Enviolet®-UV-Oxidation: A Proven Method for Bright-Nickel Plating Bath Purification

by Rudy Mathis, Ralph Dixon,* Martin Sörensen, Jürgen Weckenmann and Andreas Fath

The purpose of this article is to demonstrate the effectiveness of the UV-oxidation treatment method as compared to the traditional activated carbon/hydrogen peroxide treatment process for the 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 have surely thought, "There's got to be an easier way." There is - a completely automated state-of-the-art process, ultraviolet oxidation. It eliminates 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 nickel solutions range from 15,000 to 30,000 ppm. Solutions with TOC values above 30,000 ppm are usually 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 test, and either over- or under-treat their baths. They may find themselves with the same problems after going through a costly and messy treatment.

Aqua Concept Karlsruhe (a.c.k.), in Germany, has developed and introduced a new plating bath treatment method to the metal finishing and printed circuit board industry - 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 by many metal finishing and printed circuit board companies in the area of organic removal from bright nickel and acid copper plating baths, as well as many wastewater treatment applications, including EDTA copper, cyanides, zinc-nickel, electroless nickel, stripper/developers, etc. Furthermore, the fields of application for this unique process seem to be unlimited as new applications evolve almost daily within other industries.

The problem

Organic plating additives in nickel plating solutions change their properties because of 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. Over time, they severely influence plating bath performance (throwing power, leveling, etc.).

If a plating department is required to produce a high quality plated product at all times (*e.g.,* 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 microporous nickel bath. Every plater in this industry knows how time consuming and troublesome such a carbon treatment process is and, unfortunately, the final results achieved are rather unsatisfactory when analyzed for total organic carbon

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(TOC) content. In the case of a microporous nickel bath, a carbon treatment process is even more labor intensive because of the presence of solids, which first require 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 to 20% TOC reduction. One must realize 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 freshly prepared bright-nickel bath contains 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 (Table 1), 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. Usually, it preferentially extracts polymers with longer chain lengths but leaves the small molecules behind, of which many of these breakdown products are a part (Fig. 1).

The solution

In 1998, 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 could no 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. After six months of continuous bath treatment, the bath performance showed results equal to a freshly prepared plating bath, with exceptionally good leveling and optimal throwing power (Fig. 2 and Table 2). At that moment, activated carbon treatment was eliminated and the system was upgraded with a second UV reactor for additional capacity (Fig. 3).

Several laboratory tests were performed with Harley Davidson's nickel baths at ProdEcon's (a.c.k.'s U.S. representative) laboratory setup. The UV-treated samples were returned again and Harley Davidson analyzed the samples for any remaining organic constituents. Various Hull Cell tests were also performed, first with no 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 microporous nickel bath treatment as a first test and has future plans to implement this technology on their semi-bright and bright nickel plating baths.

An interesting observation about the microporous nickel application is that the organic additives and their breakdown products are removed in spite of the presence of microporous solids, which is another great benefit when compared with the activated carbon treatment process.

How it works

Chemistry

In principle, ultraviolet oxidation is used for the 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

