Modern Treatment Methods of Strong Chelates in Surface Technology

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SUMMARY – In modern surface finishing technologies such as those used in production of PCBs, strong chelates (e.g. EDTA, NTA and polyamines etc.) are found in nearly all important steps of cleaning and electroless plating. The benefits of the chemicals during production on the influence of the equilibrium of free (dissolved) metal ions and complexes formed, create potential problems in the wastewater treatment and recycling. Conventional methods are not able to remove/precipitate the metal ions and complexes to enable consent to discharge levels to be met, and this paper shows how modern methods such as ultraviolet treatment can solve those problems, enabling investment and cost savings to be made.

INTRODUCTION

In the metal finishing industries strongly bonded chelatants have a long tradition. The superior electrochemical properties of such chemicals as EDTA, NTA, cyanide, polyamines and others, have made these compounds invaluable during the production of plastics and metals. Some of these compounds can, however, cause considerable problems to the wastewater treatment. The limits laid down by the authorities can only be met with great difficulty or cannot be met at all times.

If the wastewater contains compounds such as polyamines, the traditional treatment is not always adequate, and newly developed methods such as the ultraviolet technique described below are needed.

Typical comparisons of the value of traditional and modern techniques in treating variously chelated processes are shown in Table I.

Because of the increasingly higher specification requirements in surface finishing, chelates based on polyamines are being introduced more extensively, and chelates such as EDTA that were largely replaced earlier, have found their way back into surface finishing technology.

This review discusses the difficulties faced when using traditional methods as against the success experienced with the newly developed a.c.k. UV-process, then presents examples, in the form of case studies, of the treatment of such complexed wastewater in existing installations. From a large number of reference sites, for the purpose of this paper, only companies based in Germany have been selected because in this market for a long time there was a great deal of scepticism to the use of the ultraviolet process.

When a.c.k. aqua concept GmbH started five years ago with the treatment of wastewater from the surface treatment industries using UV-process systems, it was not clear to the pioneers of a.c.k. how much the German market had been damaged by many non-reputable manufacturers of UV-equipment. Nearly all prospective companies approached by a.c.k. had bad experiences themselves or had heard from colleagues in other companies with similar experiences.

Table I. Chemical composition or of strongly chelated electrolytes and treatment processes.

Process	Chelators	Classical treatments	Modern method
Electroless nickel	Organic carbonates, ammonia	Rinse waters only	Rinses and concentrates *e.g.* Enviolet®
Electroless copper A	Organic carbonates (tartrate, citrate)	Rinse waters only	Rinses and concentrates *e.g.* Enviolet®
Electroless copper B	Polyaminocarboxylate (EDTA and other complexes)	Already difficult for rinse waters	Rinses and concentrates *e.g.* Enviolet®
Zinc-nickel	Polyamines (EDTA, cyanide and other complexes)	Already difficult for rinse waters	Rinses and semi-concentrates *e.g.* Cyanomat® P
Cyanide	Cyanide	Good to satisfactory	Rinses and concentrates *e.g.* Cyanomat®

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Table II. Overview of the described case study plants and waste water produced.

User	Waste water source	Method of treatment
Multilayer Technologies (PCB – manufacturer)	Electroless copper rinses and concentrates	Batch
Seidel Metallveredelung (plastic and metal finishing)	Cyanide baths and waste water Electroless nickel	Sequential
Thoma Metallveredelung (metal finishing)	Electroless Nickel Zinc/Nickel	Alternating

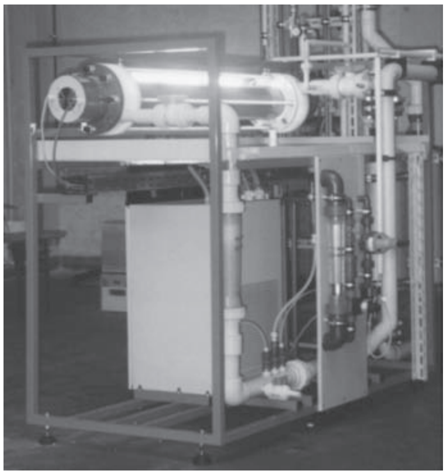

Figure 1. Enviolet® 12 UV-Reactor with process technology for optimal process requirements: In the UV- facility all necessary systems for process control and safety, also the dosing and mixing of the chemicals are fully integrated. The performance transformers of the systems are located near the reactor and are monitoring the optimal performance through a patented process.

