

ENVIOLET® the State-of-the-Art Technology for “Electroless Nickel” Wastewater Treatment

Case History, Thoma Metallveredlung, by Martin Sörensen and Jürgen Weckenmann, a.c.k., Germany
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1 Background

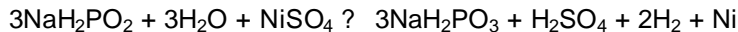
Very often electroless electrolytes contribute to wastewater treatment problems. These electrolytes are used in electroless plating processes, which contain a variety of chemicals to meet special surface treatment requirements.

Metal salts produce the base material for metal deposition and hypophosphite is delivering the electrons for the metal reduction process – it is basically the internal electric current source and, therefore, named “electroless” process. Complexing agents in the electrolytes guarantee a high metal concentration during a simultaneously high metal depletion at the diffusion layer of the plated piece.

Some typical electroless nickel (EN) bath compositions are as follows:

- Nickel salt with approx. 4-7 g/l Ni
- Reducing agent (primarily sodium hypophosphite), approx. 30-40 g/l
- Complexing agents (citrate, lactate, tartrate, acetate, etc.) 20-30 g/l
- Some bath compositions contain also ammonium, 3-5 g/l

The EN process can be expressed with the following chemical formula [1]:



A continuous phosphite buildup occurs as part of the chemical reaction during the nickel deposition process, which limits the longevity of the EN bath. For that reason, the spent EN baths must be periodically dumped and waste treated prior to sewer discharge just like the EN rinse water. In addition to the typical EN electrolyte constituents other breakdown products are generated during the deposition process as well.

According to regulatory requirements of the German government the wastewater treatment should not just be limited to the best-available-technology (BAT). It must also meet the required discharge limits shown in table 1.

Table 1: Discharge Limits for EN Wastewater

Phosphor, P *)	50 – 2.0	mg/l (ppm)
Nitrogen from NH ₃ / NH ₄ , N	100	mg/l
Chemical Oxygen Demand (COD), O	400	mg/l
Nickel, Ni	0.5	mg/l

*) may vary depending on type of discharge permit and local regulatory requirements

The reducing agent and complexing agents are causing a high level of COD concentration. Table 2 shows approximate COD concentrations of a typical EN bath.

Table 2: COD Concentrations of a Typical EN Bath

Sodium Hypophosphite	40 g/l	18,000 mg/l COD
Tartaric Acid	35 g/l	18,500 mg/l COD

Total COD 36,500 mg/l

To meet the required discharge limits (Table 1), Ni, COD (complexing agents, hypophosphite and phosphite) and phosphor (hypophosphite, phosphite and phosphate) must be reduced. Various treatment methods are available today, which all must meet the required discharge limits.

2 Treatment Methods

2.1 Conventional Treatment

A substantial amount of nickel and phosphite can be removed with the conventional lime treatment method. However, depending on the presence of certain complexing agents, substantial amounts of nickel remain in solution and the complexing agent concentrations are seldom reduced by the precipitation process, which means that the filtrate, after mechanical separation, still contains substantial amounts of nickel and complexing agents. Hypophosphite doesn't form a sparingly soluble calcium salt and thus cannot be precipitated by lime treatment.

Many tests exist regarding conversion of hypophosphite and phosphite to phosphate. Calcium hypochlorite (in excess) as well as potassium permanganate were proposed and used. Besides an excessive salting effect the use of calcium hypochlorite generates the undesirable AOX (adsorbent organic halogen compounds) compound. This leads to precipitation and filtration problems and increases the sludge volume considerably. The sludge volume is even bigger yet when using potassium permanganate for treatment. For that reason off-site treatment via a licensed treatment company is often the preferred choice.

2.2 Wastewater Treatment with UV-Oxidation, Enviolet®

With UV-Oxidation organic compounds are generally mineralized. Present inorganic phosphorous compounds, hypophosphite and phosphite are oxidized to phosphate and typical complexing agents of EN baths are oxidized to the inorganic carbon dioxide (CO₂) under moderate reaction requirements. It can be compared with a cold combustion process in liquid phase.

