Substitution of Zinc cyanide for electroplating

This case study aims to illustrate a chemical substitution process. It is based on publicly available information on company's experience as well as on substance hazards, alternatives to the hazardous substance and regulatory information. The case study is neither complete nor comprehensive in illustrating all substitution options of a substance but rather exemplary.

1 Zinc cyanide electroplating - substitution in a nutshell

Zinc cyanide is hazardous both for human health and the environment. In this substitution example its use for electroplating is addressed. Due to the severe hazards of cyanide compounds and the risks of releasing highly toxic gasses when coming into contact with acids, a substitution is needed. Alternative electroplating processes of zinc have been identified and tested in practice. The alternative processes have been tested since 1970's and the costs and benefits are well known.

2 Current situation

2.1 Hazards of zinc cyanide

Zinc cyanide (CAS-number 557-21-1; EC-number 209-162-9; scientific name: zinc, dicyanide)

Zinc cyanide is hazardous for human health and the environment. The following risk phrases are listed in the classification and labelling inventory:

- H300 (Fatal if swallowed)
- H310 (Fatal in contact with skin)
- H330 (Fatal if inhaled)
- H410 (Very toxic to aquatic life with long-lasting effects)

2.2 Regulatory status

Currently zinc cyanide does not face any legal restrictions on production, use or import.

3 Substitution process

3.1 Substitution incentives

The product manager and occupational safety/environmental specialists of the company started the substitution process. The main reason for initiating this process was a concern due to a high human and aquatic toxicity of zinc cyanide and also several other aspects connected with it. Namely: increased costs for waste disposal, raw material handling, high demands for workers' health protection and wastewater treatment. Apart from that, a modernization of technical equipment used in electroplating was planned in any case, as the existing one was operational for many years and was worn out.

The management decided on a step-wise company internal project to:

- identify alternatives on the market;
- assess the related hazards, risks and technical performance;
- commence pilot production and testing together with the interested customers in case the new product proves to exhibit different technical and/or visual properties.

3.2 The substitution project

3.2.1 Initial research and orientation in the field

The manager has set up a small team for his substitution project consisting of himself (product quality department), the technical director, a representative of the financial department and the manager of health, safety and environment. In their first meeting, they decided to start an initial orienting research on available alternatives.

3.2.2 Identification of alternatives

The team distributed tasks for the identification of alternatives. The technical director compiled information on potential alternatives identified by the team according to their suitability.

In a second meeting they reviewed the identified alternatives for further assessment. Only those that looked the most promising for the company's application were selected.

It turned out that the majority of cases of substituting zinc cyanide in metal plating describe two main alternatives – zinc chloride (acidic zinc solution method) and zinc alkalines.

The substitution team agreed that before taking a decision to invest in alteration of technical processes, evaluation and comparison of alternatives must be made.

3.3 Selected alternative and justification

The team selected several criteria that they found important, according to which the possible alternatives and the substance currently in use can be compared. The main criteria for comparison: human toxicity, environmental toxicity, availability of information on the application for metal plating based on existing cases, possible legal restrictions and possible technical limitations.

	Available	Health hazards	Env. hazards	Availability of information on hazards	Legal restrictions	Known technical limitations
Zinc cyanide	Yes	Cat 1 toxicity all routes	Very toxic to aquatic organisms	Sufficient	No	Rather low covering-power and solution rinsability. Relatively low plating speed
Zinc chloride	Yes	Skin and eye damage, harmful if swallowed	Very toxic to aquatic organisms	Sufficient	No	Corrosive solutions Possible poorer plate distribution

	Available	Health hazards	Env. hazards	Availability of information on hazards	Legal restrictions	Known technical limitations
Alkaline zinc	Yes	Skin and eye damage, harmful if swallowed	Minimal	Sufficient	No	Lower process efficiency Less ductility Lower shine of the finished product

