Enviolet®-UV-Oxidation, a Proven Method for Bright-Nickel Plating Bath Purification

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Background

The topic of this presentation is to demonstrate the effectiveness of the treatment method in comparison with the traditional activated carbon/hydrogen peroxide treatment process for removal and destruction of organic constituents in bright-nickel baths.

UV Oxidation for Nickel Purification

Have you ever cleaned and charged a large plating filter? If yes, then you surely thought, there's got to be an easier way. There is, a completely automated State of the Art Process, ***Ultraviolet – Oxidation*****.** Eliminate carbon filtration and batch treatments, controlling nickel bath purity by TOC (Total Organic Content).

Harmful organics are crunched up and expelled as carbon dioxide gas. Resulting in reduced rejects, and consistent plating quality through improved leveling and throwing power without the use of Activated Carbon. This technology works on all plating baths where harmful organics reduce plating bath efficiency.

Nickel Plating Bath Contaminants

Contaminants in nickel solutions may be broken down into four categories, good metallics, harmful metallics, good organics and harmful organics. Harmful metallics are detected by Atomic Absorption analysis, and removed by Electrolytic Purification. Organic contamination may now be analyzed by checking the TOC (Total Organic Content). By knowing the TOC of an organically clean bath, subtracting this amount from the total TOC gives us a measurement of the harmful TOC. TOC values for clean bright nickels solutions range from 15,000 to 30.000 ppm. Solutions with TOC values above 30,000 ppm usually are in need of purification. The normal procedure would be a batch carbon treatment. These treatments fall into different categories, and require additional testing to determine the correct treatment.

Straight carbon
High pH carbon
Low ph carbon
Carbon plus Hydrogen Peroxide
Carbon plus Potassium Permanganate

Unfortunately very few electroplaters take the time to perform the above, and either over or under treat their baths. They may find themselves with the same problems after going through a costly and messy treatment.

Approximate Nickel Bath TOC Values

Process	TOC Make-UP ppm	Working Bath ppm
Bright Nickel (SAS Base)	3,000	10 – 15,000
Bright Nickel (PPS Base)	2,000	10 – 15,000
Bright Nickel Iron Tolerant)	7,500	10 – 20,000
Sulfur Free Semi-Bright	2,000	6 – 8,000
Microporous	2,000	6 – 15,000

Aqua Concept Karlsruhe (a.c.k.),Germany, developed and introduced a new plating bath treatment method in the metal finishing and printed circuit board industry, by means of the Enviolet®-UV-Oxidation process for the removal and destruction of organic additives and their breakdown products. The Enviolet®-UV-Oxidation process has been successfully applied in Europe and Asia since 1998 for many metal finishing and printed circuit board companies in the field of organic removal from bright-nickel and acid copper plating baths as well as many wastewater treatment applications such as: EDTA Copper, Cyanides, Zinc-Nickel, Electroless Nickel, Stripper/Developer, etc. Furthermore, the field of applications for this unique Enviolet®-UV-Oxidation process seems to be unlimited as new applications evolve almost daily within other industries.

The Problem

Organic plating additives in nickel plating solutions change their properties due to many electrochemically induced reactions during the plating process. These changes influence the molecular structure of these organic additives and eventually accumulate as organic breakdown products, which, over time, influence the plating bath performance severely (throwing power, leveling).

If a plating department is required to produce a high quality plated product at all times, **like at Harley Davidson**, throwing power and leveling are of major concern. The standard treatment method, a combination of activated carbon and hydrogen peroxide at elevated temperatures, has been the treatment-of-choice for the aged bright-nickel and micro-porous nickel bath. Every platter in this industry knows how time consuming and troublesome such a carbon treatment process is and, unfortunately, the achieved final results are rather unsatisfactory when analyzed for Total Organic Carbon (TOC) content. And in the event of a micro-porous nickel bath, a carbon treatment process is even more labor intensive because of the presence of solids, which requires first a pre-filtration process prior to the actual carbon treatment, and then, fresh solids must be added back again to the plating solution. Typical results after a complete activated carbon/hydrogen peroxide treatment cycle show only a 10-20% TOC reduction. One should know that if organic breakdown products are of concern then TOC measurement is the recommended analysis method. Of course, TOC measures not only the breakdown products it also includes the organic additives (carrier, brighteners, levelers and wetting agents). Typically, a fresh prepared bright-nickel bath contains organic additives between 2,500 to 5,000 ppm

TOC. However, in spite of numerous activated carbon treatment cycles, TOC levels of 10,000 to 20,000 ppm have been reported, which clearly indicates that the bath is well aged and/or in serious condition. Why does activated carbon not do a better job? It is because activated carbon has its restrictions. It usually extracts preferentially polymers with longer chain lengths but leaving the small molecules behind, which many of these breakdown products are a part of (see Figure 1).

