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CLEANING PRIOR TO PVD/CVD-COATING, DETERMINATION OF THE CLEANLINESS AND CHEMICAL DECOATING OF PVD/CVD-LAYERS[1]

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Abstract

Cleaning prior to PVD/CVD coating is a key issue to achieve high yield in PVD/CVD coating processes. This article covers the principles of aqueous cleaning prior to PVD/CVD coating, describes the methods to determine the cleanliness and give a survey about the chemical decoating processes of PVD/CVD-layers.

Keywords: Ultrasonic cleaning; Cleanliness; Decoating.

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1 INTRODUCTION

About 45 years ago Borer Chemie started with the introduction of aqueous cleaning which replaces at that time the cleaning with Chromium sulphuric acid, a very hazardous and carcinogenic method, in the laboratory glass cleaning.

Since this time the aqueous cleaning processes have been developed significantly, and today they are very effective and environmentally friendly methods to achieve total residue free surfaces on nearly every substrate material. The aqueous cleaning processes replace more and more solvent based cleaning processes in the field of cleaning prior to coating.

The determination and the monitoring of the cleanliness of the surfaces prior to PVD/CVD-coating is an important issue for achieving a perfect coating.

Chemical decoating of PVD/CVD layers like e. g. TiN, TiAlN, DLC, CrC is more and more demanded in the PVD/CVD coating industry.

2 PRINCIPLES OF CLEANING

Residue-free aqueous cleaning is more than 40 years old and it is very successfully used in the following fields:

- Prior to PVD/CVD-coating;
- Precision metal parts;
- Ophthalmic and precision optics;
- Flat glass for displays;
- Photovoltaic.

For a high-sophisticated cleaning four factors are important as follows:

- Time – Usually times from 1 to 5 minutes as a cycle time are applied;
- Cleaner – They are acidic, neutral or alkaline cleaners applied;
- Mechanical effects – These can be Brownian molecular motion (soaking bath), mechanical treatment (brushing, rubbing), spray pressure (washer), cavitation (ultrasonic bath);[1-3]
- Temperature – Usually cleaning is done at room temperature up to about 90 °C.

The removal of oils and solid parts is mainly done by surfactants which have both a hydrophilic region and a hydrophobic region. This chemical structure enables the surfactant to bring the contaminations into the aqueous solution. The sequestering agents prevent the formation of deposits and prevent the re-deposition of detached particles of dirt and contaminants (above all abrasives).

This works like shown in Figures 1 and 2:

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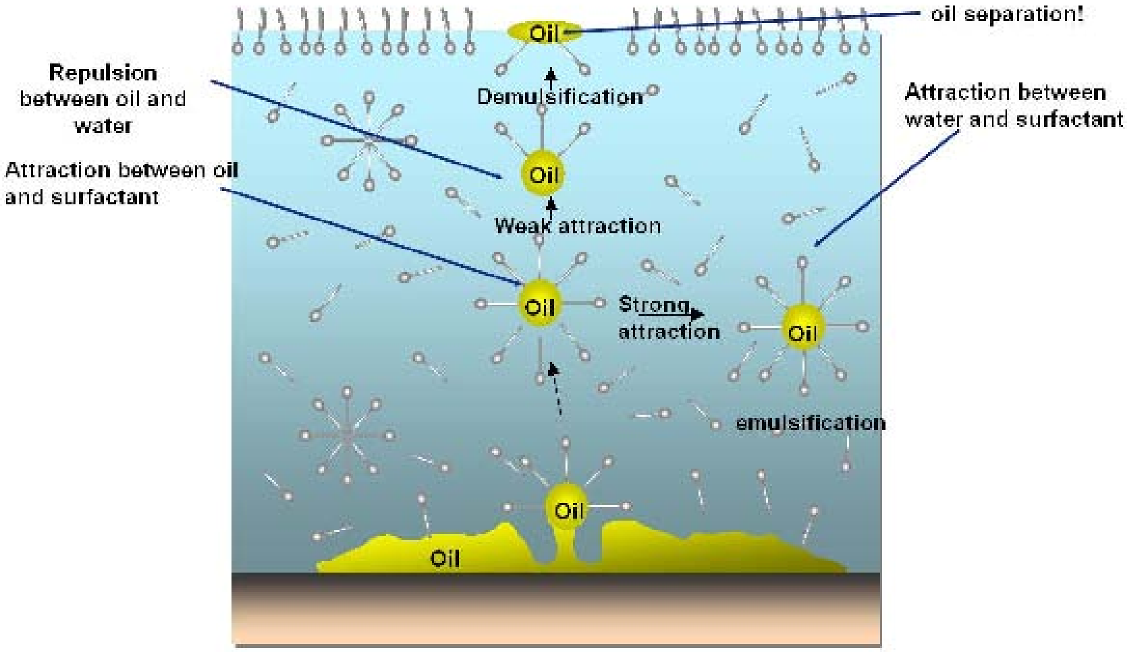