Because of this, a.c.k. had to conquer the German market by being successful abroad.

Only after many successful installations in well known companies in nearby countries satisfying the customers' requirements was a.c.k. taken seriously in its own country.

Since that time, a.c.k. has not only become a respected partner to companies with chemical complexant problems, and plant manufacturers, but also to the many suppliers of technical equipment for the surface finishing industry.

In the following section different disposal methods for electrolyte chelates are compared and evaluated and then, in the case study section, the fully-automated wastewater treatment plants of the companies *Multek Europe, Seidel Metallveredelung* and *Thoma Metallveredelung* are described.

TREATMENT METHODS

Conventional Treatment of Electroless Nickel

With the classic lime precipitation a large amount of nickel as well as phosphite can be separated. Depending on the concentration of the chelates, a significant amount of nickel still remains in the solution. The concentration of the chelates can rarely be reduced through the precipitation. Thus, the filtrate of the wastewaters still contains large amounts of nickel and chelates.

Hypophosphite does not build a low dissolving calcium salt like phosphate. It also cannot be separated with lime.

There have been many attempts to change hypophosphite and phosphite to phosphate. It was found necessary to add calcium hypochlorite in excess. Permanganate has also been suggested and tried.

The use of calcium hypochlorite, as well as creating unwanted AOX, causes a strong increase in salt load. This causes problems during flocculation and filtration as well as increasing the amount of sludge significantly. Using permanganate, the sludge quantity is even greater. In practice, the disposal of rinsewaters and used baths is often undertaken by special waste disposal companies.

EDTA Recovery

The recovery of EDTA is preferred by the Legislators, however it falls down in practice: the quality requirements of the bath manufacturer make the recovery so expensive and complicated that this alternative has no significant technological advantage. In the end what normally happens is the incineration of the precipitated EDTA. Further disadvantages are the high emissions from the recovery and the associated safety requirements for the people involved in the procedure.

Sulphide precipitation

A frequently practised method is the precipitation of the metals with sulphide chelate breakers. The disadvantages of this very simple procedure are well known: the chelates remain substantially unbroken. Therefore, the water containing chelates has to be treated by sulphides, otherwise a mixture of a back solution, or a strict separation of the wastewater streams is necessary to properly control the problem. Further disadvantages are the poor or inconsistent meeting of the consent levels, the condition of the filtration media (particularly, during the precipitation of copper and nickel, colloids can be formed which cannot always be separated totally by filtration) and high running costs.

In addition, the sulphide flocculation decreases the life of the post-treatment selective Ion Exchanger considerably, due to a proportion of the heavy metals settling irreversibly in the selective Ion Exchanger.

Electrolysis of "Electroless Copper" bath

Up to now, electrolytic methods have been installed for some applications. Electrolysis separates the dissolved copper metallically. However, the chelates still remain or are changed electrochemically to other chelates. EDTA "disappears" to a great extent, but under detailed analysis, is found to be replaced by other homologues of EDTA, for example: EDTriA, EDDA-N,N, EDDA-N,N', EDMA as well as IMDA that are formed through the electrolysis. In this case the separation of the stream prior to treatment is also necessary to achieve the consent levels. Because not all the chelates are destroyed, this leads to subsequent problems in the effluent treatment plant, for example, remobilisation of the heavy metals from the precipitate[1]. On top of this, the high energy requirements and long treatment times of the process do not make the process popular. A few electrolytic systems have taken months after commissioning before the customer could operate the system with a certain degree of confidence.

Table III. Contents of the electroless CuEDTA bath and levels at Multek after treatment with the a.c.k. UV-process.

	concentration in the bath	Concentration after alkaline precipitation
Copper	5,000 – 6,000 mg dm^{-3}	0.2 – 0.5 mg dm^{-3}
EDTA	25,000 – 35,000 mg dm^{-3}	< 10 µg dm^{-3}
Formaldehyde	6,000 mg dm^{-3}	n.n.
COD	43,000 – 60,000 mg dm^{-3}	Approx. 1,000 mg dm^{-3}

Table IV. Wastewater configuration at Seidel.

Total volume of the batch: 2 x 6 m³	Content of the batch /m³	Chelates in the wastewaters	Concentration of the chelates
Regenerates	4	Cyanide	500 – 800 mg dm^{-3}
Cyanidic wastewater	3	Cyanide	approx. 1,000 mg dm^{-3}
Stripper	0.1	Cyanide	10,000 mg dm^{-3}
Electroless nickel	2	Carboxylates	approx. 2,000 mg dm^{-3}

Figure 2. The treatment plant for the detoxification of Cu EDTA at Multek, completely delivered and installed by a.c.k.

