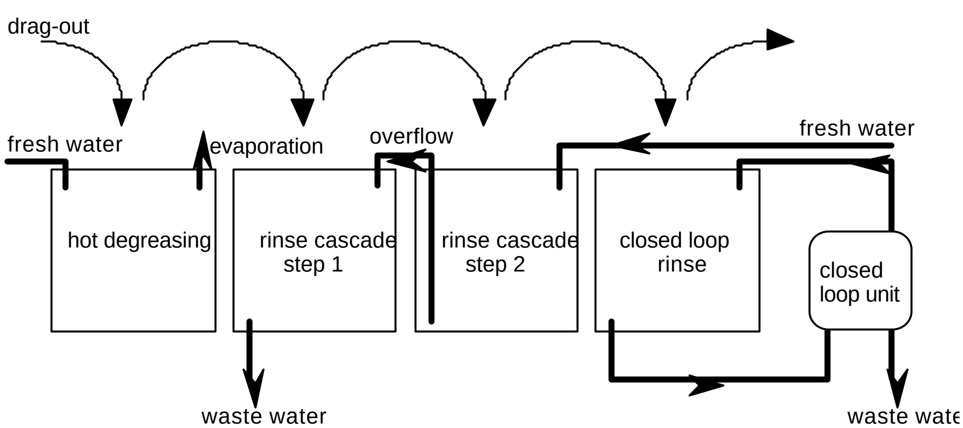



**Fig. 7:** Fluid flow in a hot degreasing with double cascade and closed loop rinse

The rinsing bath was supplied with DI water from the central ion exchange unit. Although the rinsing volumes were optimized, the amount of DI water produced in the ion exchange unit was not sufficient. To solve this problem a zero discharge rinsing technique with recycling equipment containing an oil separator and a micro filtration was installed. To ensure that the whole line worked successfully, the cleaners were changed to a modular cleaning system and the temperature was lowered from 80 °C to 75 °C.

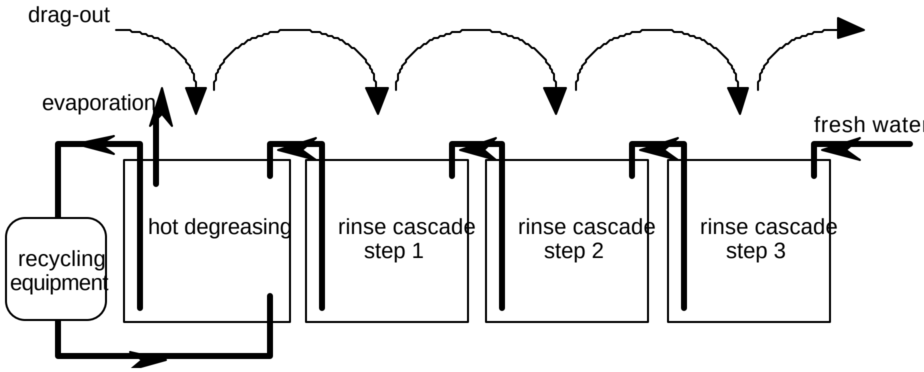



**Fig. 8:** Fluid flow in a hot degreasing with triple cascade and feedback

The amount of waste water was reduced to 1/40 th, the consumption of fresh water was lower and the economic efficiency increased.

**Conclusion:**

High quality cleaning, effective recycling and extended cleaner life cannot be achieved with conventional emulsifying type systems. Because of the frequent dumps associated with their use, these systems need to be priced at less than 0.5 EUR/Kg to be competitive with the more advanced modular demulsifying systems.

| **Barrel Zinc Plating** | | | | |
|---|---|---|---|---|
| cycle | 6 min | 24 h/d | 5 d/w | |
| drag-out | 2.5 l/barrel | 25 l/h | 100 kg fastener/barrel | |
| hot degreasing | 3 bathes, total 5200 l volume, 6,5 $m^2$ bath surface | | | |
| temperature | 75 °C | | | |
| evaporation loss | 73 l/h | | | |
| **process technology** | | | | |
| rinse | double cascade and closed loop rinse **(Fig.7 )** | | triple cascade (**Fig. 8**) | |
| make up | 50 g/l emulsifying cleaner | 2.5 EUR/kg | 50 g/l Builder + 5 g/l surfactant | 5 EUR/kg |
| service live | 2 weeks | | 12 weeks | |
| **fluid flow** | | | | |
| fresh water* | 154 l/h | 0.20 EUR/h | 113 l/h | 0.20 EUR/h |
| waste water (cascade, step 1)** | 67 l/h | 0.23 EUR/h | – | – |
| waste water (cl-regeneration)*** | 42 l/h | 0.20 EUR/h | – | – |
| waste water (make up, prop.)*** | 22 l/h | 0.10 EUR/h | 3.6 l/h | 0.01 EUR/h |
| waste water/costs (total) | 131 l/h | 0.73 EUR/h | 3.6 l/h | 0.21 EUR/h |
| **concentrations** | | | | |
| rinse 1 | 16.9 g/l | 169 mval/l | 13.86 g/l | 126 mval/l |
| rinse 2 | 4.6 g/l | 46 mval/l | 3.08 g/l | 28 mval/l |
| closed loop rinse / rinse 3 | 0.1 g/l | 1 mval/l | 0.55 g/l | 5 mval/l |
| **economic efficiency** | | | | |
| cleaner consumption (drag out) | 0.713 kg/h | 1.75 EUR/h | 0.013 kg/h | 0.07 EUR/h |
| cleaner consumption (regeneration) | – | – | 0.083 kg/h | 0.42 EUR/h |
| cleaner consumption (make up) | 1.100 kg/h | 2.75 EUR/h | 0.200 kg/h | 1.00 EUR/h |
| cleaner consumption (total) | 1.813 kg/h | 4.52 EUR/h | 0.300 kg/h | 1.50 EUR/h |
| **overall costs** | **5.26 EUR/h** | | **1.71 EUR/h** | |

**Tab 1:** Balance sheet of a hot degreasing with different rinse techniques:
#1: emulsifying cleaner, s.a. fig. 7
#2: demulsifying cleaner + equipment + rinse flow back, s.a. fig. 8
*fresh water costs = 1.25 EUR/$m^3$, **waste water costs = 3.50 EUR/$m^3$, ***total costs for water = 4.75 EUR/$m^3$

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