Comments by

The Central Association of Surface Treatment Professionals Germany (ZVO)

on the subject of

Proposals for Prioritising ***Cobalt (II) Sulphate, Cobalt (II) Dinitrate, Cobalt (II) Dichloride and Cobalt (II) Acetate*** for Inclusion in Appendix XIV of the REACH Regulations

in connection with the

public consultation

up to 14 September 2011

Application of divalent cobalt salts in

Conversion layers

in the European electroplating Industry

1 Preamble

The electroplating and surface treatment industry is, at the same time, both a key technology and a cross technology and, as a result, a driving force for technological advancement.

Within the overall field of electroplating, zinc and zinc alloys and their subsequent conversion layers for the cathodic corrosion protection of steel components represent a particular area of focus which is of growing importance.

To save resources and reduce CO_2 one has to have durable products with optimised technical properties. Zinc and zinc alloy coatings with the conversion layers deposited on them make a considerable contribution to achieving these aims as a result of their corrosion-protection properties. It can be generally said that zinc & zinc alloys provide optimum corrosion protection for a minimum use of materials and at low costs.

The use of cobalt (II) salts with its importance for the surface treatments industry, machine and plant engineering, automotive, improving the adhesion of paint layers when they are applied and other industrial sectors, such as the construction industry in Europe, must have a future in order to maintain the specific properties achieved with the application of electrochemical corrosion protection systems using zinc and zinc alloys with subsequent conversion layers.

Because of the following reasons the Central Association of Surface Treatment Professionals Germany (ZVO) cannot follow the arguments to inlcude the Cobalt Salts (cobalt(II)-sulphate, cobalt(II)-nitrate, cobalt(II)-chloride and cobalt(II)-acetate) into the Appendix XIV of the REACH regulations.

In the event that these substances are included in Appendix XIV of the REACH regulations we demand that there has to be an exception to the rules to allow the use of Cobalt(II)-Salts for the purpose of anti-corrosion, decorative, bright Cobalt-Alloy-Plating.

2 General remarks

In the generation of conversion layers, the galvanized components are dipped in a treatment solution containing either trivalent or hexavalent chromium compounds. The solutions react chemically with the metal surface and generate thin conversion layers approx. 30 to 1,000 nanometres (nm) thick, which are called conversion or passivating layers.

The durability of many components depends to a considerable extent on the additional corrosion protection effect of the conversion layers. Conversion layers delay the initial attacks on the metallic protective layer made of zinc or zinc alloy. For this reason, they are used mainly for improving the corrosion resistance of zinc plated components in vehicles, for example.

2.1 Chemical processes for generating conversion layers based on Cobalt compounds

Solutions based on hexavalent chromium compounds were in use as early as the 1930s for creating corrosion protection conversion layers.

EU Directive 2000/53/EC relating to end-of-life vehicles passed by the European Parliament and the subsequent EU Directive 2002/95/EC (RoHS Directive) prohibited the use of chromated coatings for cars and electronic components.

Due to the extensive efforts of the supplier industries, coatings firms and the automotive industry, passivation coatings, hitherto only available as laboratory tests based on trivalent chromium compounds, were developed to the point where they could be offered to the market.

During the process, it was discovered that the degree of corrosion protection that is provided by hexavalent chromating can only be achieved by adding cobalt salts to the trivalent passivation solutions.

With effect from 1 July 2007, only trivalent conversion coatings were permitted to be used for the aftertreatment of galvanized / zinc alloy coated components for new registrations of standard cars. For most other applications, these systems have now been adopted throughout the market.

The solutions used to generate the conversion layers still contain normal salts, which are found to some extent in food processing. Amongst others, sodium fluoride (tooth paste) and sodium nitrate are well known examples. Together with the normal salts, the trivalent chromium compounds in use form complexes which react with the metal surface of the immersed component. This process produces suitable conversion layers free of chromium (VI).

It became apparent that Cr(III) based conversion coatings with high levels of corrosion protection are only possible if cobalt salts are added to the application solutions and cobalt is included in these as a hydroxide (damp) and oxide (dry) in proportions of < 2% with reference to the conversion layer.