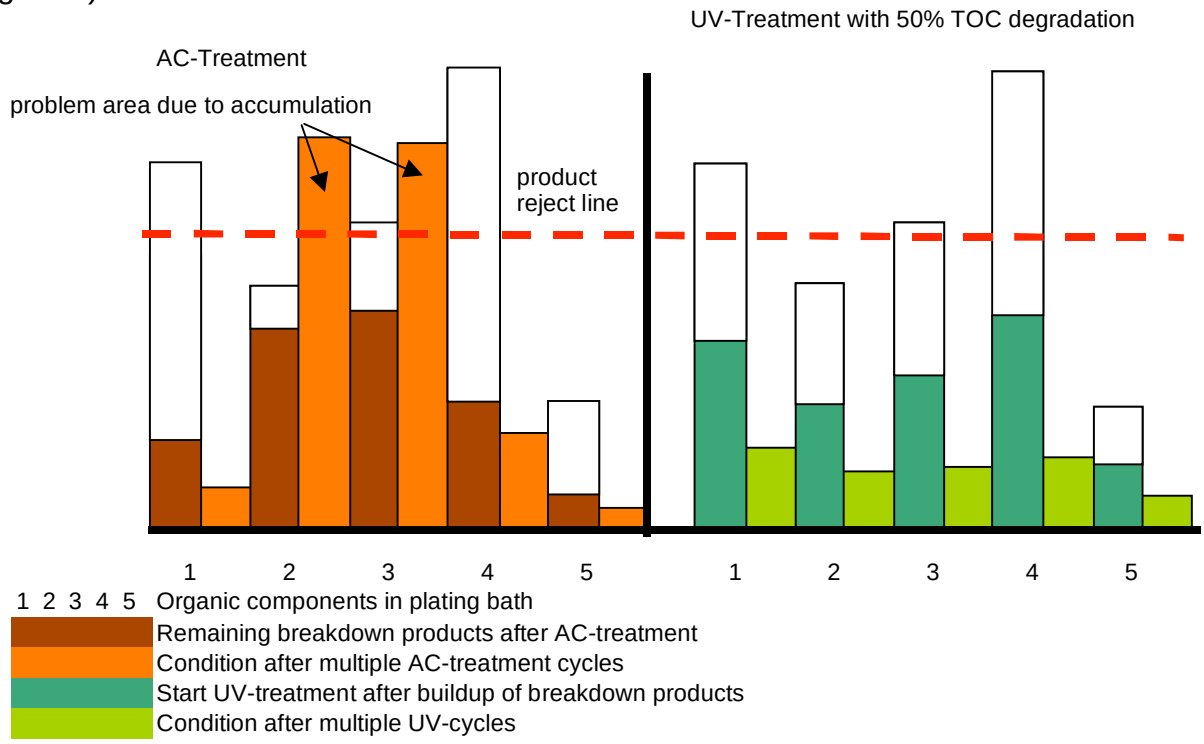


Figure 1: Chart shows precise comparison between activated carbon (AC) and UV-treatment over a prolonged time period. While with AC-treatment the poorly adsorbed organic compounds keep accumulating, they are reduced to a controlled level below the “product reject line” with UV-treatment.

The Solution

In 1998, eight (8) years ago, a.c.k. installed their first Enviolet®-UV-Oxidation process at Hansgrohe AG in Germany, which is a major faucet manufacturing company worldwide. The traditional activated carbon treatment process just could not any longer sustain the bright-nickel bath purification requirements. It was not a dependable process and lacked repeatability. Shortly after startup of the UV-Oxidation process the quality of nickel deposition was substantially improved and after six (six) months of continuous bath treatment the bath performance showed results equal to a fresh prepared plating bath; exceptionally good leveling and optimal throwing power (see Figure 2 and Table 1). At that moment activated carbon treatment was eliminated and the system was upgraded with a second UV reactor for additional capacity (see Picture 1).