Nickel in the wastewater remains dissolved during the UV-Oxidation process and is removed by means of conventional lime treatment after the UV-Oxidation process. The complexing agents are destroyed and consequently previous strong nickel complexes are not present anymore. Furthermore, with subsequent lime treatment the formed phosphate is precipitated as calcium phosphate.

Therefore, with the aid of the UV-Oxidation process the COD concentration is substantially reduced and a simple precipitation of the dissolved nickel ions is feasible. After the precipitation a mechanical separation process (sludge filtration) is necessary. This process works now very fast and is simple since the solids precipitation is very compact resulting to a high sludge density. The main reason for this improvement is the minimal salt increase when treated with the UV-Oxidation process.

Another advantage of this process is that some other spent electrolytes may be mixed together for simultaneous treatment, which is an additional justification for the system purchase since that would shorten the ROI (return of investment) tremendously [2, 3]. But when treating such concentrated chemicals, UV-reactor performance requirements are very critical. However, the UV-reactors, type Enviolet®, see picture 1, were specifically designed for such applications and fulfilling exactly these requirements:

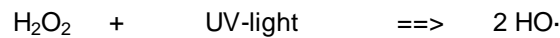


Picture 1:
Enviolet® - 12 UV -Reactor with integrated process technique for performance optimization. Besides the necessary monitoring and safety features there are also reagent metering with in-line mixing integrated. The power supply is next to the UV-reactor and is continuously regulated for optimal performance.

- The rotational flow pattern prevents particle deposition on the UV-module (unit of quartz glass tube and radiator).
- Therefore, the created high turbulence enhances the chemical reaction and is providing even with dirty and/or high turbidity solutions optimal treatment conditions.
- Due to high quality material selection, acidic and chloride containing solutions can be treated at high temperatures.

The UV-oxidation system operates as a batch treatment process. The wastewater circulates in a closed loop through the Enviolet-UV system whereby the ultraviolet light initiates various reactions:

- The nickel complexes are absorbing UV-light and as a result a chemical reaction is induced, which leads to decomposition of the complexing agents (photolysis).
- The added hydrogen peroxide (H₂O₂) is absorbing UV-light and as a result is splitting the chemical bond by generating very strong oxidizing HO·-radicals:



- These HO·-radicals are so reactive that they generate reactions, which lead to complete mineralization, i.e. formation of carbon dioxide (CO₂) [4].

Furthermore, the HO·-radicals also react with hypophosphite and phosphite by formation of phosphate. And with the addition of catalyzer reagents, the UV-oxidation process can be accelerated for the treatment of some electrolytes.

Some EN treatment baths may also contain ammonium (NH₄) besides organic complexing agents. In that case, an additional treatment step may be required after the UV-Oxidation process (oxidation of organic and reduced phosphorous compounds) for the elimination of ammonium. The necessary process step will enhance the UV process without increase of the operating cost if properly integrated with the UV system design.

3 Case History

3.1 Thoma Metallveredelung GmbH, Germany

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Thoma Metallveredelung is a very traditional and renowned company in the metal surface treatment industry. Theodor Thoma founded the company in 1924 and still today it remains a very successful family enterprise. In 1999 the company celebrated with great pride its 75 year anniversary [5]. Innovative concepts and the futuristic vision of Ferdinand Thoma have made this enterprise to a showcase plating company.

The following metal finishing processes are Thoma's core business:

Zinc plating with subsequent finish
Zinc-Nickel plating
Hard chrome plating
Electroless nickel plating (EN)
Copper-Nickel-Chrome-Tin plating

EN plating in combination with hard chrome produces a surface that is extremely corrosion and abrasion resistant.