Treatment of cyanide contaminated process waters

The traditional process, up to now, uses hypochlorite for treatment. This method in practice produces acceptable results as far as the metal levels are concerned; however, a few parameters such as AOX are well over the legal limits after treatment. If the wastewater contains metals such as nickel or silver, these, as a rule, can cause major problems. In addition this treatment has another disadvantage in that the transformation of cyanide with hypochlorite creates large amounts of toxic chloramines. The chloramines result from the reaction of the excess of hypochlorite with ammonia created in the process. Chloramines react particularly in the post treatment biological phase causing a lowering of performance at the sewage treatment works.

Waste water treatment using Enviolet® – UV-oxidation or Cyanomat®

During UV-oxidation the organic chelates and cyanides are generally broken down. The inorganic phosphoric substances (hypophosphite and phosphite) can be oxidised to phosphate. Properly applied, this process can be used for all strong chelates. The cyanide treatment has already been discussed in some detail elsewhere[4], and will not be repeated here.

The electrolytes containing chelates (for example, EDTA, tartrate, citrate, *etc*.) or the chelates of Zn-Ni electrolytes are oxidised through UV-oxidation under standard reaction conditions to the inorganic carbon dioxide (CO_2). This process can be compared with the "cold" combustion in the water phase.

The metals and solvent in the wastewater remain contained during the UV-oxidation. After the UV-oxidation the metals are precipitated with a traditional alkaline flocculent, whereas for chemical nickel a lime flocculent is offered to eliminate the phosphates and calcium phosphate. This is now possible because the chelates have been eliminated and there are no more strongly complexed metals in the water, and all phosphorus-containing substances are oxidised to phosphate.

This process is also effective for the elimination of other chelates; it is quick, reliable, and cost effective[2,4,5], as is described in the following example for EDTA.

The total break-down of EDTA has been shown by analysis of an HPLC-Process on the RP C18 reverse-phase with DA-detector[2]. In this case well defined peaks were shown in the spectral analysis of the strongly diluted (1:2000) old plating bath. In the diluted (1:100) sample analysis, after 2 hours of treatment, it was clearly seen that during the breaking down process, various high-molecular products are created. The analysis of the undiluted sample after about 4 hours treatment showed clearly that not only the EDTA but also the high molecular by-products are totally destroyed.

The treatment plant consists basically of a batch-tank, the Enviolet® – UV-reactor, and a chemical dosing station and an additional process stage. The plant is fully automatically controlled, because only in this way can the sequence of the process parameters in excess of 10 steps be properly completed. In this way a.c.k. has been able to prove repeatedly, that the combination of a UV-high performance reactor with a intelligently developed process and control, that have been sequentially tested in a.c.k.'s R&D department to established parameters, lead to a successful outcome.

With the present technical processes we believe not only is there a working technology but clients can also be offered a technology that has already got the required statutory approvals.

Thus, with the help of UV-oxidation, we can also achieve much lower COD values as well as a simple flocculation of the loose metals ions.

The mechanical separation is made afterwards through filtration of the precipitate.

This process leads to a very quick and easy filtration, because the sedimentation of the sludge is very compact. The reason for this is due to the low salt levels associated with the UV-oxidation process. High sludge density is the result leading to lower landfill charges.

A further advantage of the process is the possibility of treating old baths (concentrates). In this way, the customer can get a short pay back on the installation. There is a great savings potential in the combined treatment of the concentrates, which were usually disposed of by tankering away.

Particularly during the treatment of concentrates the UV-reactors are placed under extreme performance requirements. These requirements are optimally achieved by the Enviolet® series:

- The abrasive rotational stream avoids the UV-module from getting dirty (unit has quartz glass tubes and UV-lamp).
- The induced high turbulence guarantees a very good material transfer and gives an optimal process treatment even in very dirty and turbid media.