Figure 1. Principle of the emulsification and demulsification of oils.

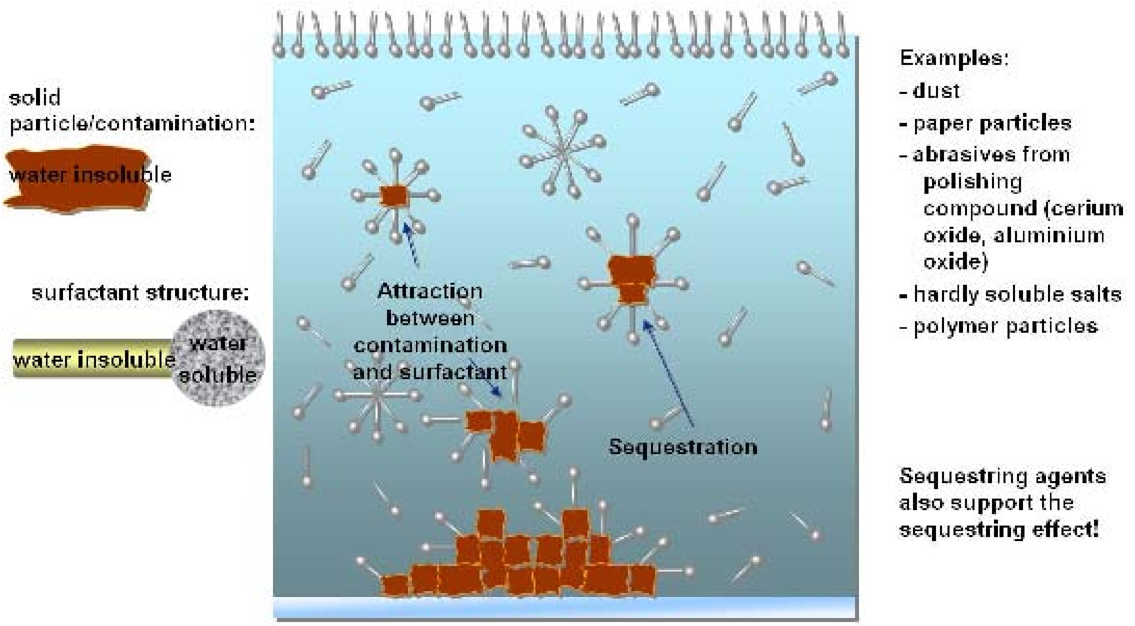

Figure 2. Principle of the suspension of solid parts.

The alkaline detergents undergo chemical reactions with the organic contaminations like as:

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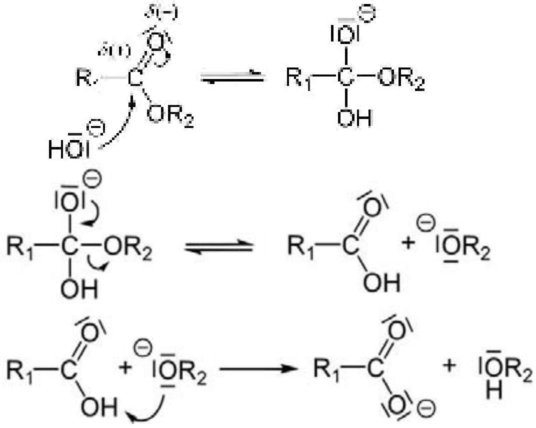
- Alkaline hydrolysis (Saponification):



- Alkaline «deprotonation»

Both reactions lead to better water soluble contaminations.