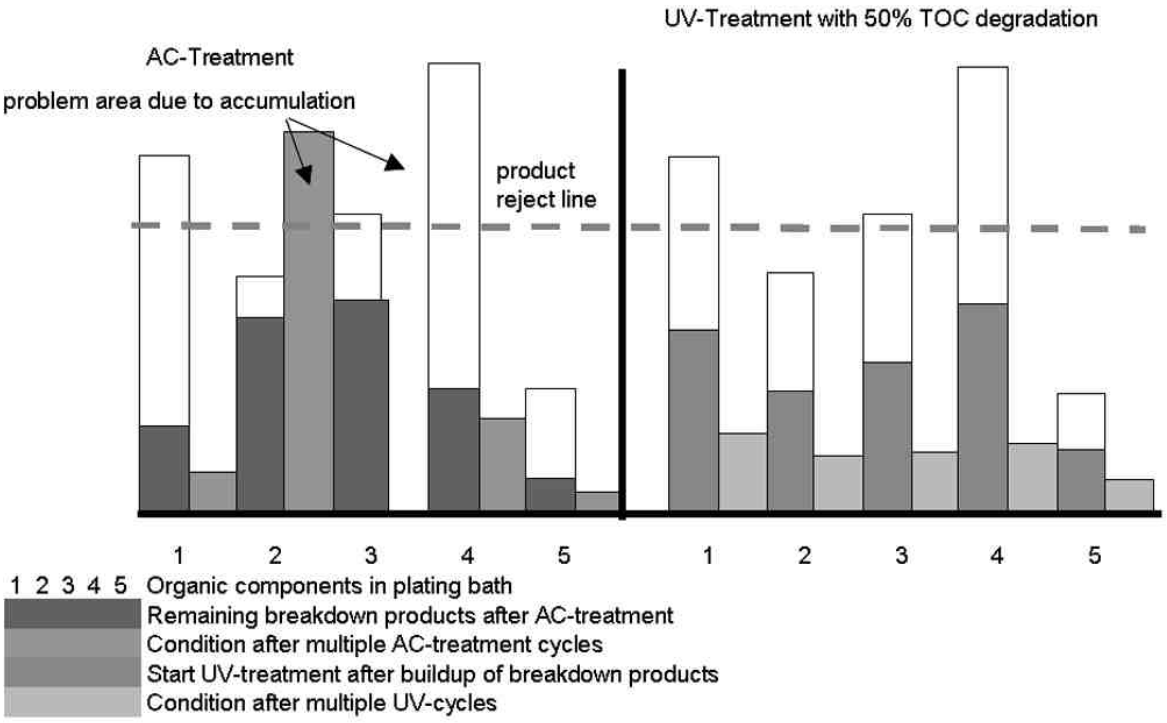

Figure 1—Chart shows precise comparison between activated carbon (AC) and UV-treatment over a prolonged time period. While with AC-treatment the poorly adsorbed organic compounds keep accumulating, they are reduced to a controlled level below the "product reject line" with UV-treatment.