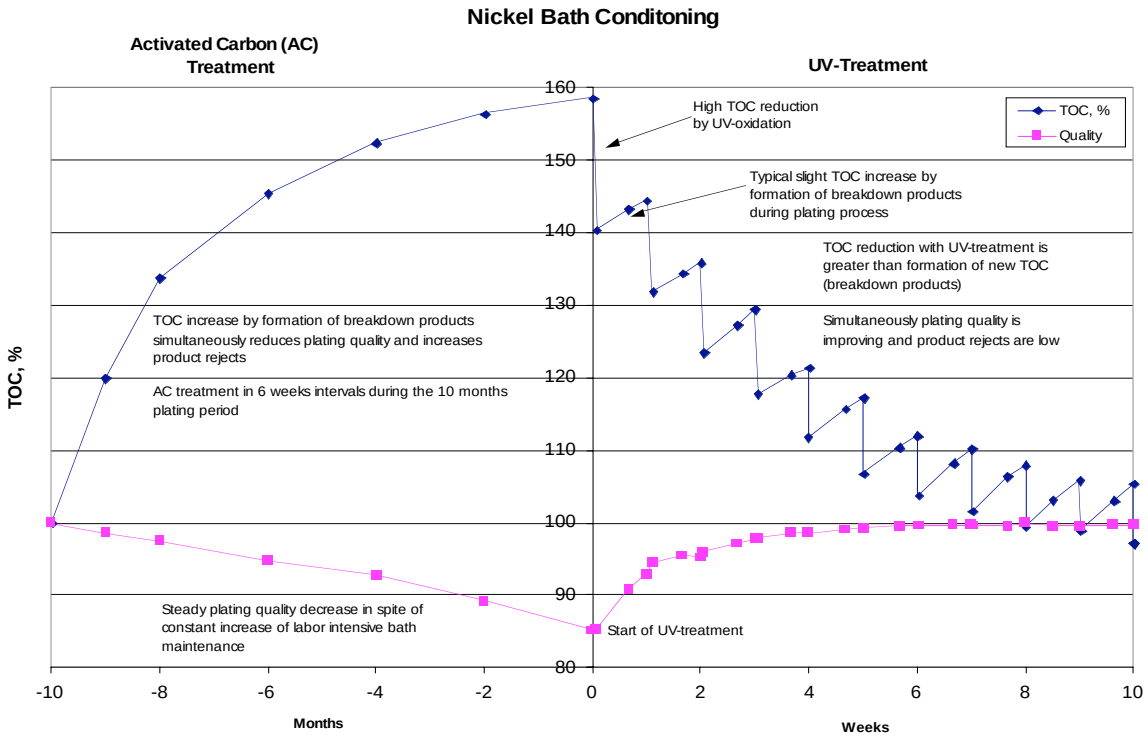


Figure 2: Left: Increase of TOC due to buildup of breakdown products and decreasing plating quality with increasing TOC concentration in plating bath.

Right: Oscillating TOC decrease due to off-line UV treatment cycles. The noticeable TOC increases result from the plating process, whereas the decreases are the result from the UV purification process. Depending on the UV system capacity, noticeable quality improvements are already accomplished after just a few treatment cycles and after multiple purification cycles consistent high plating quality is achieved.

Table 1: Comparison of AC Treatment vs. UV Treatment

	With AC Treatment	After 6 Months UV Plating Bath Maintenance
TOC, total g/l	9.7	4.8
TOC, original organic additives, g/l	4.5	4.4
TOC, breakdown products, g/l	5.2	0.4
Reject Rate, %	3 - 7	< 0.3

Picture 1: Typical Enviolet® UV System for Plating Bath Maintenance

Several laboratory tests were performed with Harley Davidson's nickel baths at ProdEcon's (a.c.k.'s US representative) laboratory setup. The UV treated samples were returned again and Harley Davidson analyzed the samples for any remaining organic constituents as well as performing various Hull Cell tests, first without any organic additives and then with new additives. All Hull Cell test panels showed very good and encouraging results. Harley Davidson, York, PA, entered into an agreement with ProdEcon Inc. and is now using a.c.k.'s Enviolet®-UV-Oxidation process for their micro-porous nickel bath treatment as a first test and has future plans on implementing this technology also on their semi-bright and bright nickel plating baths. An interesting observation about the micro-porous nickel application is that the organic additives and their breakdown products are removed in spite of the presence of micro-porous solids, which is another great benefit when compared with the activated carbon treatment process.

How it Works

Chemistry

In principle UV-Oxidation is used for destruction of organic chemical compounds by using UV light together with a standard oxidizing agent, such as hydrogen peroxide, to boost treatment performance over that performed with hydrogen peroxide alone. UV light is used to split the hydrogen peroxide molecule by producing highly reactive radicals (OH·). It is these hydroxyl radicals which then react quickly with the organic molecules by oxidizing them and breaking them down into carbon dioxide and water. Thus, this process will completely break down (mineralize) virtually all organic compounds to carbon dioxide and water, whereas sulfur

compounds are converted to sulfate and, therefore, at the end of the process, there are no waste disposal products (sludge) to deal with, which makes the Enviolet®-UV-Oxidation method a much more effective process as compared to traditional activated carbon/hydrogen peroxide treatment.