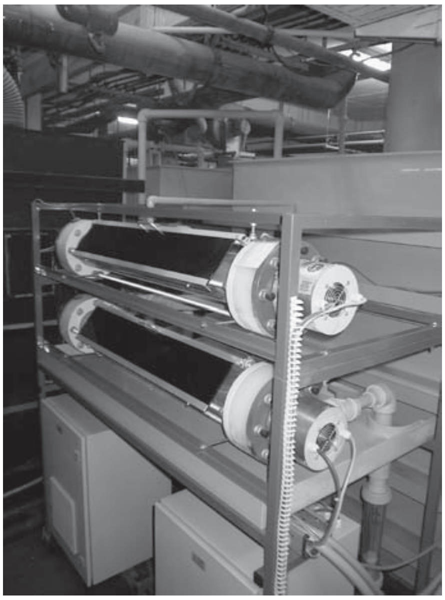

Figure 3. Cyanomat® for the treatment of complexed wastewaters at Seidel.The Enviolet® – UV-oxidation reactor is at the front, all other treatment components (stacked containers, batch containers, energy recovery, dosing stations, control panel, etc.*) are located behind.*

- Due to the high quality of the components chosen, even acidic and chloride solutions can be treated at higher temperatures, without corrosion being a problem.

The treatment from UV-oxidation is conducted by recycling the water in a batch process through the Enviolet® system. In this way the ultraviolet light starts a number of reactions:

- The chelates absorb the UV-light and this induces chemical reactions which lead to the degradation of the chelates (*via* photolysis).
- The added hydrogen peroxide absorbs the ultraviolet light, with the formation of highly oxidising radicals.

These radicals are so reactive that under ambient temperature other reactions (thermal processes) occur resulting in a complete breakdown of organic materials to oxides of carbon. Furthermore, these radicals react with hypophosphite as well as phosphite, in the formation of the phosphate. By adding catalysts, the UV-oxidation can be significantly accelerated.

For baths that, in addition to containing

Table V. Effluent streams and the important chemical components at Thoma Metallveredelung

Total volume of the batch: 12 m³	Proportion in batch in m³	Chelates in effluent	Concentration chelates /mg dm^{-3}
Electroless nickel	4 – 5	Carboxylates, Gluconates	1,000 – 4,000
Zinc pickling	2	Aromatic Carboxylates	1,000 – 2,000
Acid pickle (HNO_3)	2	Ammonium, Carboxylates	max. 500
Ammoniumbifluoride	2	Ammonium	2,000 – 3,000
Zinc – nickel	9	Aminocarboxylates, Cyanides	Approx. 8,000

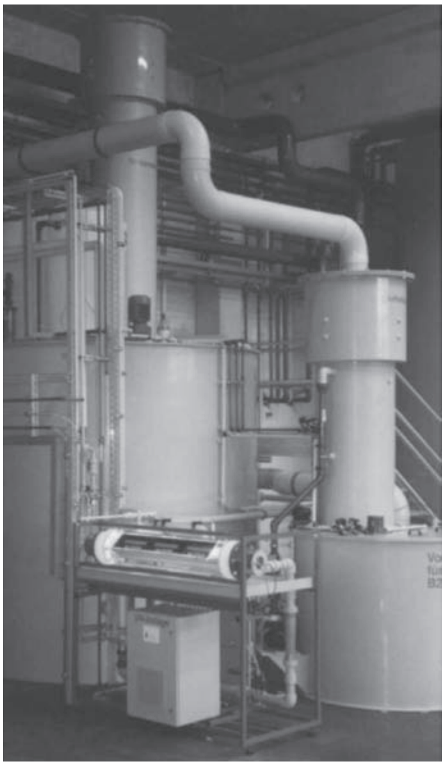

Figure 4: Enviolet® installation at Thoma for the treatment of waste waters of electroless nickel, and zinc/nickel as described in Table V. The treatment takes place in a 12m³ batch due to an automatic treatment sequence, which eliminates all chelates. Not shown are the dosing station and the electric cabinet. The installation can be upgraded easily to the three fold daily capacity without taking additional space.

organic chelates, also contain the ammonium ion (NH_4^+), a further step after the oxidation of the organic substances and the reduction of phosphorus compounds is required. The required process complements the UV-process and does not increase the treatment costs, as long as it is integrated into the whole process.

CASE STUDY REFERENCE INSTALLATIONS

All companies discussed have achieved the desired breakdown result, beneath the consent levels of the metals, and also other consent limits such as phosphate, AOX and chelates. In this way all relevant and important limits are met.

Multilayer Technology GmbH&Co. (Böblingen)[3]

Multek Europe in Böblingen is a subsidiary of Flextronic International Ltd., manufacturing multi-layer high quality printed circuit boards. With thirteen production sites in four continents, Multek is represented in all important global markets. The Böblingen site specialises in the production of complex, multi-layer printed circuit boards. Because of the increase in production requirements, a new electroless copper line was required and the decision fell in favour of an electrolyte based on EDTA.