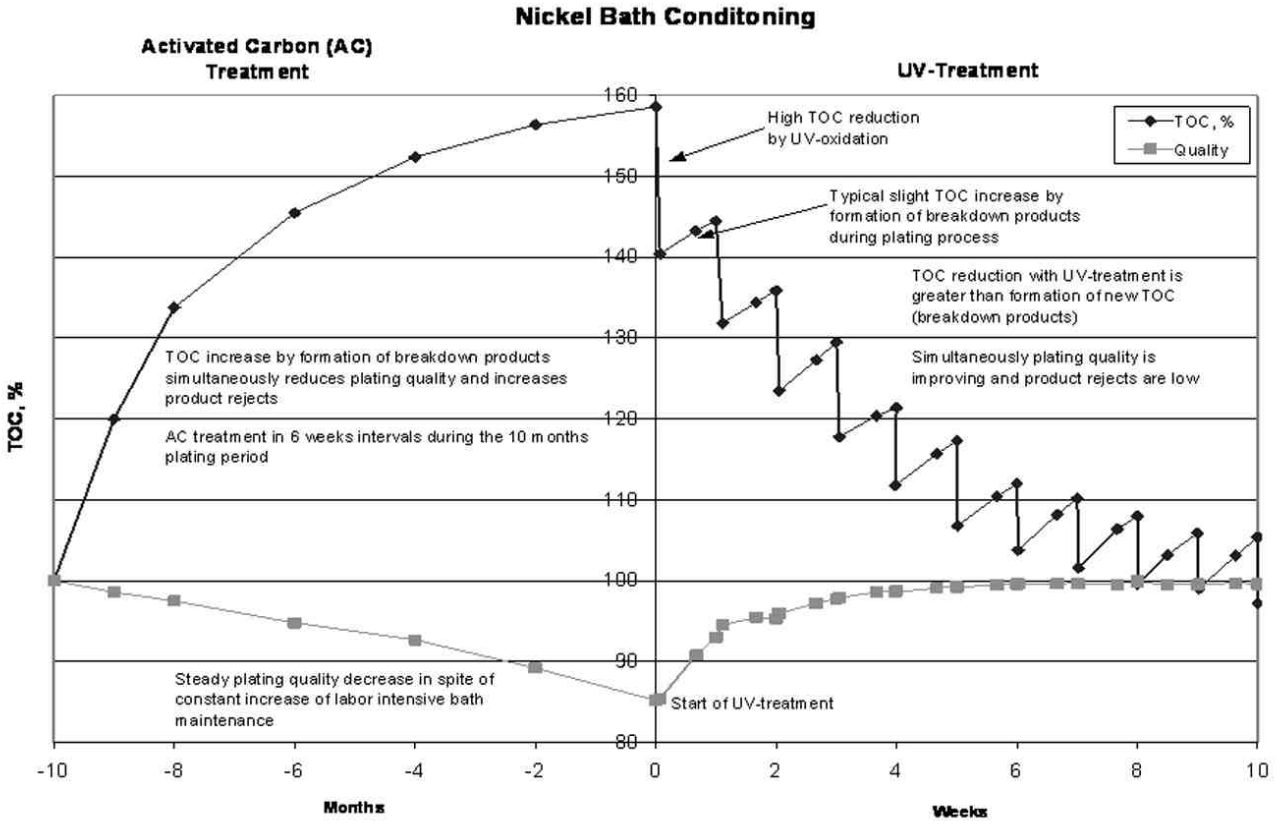

Figure 2—*Left:* Increase of TOC due to buildup of breakdown products and decreasing plating quality with increasing TOC concentration in plating bath. *Right:* Oscillating TOC decrease due to off-line UV treatment cycles. The noticeable TOC increases result from the plating process, whereas the decreases 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.

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. This makes the Enviolet®-UV-Oxidation method a much more effective process as compared to traditional activated carbon/hydrogen peroxide treatments.

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 to 15% of the plating bath volume is required for treatment per week in order to maintain consistent TOC concentration in the bath and produce consistent plating quality. The specified volume is pumped from the plating tank to the UV batch treatment tank. Of course, when the UV treatment process is first put into operation, that volume loss in the plating bath has to be replaced with fresh bath makeup. The UV treatment process is then started and, in a fully automatic mode, treats the plating bath until the desired TOC concentration is reached. The organic degradation chart shown in Fig. 4 shows how the TOC is reduced during a typical UV treatment process.

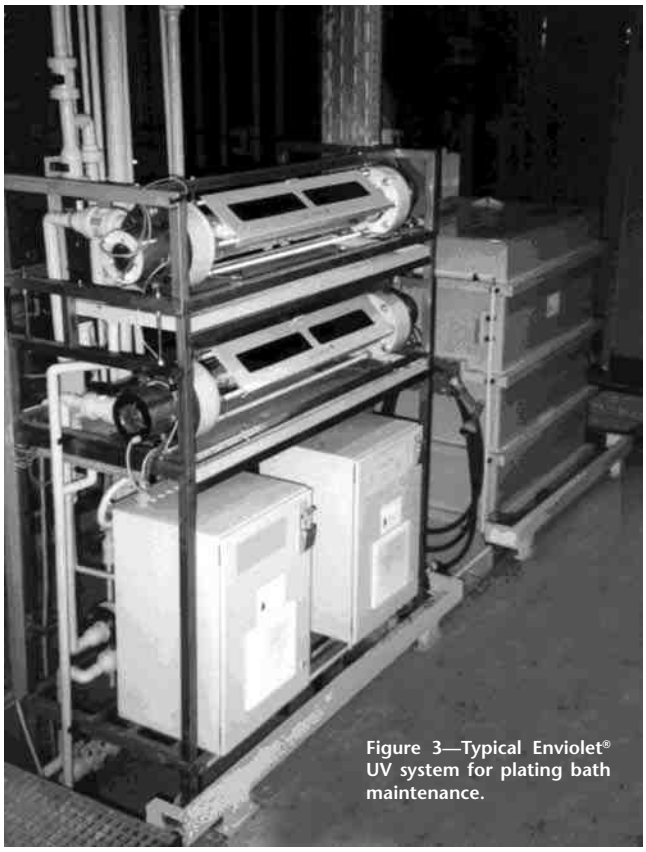

Figure 3—Typical Enviolet® UV system for plating bath maintenance.

Table 1
Approximate nickel bath TOC values

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

Table 2
Comparison of AC treatment vs. UV treatment

	With AC Treatment	After 6 Months of 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

During the final step of the treatment process all excess oxidizing agent is removed. The UV-treated solution is then ready for inspection. Figure 5 shows a series of Hull cell test panels which clearly illustrate the changes before and after the UV treatment process. The treated plating bath 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 be next to undergo the UV treatment process.