The addition of cobalt salts is necessary in particular if corrosion protection is required in warm or hot environments (e.g. engine spaces, brakes, gearboxes etc. and in electrical parts in housings etc.). In these cases, solutions containing cobalt are state-of-the-art and indispensable up to now for zinc layers, zinc nickel and zinc iron alloys.

3 Potential health hazards

3.1 Potential health hazards where cobalt (II) salts are applied

Acute dermal toxicity:

There are no figures available for absorption of soluble cobalt salts through the skin, but a sensitising effect on the skin is believed to exist.

Acute inhalation toxicity

No figures on acute inhalation toxicity of soluble cobalt compounds are available. However, two-year tests on rats indicate that there may be a hazard of chronic toxicity including damage to the respiratory tract.

3.1.1 Evaluating the readings

Health hazards through unintentional oral intake of soluble cobalt salts do not exist. Wherever cobalt salts or compounds containing cobalt salts are handled, there are strict prohibitions in force to prevent eating, drinking and smoking. Unintentional intake can, therefore, be discounted.

Sensitisation of the skin can also be excluded. Sufficient protection exists by applying personal protective equipment (PPE). Employers are required to monitor the compliance of staff with the prescribed use of PPE.

Any potential risk from inhaling aerosols containing cobalt salts or particles is counteracted by the provision of extractor systems. The effectiveness of these protective measures is ensured by regular workplace measurements performed by the technical monitoring services of the Occupational Accident Insurance Associations. Measurements took place at a number of places in a company in 2004 that uses passivation substances containing cobalt sulphate for passivating electrochemically deposited layers of zinc. The results were as follows:

Measuring point	Cobalt reading
1	<0.001 mg/m³
2	<0.00063 mg/m³
3	<0.00061 mg/m³
4	<0.00059 mg/m³

The limit value applicable in 2004 as the Maximum Exposure Limit was <0.1 mg/m³.

The measured values show clearly that, provided appropriate technology is applied on-site, the MEL applicable then could be adhered to with ease and no exposure of staff working on these installations where there were respirable fractions of cobalt compounds was possible.

3.2 Persons at risk

If existing safety regulations are not adhered to, there are potential health hazards in handling cobalt (II) salts in day-to-day production environments, which is why workers must be subjected to regular health checks in order to detect any possible health damage at an early stage. It is important to note that, in coatings firms, only fluid mixtures are used for generating conversion layers.

Preventative health checks are required for workers who may be at risk from inhalation of cobalt compounds in the shape of respirable dust or aerosols or who may have skin contact.

3.4 Protective measures in the workplace

To protect its workers, companies are required to take suitable measurements in the workplace to determine the extent of any effects of cobalt compounds and, in this way, to monitor the long-term effectiveness of the protective measures implemented – e.g. the efficiency of air extractors.

The employer is required to commission an approved doctor to carry out the preventative examinations. The requirement for an "approved" doctor is to ensure that he/she has the necessary technical knowledge, understands the technical equipment and work environment and is able to implement the regulations as required.

4 Environmental protection when dealing with conversion layers

4.1 Environmental protection when using solutions containing cobalt

Solutions containing cobalt for generating chromium (III) based conversion layers do not require electricity. The application usually takes place at temperatures between 25 and 40°C, in some cases up to 65°C. Where appropriate technical equipment has been installed on site, such as an air extractor, this manufacturing process does not generate any hazardous aerosols and the air in the workplace will not be contaminated in fact, refer also to 3.2.1.

Preventative actions can be taken in the interests of personal and environmental protection. To ensure the regulatory requirements in the workplace and the environment are met long-term, companies implement, monitor and document these measures:

- Regular monitoring of the performance and function of extractor systems and, if necessary:
- Repeated annual safety instruction for staff
- Use of personal protective equipment (PPE)
- Smoking, eating and drinking prohibitions in the work place
- Repeated, regular room-air measurements
- Annual health check-ups for staff.

Where the above-mentioned measures are conscientiously applied, the result will be that neither the employees nor the environment will come into contact with cobalt (II) salts. This safely prevents harmful contact with people and the environment.

4.1.1 Cobalt (II) salts in waste water

Cobalt is found in aqueous solutions as a cation. By adjusting the pH value to the alkaline range, the cobalt can be precipitated out as cobalt hydroxide at < 1 mg/L. There is currently no limit value in the German Waste Water Regulations for electroplating firms or in Appendix 40 to the regulations.