The principle of solvent cleaning is a homogeneous dissolution of the contaminations in the solvents. Solvents are not able to perform chemical reactions with the contaminations removed.

Aqueous cleaning is a totally different philosophy of cleaning and has some mayor differences compared to solvent degreasing. With aqueous cleaning, chemical reactions become possible. Chemical reactions support the cleaning process tremendously.

3 STEPS OF CLEANING PRIOR TO COATING

The aqueous cleaning process prior to coating is usually a nine step process like shown in Figure 3 and 4:

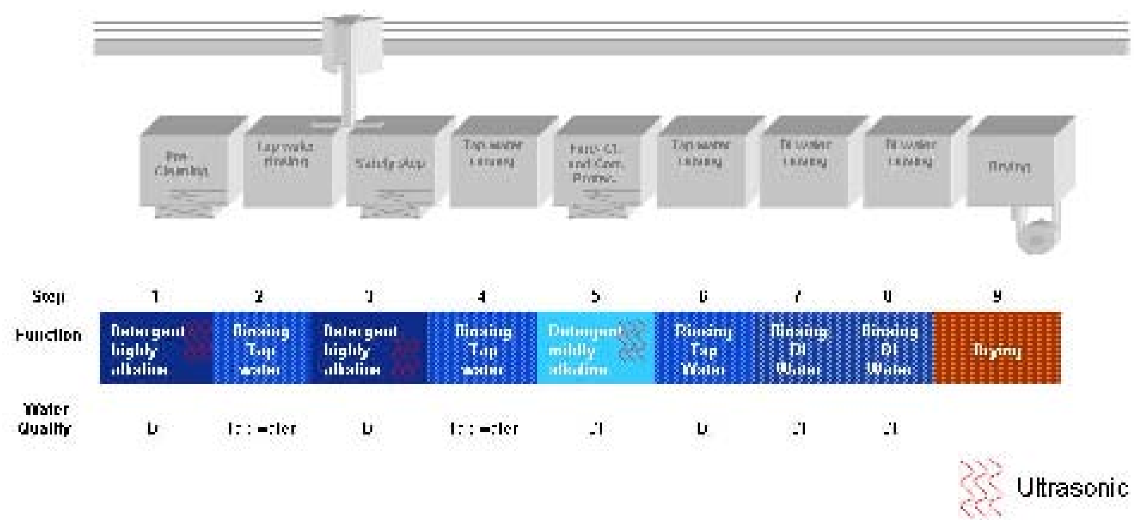


Figure 3. An example of an optimal degreasing process.

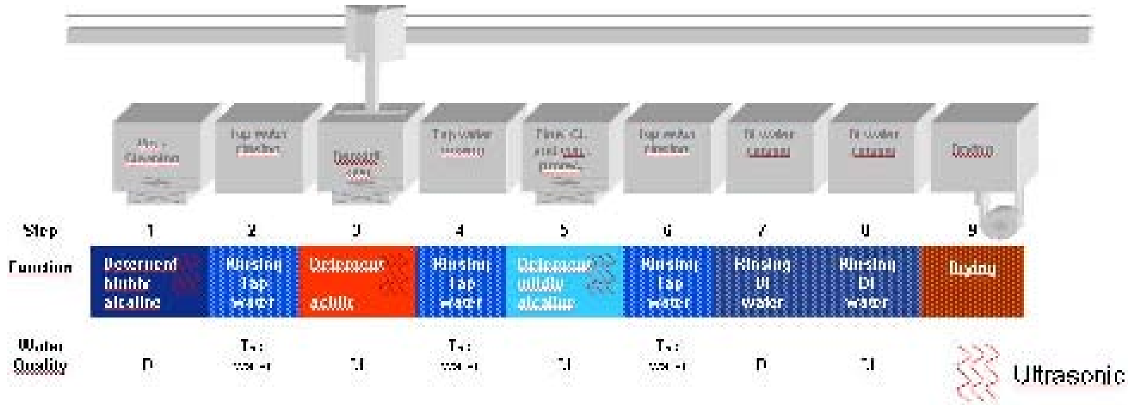


Figure 4. An example of an optimal degreasing and deoxidation process.

Bath 1 is for pre-cleaning, thereby removing most of the contaminants take place. The use of an oil separator is strongly recommended in this step.