Conclusion

At Hansgrohe, the goal for permanently achieving 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 enormously reduces the cost of the mechanical pretreatment (grinding, polishing/buffing) steps.

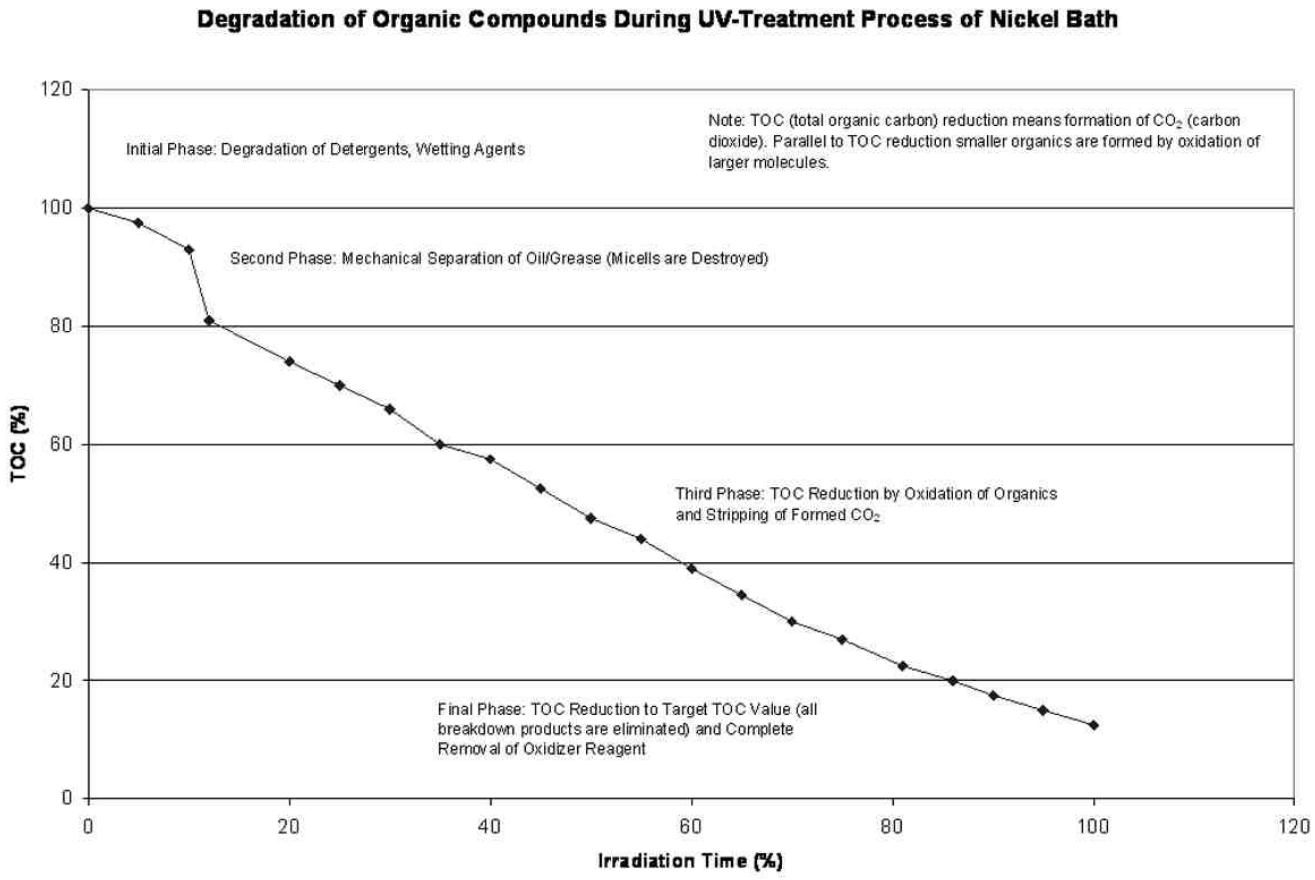

Figure 4—Typical TOC degradation chart of a Watts nickel plating bath.

Plating bath purification 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 well and has been depending solely on this plating bath maintenance process with no additional purification concepts.