5 Economic importance of conversion coatings on zinc and zinc alloys

5.1 Economic importance of electroplating firms for Europe

Sales of passivating solutions (chromium (III) based) and chromating solutions (chromium VI based) alone for electrochemical galvanising in Europe amount to approx. € 40 m per year, of which approx. € 16 m are in Germany. This equates to a turnover and cost proportion of around 2.5% among electroplating firms applying zinc coatings. This is equivalent to a total production volume in coatings firms throughout Europe of around € 1.6 bn.

The approx. € 1.6 bn of added value generated Europe-wide by companies involved in electrochemical galvanising would be directly affected by a decision to prohibit the use of cobalt (II) salts in Europe.

- The proportion of cobalt-relevant applications amounts to around € 1.2 bn.

The proportion of the European market covered by German companies is approx. 40% so the production volume generated by galvanising companies in Germany amounts to approx. € 640 m.

- The proportion of this amount accounted for by cobalt-relevant applications is about € 480 m.

5.2 Macroeconomic importance of conversion coatings

5.2.1 The German automotive industry as an example

A sales volume of approx. 45% of the parts coated by galvanising firms is destined for the automotive industry, e.g. for housings, rails, brake parts, piping, safety clamps, gearbox and shock absorber caps, fuel pumps, screws etc. According to the VDA (as at 25 March 2011), 5,552,409 cars and 353,576 commercial vehicles were built in Germany in 2010.

Assuming an average sales price for cars made in Germany of approx. € 25,000 (VDA assumption), this equates to a total production volume of € 140 bn in the German automotive industry alone, which necessitates numerous galvanised components to secure the durability and functional safety of those vehicles (estimate: approx. 500 -1,000 components with conversion coatings on zinc or zinc alloys per vehicle).

Leaving aside the financial impact, and considering only the components used in the German car-making industry, the number of treated parts amounts to > 500 per vehicle, which means that, without the electrochemical galvanising processes, there would be more than 2.8 billion components per year that would not be handled by electroplating firms.

5.2.2 Window fittings manufacture as an example in Europe

Around 20% of the sales turnover of parts handled by galvanising firms is for the manufacture of fittings for windows. The total demand of chemicals for electrochemical surface treatments in Europe amounts to approx. € 25 m per year, of which around € 8 m is for conversion coating using cobalt.

A majority of the coatings is performed in Germany, France, Slovenia and Austria. Electrochemical treatments contribute to the European domestic product to the tune of approx. € 100 m per year and, as a result of the high proportion of manual labour involved, provides safe jobs for around 3,000 people.

All in all, European manufacturers of window and door fittings generate annual sales of approx. € 3 – 4 bn and employ between 16,000 and 20,000 workers.

6 Conclusions

Cathodic corrosion protection using zinc and zinc alloys is an indispensable characteristic of coated steel components as used in all fields of industry, the trades and in households, and this protection is reinforced and maintained by conversion layers. Electrochemical anti-corrosion coatings extend the lifetime of steel parts by a factor of 20 – 100 and, as a result, make a valuable contribution to enabling resource-saving industrial and economic processes.

There is little practical research available on the application of cobalt-free conversion coatings. In this context, comprehensive testing by electroplating firms is needed; optimisation and adjustment of applications need to be developed. In addition to this, it is necessary for end users to carry out function testing and day-to-day testing to determine and secure the properties of the coatings in realistic conditions. In many contexts, there

are also safety aspects to be taken into consideration. On the market you cannot find cobalt free conversion coatings with nearly the same results than including cobalt.

Prohibiting the use of cobalt salts in conversion coatings would considerably reduce the corrosion protection of the parts so coated and that would have negative effects on the durability and sustainability of industrial efforts in Europe. The result would be increased consumption of resources and energy and this, in turn, would jeopardise the European targets for climate protection and efforts to reduce CO_2 emissions.

As described in the statements above the Central Association of Surface Treatment Professionals Germany (ZVO) cannot follow the arguments to include the Cobalt Salts (cobalt(II)-sulphate, cobalt(II)-nitrate, cobalt(II)-chloride and cobalt(II)-acetate) into the Appendix XIV of the REACH regulations.

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