"Surfaces for the Future" is Thoma's slogan, which calls constantly for new and innovative processes. This is the reason for the recent production expansion of zinc-nickel and EN plating of aluminum.

Besides the addition of 10,000 m² (100,000 sqft.) space, also an investment for new automated plating lines was made. Furthermore, a new customer oriented and air conditioned material handling center, including loading/unloading area, of 2,200 m² (22,000 sqft.) was added as well, which assures a fully controlled environment.

These changes and the consequent integration of the Best-Available-Technologies (BAT) were the building blocks for "Clean Technologies", which, besides optimal manufacturing conditions, also environment and safety included in the production process. Such a working environment is very motivating for the 100 employees and is proving very positive results towards company performance.

The environment conscious company management has once again confirmed that surface finishing processes and pollution control can work together. Applied wastewater minimization concepts allow the use of recycling systems and the reclamation of valuable chemicals.

Due to these efforts, Thoma was selected by the Environmental Department of Bayerischen Landesamt from a number of candidates for the research and development project "Energy Efficiency in the Plating Industry", which results were published in June 2002.

During the expansion of the plating plant it was also desired to improve the EN wastewater treatment system to a more modern and reliable process. Simultaneously, this system should also be capable of treating the wastewater from the new zinc-nickel plating line.

It was then when Thoma's EN chemical supplier has recommended the a.c.k. company to Thoma, since a.c.k. already had successful installations with similar applications in place.

First, a.c.k. performed a feasibility study at the laboratory in Karlsruhe (Table 3) and proposed a treatment concept accordingly. Besides meeting the required sewer discharge limits, also system expansion capability for future capacity was required.

The system should exist of a large batch treatment tank so that all treatment steps, pre-treatment, main oxidation, post treatment and precipitation conditioning, can be performed in this sequence. The Enviolet® UV system was sized so that the current wastewater volume could be treated. However, the system could be expanded later on to more than 100% capacity increase without any additional floor space.

a.c.k.'s proposed concept did convinced the customer, Thoma, and was implemented accordingly because it fulfilled Thoma's futuristic company philosophy. a.c.k. delivered all main components for the EN treatment process and Thoma's contractor integrated the a.c.k system into the existing wastewater treatment system (Picture 2).

Table 3: Wastewater Volume and Constituents

Wastewater Type	Volume (m ³) per Batch Treatment	Complexing Agents in Wastewater	Complexing Agent Conc. (g/l)
EN	4 – 5	Carboxylate, Gluconate	1 – 4
Zincate Acid Dip	2	Aromatic Carboxylate	1 – 2
Nitric Acid Dip (HNO ₃)	2	Ammonium, Carboxylate	max. 0.5
Ammoniumbifluoride	2	Ammonium	2 – 3

The UV batch treatment performance has been flawless ever since system startup. Since system startup, batch treatment wastewater limits are achieved without sulfide precipitation and prior to the effluent ion exchange polishing system (Tab. 4). In addition there is a pleasant side effect with the conversion of hypophosphite to phosphate, which keeps the phosphate limits within the required discharge limits.

Table 4: Typical Metal Concentrations Before and After UV Treatment at Thoma

Metal	Concentration (mg/l)	
	Before Treatment	After Treatment
Nickel	2,500	0.2 – 0.5
Zinc	1,000	0.2 – 0.4
Chrome	200	0.1 – 0.3
Aluminum	200	0.1 – 0.3



Picture 2:
Enviolet® UV-Oxidation system for treatment of EN (electroless nickel) wastewater as described in table 1. Treatment is performed in 12 m³ batches with a process sequence that all complexing agents are eliminated. The picture does not show the chemical metering unit and control system. The system is expandable to a threefold daily capacity without additional floor space by the stacking of up to three UV reactors.

Futher info:

In 2005, Thoma upgraded the UV-unit due to significant increase of the EN business volume (doubled). The upgrading was simple since the Enviolet® UV concept is of such a modular design that no additional floor space was required.

Literature

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