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

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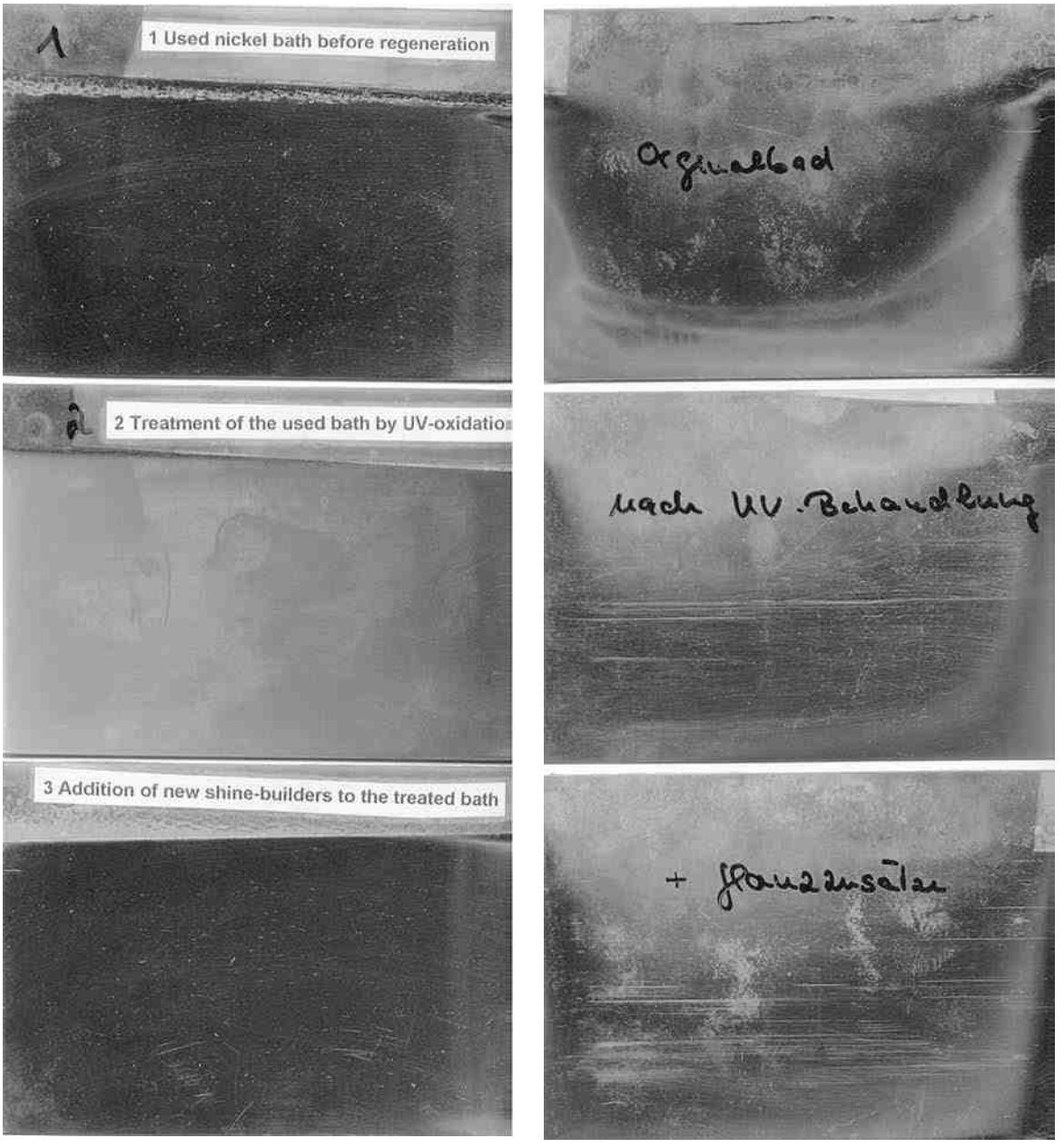

Figure 5—Illustration of various Hull-Cell Test Panels: *Left:* Test Panel Front Side; *Right:* Test Panel Rear Side. A significant increase of throwing power can be noticed with the UV-treated bath and subsequent brightener addition: Top: before UV treatment of aged bright-nickel bath. *Middle:* after UV treatment, without organic additives addition. *Bottom:* after UV treatment, with organic additives.