Bath 2 prevents from carry-over of product and contamination from Bath 1 to Bath 3, this leads to a longer useful lifetime for Bath 3. An additional advantage is that the product compatibility does not have to taken so much into account.

Bath 3 is for fine cleaning and safety step with high input of contamination in Bath 1 or if Bath 1 is nearly exhausted. Alternatively Bath 3 can be used for a deoxidation process, therefore an acidic detergent is used.

Bath 4 prevents from the carry-over of product and contamination from Bath 3 to Bath 5.

Bath 5 fulfils various functions as follows. When an alkaline product is used in Bath 3, the bath is a final cleaning step. When an acidic product is used in Bath 3, the bath is a second alkaline fine cleaning step. The bath also prepares the parts for final rinsing, where they have to be protected against possible corrosion.

Bath 6 improves the rinsing off process of the cleaner used in Bath 5 and prevents the pure water reprocessing system from becoming too heavily contaminated with cleaner components.

Bath 7 and Bath 8 are connected in cascade and have the function of the final rinsing with demineralized water.

The step No. 9 is the drying step.

To prevent corrosion the cycle times in the rinsing steps often have to be adapted to the corrosion sensitivity of the parts.

To prevent the formation of spots in final rinsing, the following points also have to be taken into account. The DI water quality used must be better than < 0.5 µS/cm. The replacement rate of the DI water in the rinsing baths should be one time per cycle time per bath (including lift-out). The basket design for the parts is very important to minimize the carry-over of pure water into the drying step and the drying system, which is used, must be powerful enough.

The residue-free cleaning of the parts is of utmost importance for the following PVD/CVD coating process. Without a totally clean surface the resulting PVD/CVD coating will not be perfect. Even, if cleaning is not the key process in the PVD/CVD coating process – a perfect cleaning process is the key success factor to be able to achieve a perfect PVD/CVD coating. The better the cleaning is, the higher the yield rate of the PVD/CVD coating process will be.

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4 ANALYSIS OF THE CLEANLINESS

It is important to analyze and to monitor the cleanliness of the substrates before coating.

This can be done mainly by four methods as they are:

IR-Spectroscopy

IR-Spectroscopy is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture. Figure 5 shows the comparison of the IR-Spectra of a uncleaned and a cleaned sample

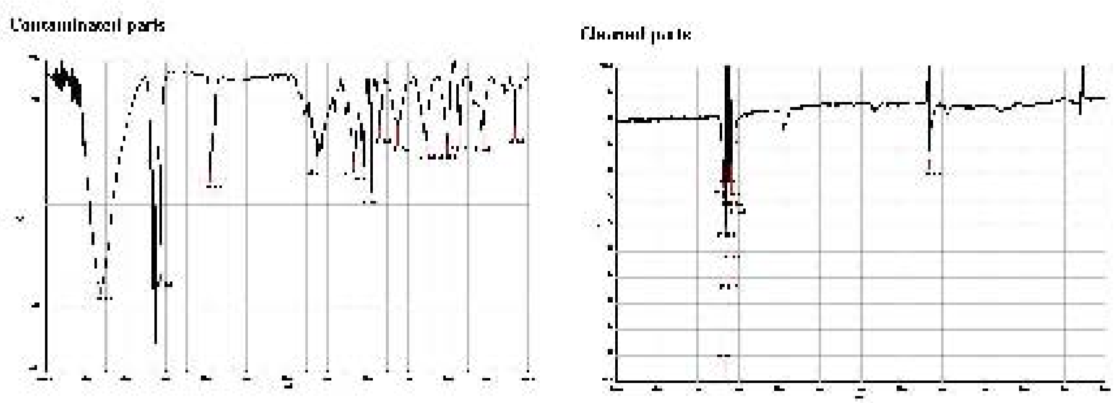

Figure 5. An example of an IR-Spectrum of an uncleaned compared with a cleaned sample.