As it can be seen, all options are similar in terms of availability and legal regulation. Health hazards are the highest for the cyanide process, which was one of the original reasons for searching for substitutes. Substances used in alkaline zinc plating pose lower environmental hazards. Both zinc chloride and alkaline zinc processes have their technical advantages and drawbacks, so the substitution team made a list of known benefits and disadvantages of these two processes, as illustrated below:

Zinc chloride		**Alkaline zinc**	
Pros	**Cons**	**Pros**	**Cons**
Superior brilliance and leveling, rivaling that of nickel-chrome	The solutions are corrosive, and therefore this is a more expensive option, due to the need for corrosion-resistant equipment	Better zinc deposit ductility and chromate receptivity compared to chloride process	Plating efficiency of ~50%
Plating efficiencies of 95–100%	Throwing power* of the systems is only fair, resulting in poor plate distribution	Bath does not exhibit chipping or star-dusting when operated properly	Lower brilliance of finished product
Ability to plate substrates such as cast iron and steels that have been hardened using any out of different methods		Good zinc distribution	Not suitable for cast iron products
Fast plating process			
Suitable for hardened and high-carbon steels			

** electroplating solution's ability to plate to a uniform thickness over an irregularly shaped cathode*

The evaluation of technical properties of both processes lead to a conclusion that the choice between the two come down to the specific product that is being plated. As the company was mostly plating hardened steel products with high carbon content, the final choice fell upon zinc chloride process, even though the operation costs were estimated to be slightly higher than for the alkaline process.

It was also found out that the workflow for the cyanide and chloride methods is not quite the same, because the acid zinc method contains significantly more process steps. Nevertheless, the time consumption for the two processes is overall identical, since the cleaning step in the acid zinc method is more efficient. In addition, as the change of equipment was already initially planned, a more corrosive-resistant baths, pipes, etc. were bought to fit the zinc chloride process.

3.4 Implementation

Implementation of the alternative process involved mostly technical and logistical adaptations:

1. Installation of new baths
2. Adaptation of the washing and waste collection/disposal system
3. Training employees on new technical steps of plating
4. Contracting suppliers of new substances
5. Amending the environmental permit in accordance with the new technical processes

The first test batches produced with the new method proved that there is not much difference with regard to the visual and technical qualities of the final product. Therefore, the production process could be launched at full scale, avoiding extensive communication and negotiations with customers.

3.5 Evaluation

It can be concluded that the substitution of zinc cyanide is well-tested by numerous companies worldwide and, therefore, fully possible. The overall operating costs of alternative processes do not much differ from the cyanide process and provide nearly identical technical and visual properties for the end product. At the same time the use of highly toxic cyanide compounds is avoided. The final selection between acidic or alkaline zinc plating is mostly dependant on characteristics of the materials to be plated. Concrete costs of necessary technical equipment (electroplating baths, pipes, etc.) are a subject to change and depend on the scale of production, location of the facility and numerous other factors.

4 References

Biddulph, C. 2011. *Zinc Electroplating. Choosing the best process for your operation*. Available at: http://www.pavco.com/upload/file/zincelectroplating.pdf (viewed in April 2016).

ECHA. 2016. *Substance information. Zinc cyanide*. Available at: http://echa.europa.eu/substance-information/-/substanceinfo/100.008.331 (viewed in April 2016).

ECHA. 2016. *Substance information. Zinc chloride.* Available at: http://echa.europa.eu/substance-information/-/substanceinfo/100.028.720 (viewed in April 2016)

National Metal Finishing Resource Center. *Pollution Prevention and Control Technologies for Plating Operations. Cyanide use reduction/elimination.* Available at: http://www.nmfrc.org/bluebook/sec54.htm (viewed in April 2016).

Substitution Support Portal. 2012. *Galvanic processes with acid zinc instead of cyanide zinc*. Available at http://www.subsport.eu/case-stories/067-en (viewed in April 2016).

The project "Baltic pilot cases on reduction of emissions by substitution of hazardous chemicals and resource efficiency" (LIFE Fit for REACH, No. LIFE14ENV/LV000174) is co-financed with the contribution of the LIFE financial instrument of the European Community.