Process Description

The Enviolet®-UV-Oxidation system is a fully automated batch treatment process. All process operating parameters are programmed at the factory according to the previous lab test results. However, the system is designed with such flexibility that by changing operating conditions adjustments can be made easily on the touch screen. Typically, 10-15% of the plating bath volume is required for treatment per week in order to maintain consistent TOC concentration in the bath and producing consistent plating quality. The specified volume is pumped from the plating tank to the UV batch treatment tank. Of course, for the first time when the UV treatment process is put into operation, that volume loss in the plating bath has to be replaced with fresh bath makeup. Now the UV treatment process is started and in a fully automatic mode treats the plating bath solution until the desired TOC concentration is reached. The organic degradation chart below (Figure 3) shows how the TOC is reduced during a typical UV treatment process.

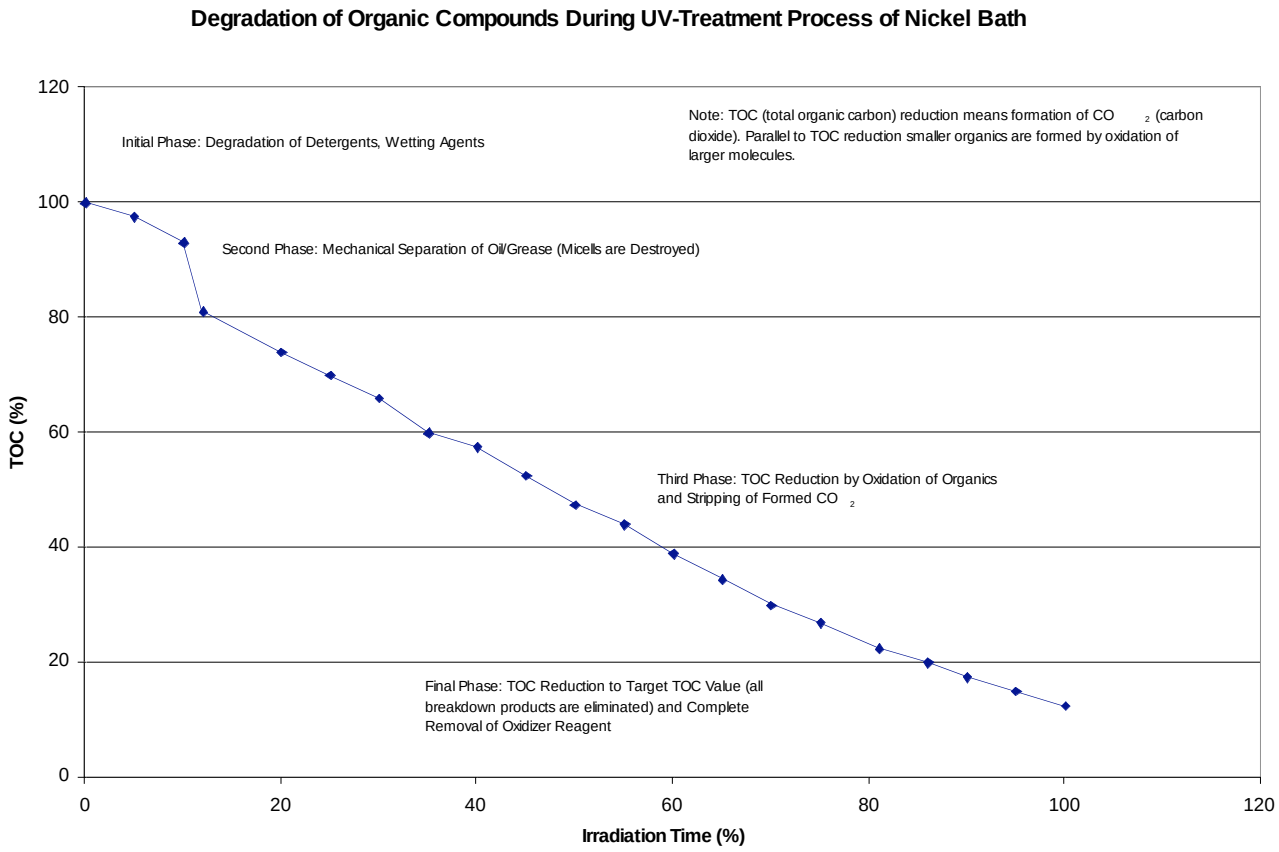
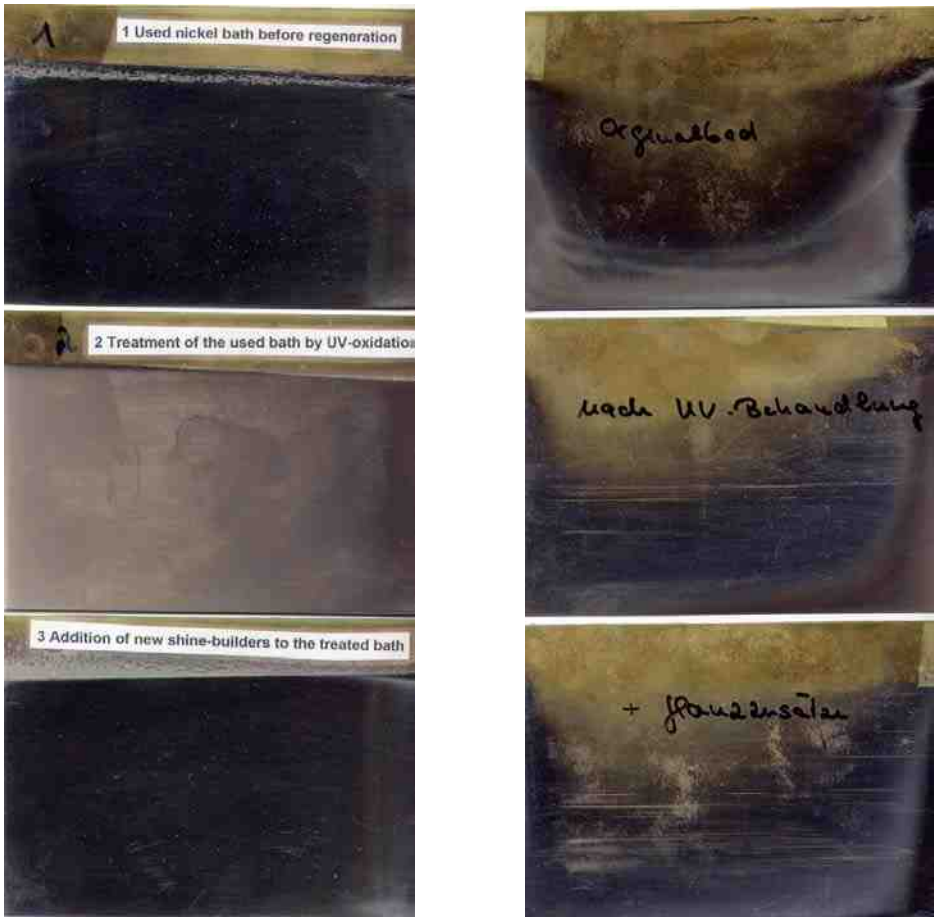