Because the recovery of EDTA was considered too intensive and expensive, also not yet a proven method, an alternative process was considered. An electrolysis plant was out of the question; companies connected with Multek that had tried using this process advised against it.

At this stage Multek was aware that a.c.k. was offering a process that had been successfully used in both the Far East and also other parts of Europe. After checking the references where metal-EDTA-electrolytes had been treated in different applications, a more in-depth investigation was set in motion.

a.c.k. presented the advantages of the technology and convinced the suppliers of the electroless copper (Shipley) and also Multek with results from similar applications. At this stage it was revealed that Shipley already used this process in the Switzerland located production.

In the course of the trials, Multek proved that no EDTA left the works. Furthermore, it has never occurred, in any of the treatments since commissioning, that metal limits have been exceeded. Table III shows the average readings taken by Multek during the trials.

At Multek 8.5 m^3 batches are treated. The stored concentrates from the processes of 27 m^3 were treated together with the waste water from the production, and were totally treated within 2 weeks.

Otto Seidel GmbH (Karlsruhe)[4]

Seidel is a leading company in the surface coating of ABS-Plastics and metals such as brass, iron/steel, stainless steel, sintered metal, copper, zinc and also aluminium. These basic materials can be further processed and plated with bright nickel, duplex nickel, satin nickel, electroless nickel, bright chromium, black chromium, gold and zinc.

In the process of modernising the Water Treatment Plant it was decided to install a process to treat effectively all the problematic wastewater. In this case both cyanidic and also organic chelates had to be treated to ensure the discharge levels of cyanide and the metals were within the consent levels. In addition, the limits for AOX and phosphate after treatment also needed to be below the consent levels.

The treatment, because of time and space requirements, takes place as a sequential batch. Two batch containers connected in series treat the cyanides first and later the organic complexes. The effluent is collected in a total of 4 stacked containers. The process control takes the specific treatment and the relevant wastewater into the batch and runs the process fully automatically. For the treatment and for environmental reasons, some of the old chemicals (*i.e.* old acids) are used; the chelates contained in these can also be treated with the UV-process. This also cuts the disposal costs of the company for these substances. After the treatment a simple precipitation is sufficient to keep within the consent levels. Additionally incorporated in the plant, an energy recovery system is integrated to recover the heat generated by the oxidation process and used for other purposes.

Alongside the treatment for the process and rinse water (Table IV) the microbes in the water from the rinses and the recycling were also treated with another UV-process, using very few chemicals. Bacteria very often lead to a poor finish of the surface and serious operational difficulties. These problems were also solved, at the same time, leading to ongoing customer satisfaction at Seidel.

Thoma Metallveredelung GmbH (Heimertingen)[5]

Thoma Metallveredlung is a traditional and well respected company in the plating and surface treatment of metals. The company was established in 1924 by Theodor Thoma and is still run as a family owned enterprise, employing around 200 people.

The continuous improvement of the surface treatments and subsequent integration of “Best Available Technology” were simultaneous steps into “Clean Technologies”, a concept that alongside optimal finishing procedures, well trained people and environment considerations were all integrated parts of the improvement process. During the expansion of the plating production, the treatment of the wastes from electroless nickel also needed to be improved and brought up to a modern and reliable standard. The new plant should also be capable of treating the process water from the new zinc-nickel line.

At the beginning of the planned expansion of the effluent treatment plant, the supplier of the process chemicals for the electroless coating process recommended the Karlsruhe a.c.k. site, which had already provided solutions for them and other clients in similar demanding projects.

The process requirements of Thoma were researched and set up in the a.c.k. laboratory, design plans agreed and the process and its plant produced.

The plant was installed and used in the first few months to deal exclusively with the electroless nickel effluent (Table V).

After successful runs with EN effluent, the plant was also used to treat the effluent from the zinc-nickel (1:3 concentrate). The results achieved for the Zn-Ni-process were so effective that the supplier of the chemicals, who had written off the possibility of UV-treatment for this type of effluent, was both impressed *and* surprised!

CONCLUSION

The advanced UV-technology of a.c.k. is shown to be a powerful tool for the disposal of complexed concentrates and wastewaters in the surface technology sector, leading to a simple, safe, and cost effective solution of well-known chelating wastewater problems.

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