Particle analysis

A particle analyzer makes it possible to analyze and document filters (on which particles have been collected after the cleaning process). Particle numbers and sizes can be determined after the components are cleaned and the cleaning fluid passed through a membrane or mesh filter. The results of a particle analysis are shown in Figure 6:

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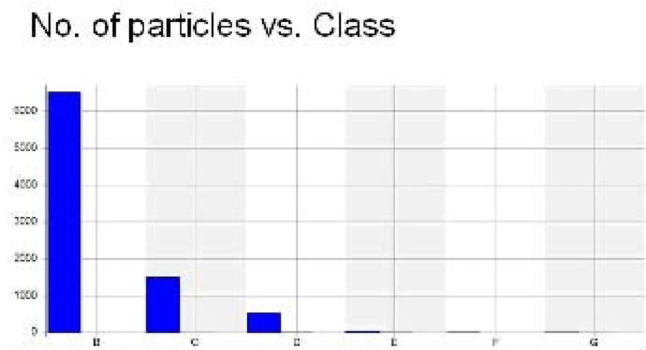
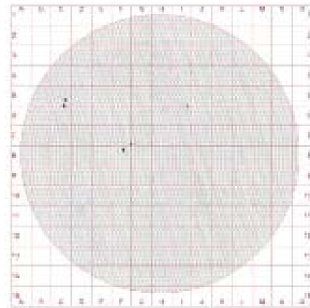


Class	Size of Class	Thereof Fibers	Total
B	5 < ... <= 15	0	6517
C	15 < ... <= 25	2	1510
D	25 < ... <= 50	7	536
E	50 < ... <= 100	4	45
F	100 < ... <= 150	0	8
G	150 < ... <= 100000	2	8
SUM			8624

Filter plate for particle count



Microscope picture

Figure 6. Result of a particle analysis.

Contact angle

The contact angle is the angle at which a liquid/vapour interface meets a solid surface. The contact angle is specific for any given system and is determined by the interactions across the three interfaces.The measurement of the contact angle of a water droplet is a quick and simple way to evaluate cleanliness of a solid surface. The correlation of cleanliness and contacts angle is shown in Figure 7.

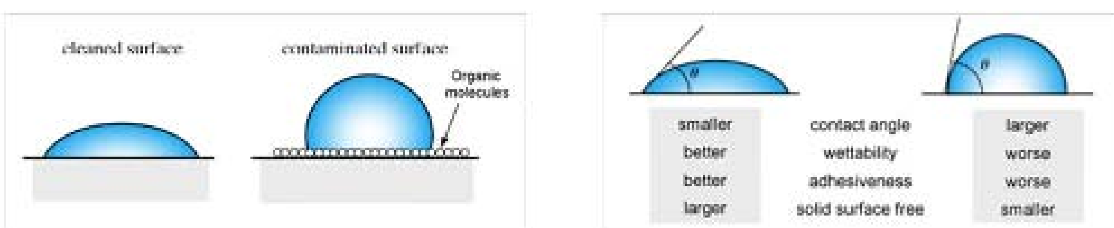


Figure 7. Significance of the contact angle[4]

Figure 8. Pictures of the contact angle measurements.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TOC-Analysis

Total organic carbon (TOC) is the amount of carbon bound in an organic compound and is often used as a non-specific indicator of water quality or cleanliness of pharmaceutical manufacturing equipment. Virtually all TOC analyzers measure the CO_2 formed when organic carbon is oxidized and/or when inorganic carbon is acidified. Subtracting the inorganic carbon from the total carbon yields the TOC.

5 DECOATING

De-coating processes are of natural interest to the industry, because of the following facts. Carbide substrates are very expensive. Tools can be re-coated several times in case of correct handling. De-coating followed by applying new coatings is cheaper compared to simply coat new tools. To save new tools coated by mistake (e.g. by break of coating oven, wrong coating applied) chemical decoating is a very helpful tool.

The chemical decoating has, compared to the sand blasting method, the advantage, that there is less labour cost and no attack on the substrate.

The following systems can be successfully chemically decoated:

Layers	TiN TiCN TiSiN/AlTiN	TiAlN-Multilayer TiAlN AlTiN AlTiSiN	WC/C	DLC	Cr CrN	ZrN	Si SiC Si3N4
Carbides + Composites of carbides	✓	✓		✓		✓	
HSS + other tool steels	✓	✓	✓	✓	✓	✓	✓

6 CONCLUSIONS

Cleaning prior to PVD/CVD coating is a key issue to achieve high yield in PVD/CVD coating processes. This article covers the principles of aqueous cleaning prior to PVD/CVD coating, describes the methods to determine the cleanliness and give a survey about the chemical decoating processes of PVD/CVD-layers.

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