Figure 3: Typical TOC degradation chart of a Watts nickel plating bath

During the final step of the treatment process all excessive oxidizing agent is removed. Now the UV treated solution is ready for inspection. Below is a picture (Picture 2) of a series of Hull cell test panels which illustrate clearly the changes before and after the UV treatment process. The treated plating bath solution can now be discharged to a holding tank where it is available for exchange with an equal volume of spent nickel plating solution that will undergo the UV treatment process.



Picture 2: Left (Test Panel Front Side), Right (Test Panel Rear Side)
Illustration of various Hull-Cell Test Panels
Significant increase of throwing power can be noticed with UV treated bath and subsequent brightener addition:

Top:	before UV treatment of aged bright-nickel bath
Middle:	after UV treatment, without organic additives addition
Bottom:	after UV treatment, with organic additives

Conclusion

At Hansgrohe the goal for a achieving permanently a consistent and optimal bright-nickel deposit was realized. However, the biggest savings potential is in the improved utilization of the organic brightener additives. As demonstrated by the customer the organic brightener additive concentration can be significantly increased in the nickel bath, which reduced cost enormously for the mechanical pretreatment (grinding, polishing/buffing) steps.

The plating bath purification process with the Enviolet®-UV-Oxidation method has now been proven for many years in various operations. Hansgrohe in particular has proven that this technology works remarkably and has been depending solely on this plating bath maintenance process without any additional purification concepts.

Furthermore, a.c.k. has gained a lot of experiences since and has improved the process even further. The UV-Evaporator system was developed, which has a significant impact for the plating bath purification process because it allows reclaiming of rinse water dragout back into the plating bath, which improves the economics of the system operation even more. This treatment concept has been proven already in many printed circuit board (PCB) manufacturing companies worldwide.

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