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

Application of divalent cobalt salts in Cobalt and Cobalt-Alloy-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.

In the field of electroplating, cobalt salts are used in particular in the manufacture of coatings made of metallic cobalt-alloys. Cobalt- and cobalt-alloy-plating is a field of special interest whose importance continues to grow from both an economic and technical point of view. The added value gained from refining surfaces contributes to a strengthening of Europe as an economic region and secures the competitive edge of European products on the world's markets.

The need to save resources necessitates the ability to produce durable commodities which have optimised technical properties. As a result of their mechanical properties, e.g. high hardness levels in gold application, cobalt including coatings makes a crucial contribution to these aims.

These comments are aimed at the European Chemicals Agency (ECHA) and refer to the proposals for prioritising the inclusion of cobalt(II)-sulphate, cobalt(II)-nitrate, cobalt(II)-chloride, cobalt(II)-acetate and cobalt(II)-carbonate in Appendix XIV of the REACH regulations. The use of the substance and its importance for the surface treatments industry, electronic and plant engineering, bathroom and furniture fittings, consumer articles, the watch and clockmaking and jewellery industries, medical technology and many other industrial fields in Europe will be referred to and the specific reasons explained as to why electrochemical cobalt- and cobalt-alloy-plating must remain an option in the future.

Because of the following reasons 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, cobalt(II)-acetate and cobalt(II)-carbonate) 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 functional, decorative and bright Cobalt- and Cobalt-Alloy-Plating.

Electrochemical processes for depositing metallic cobalt from solutions containing cobalt salts

General

These processes involve immersing the components to be coated in an aqueous cobalt salt solution. Metallic cobalt is deposited by the process of electrochemical reduction as metal themselves or in cobalt-alloys.

The result of this coating process is that the final surface of the component contains only metallic cobalt, which is a completely harmless substance from a consumer viewpoint.

Electrochemical processes for depositing metallic cobalt from solutions containing cobalt(II)-sulphate, cobalt(II)-nitrate, cobalt(II)-chloride, cobalt(II)-acetate and cobalt(II)-carbonate are mainly to be found in functional and bright cobalt or cobalt-alloy-plating.

Functional and decorative Cobalt plating from solutions containing cobalt(II)-sulphate, cobalt(II)-nitrate, cobalt(II)-chloride, cobalt(II)-acetate and cobalt(II)-carbonate

In functional and bright cobalt plating, metallic cobalt is deposited in thicknesses of 0.4 – 10 microns (µm) by an electrochemical process from solutions containing aqueous cobalt(II)-sulphate, cobalt(II)-nitrate, cobalt(II)-chloride, cobalt(II)-acetate and cobalt(II)-carbonate. These coatings are known for their high degree of hardness in alloys and corrosion resistance. For these reasons, they are frequently used as wear and corrosion protection in numerous industrial fields:

- Electronic-Industry
- Sanitary fittings
- Furniture making
- Consumer articles (e.g. household articles)
- Watch, clockmaking and jewellery
- Medical technology
- Machine and plant engineering.

Apart from technical and commercial importance hardness, resistance to wear and corrosion and the following properties are of crucial commercial and technical importance:

- Optically attractive, metallic gloss
- Chemical-resistant
- Thermally resistant
- Recyclable and of no concern from a toxicological viewpoint
- Good solderability
- High availability.

When the full range of properties of technical and bright cobalt or cobalt-alloy-coatings manufactured from solutions of cobalt(II)-sulphate, cobalt(II)-nitrate, cobalt(II)-chloride, cobalt(II)-acetate and cobalt(II)-carbonate are considered, it becomes apparent that this a pivotal technology which cannot be replaced by a direct alternative in many applications. Here are a few examples of typical coatings:

- Corrosion protection in conjunction with wear protection and decorative requirements in the electronic-industry, sanitary installations and furniture-making industries, jewellery and a host of other fields.

- To prevent abrasive wear caused by fibres, such as in Cleaning in sanitary environments

- No abrasive wear by electronic connectors

- Protection against corrosion from sweaty skin
- Antiallergenic surfaces for jewellery and watches
- Thermal loading: effects of sunlight, hot water, kitchen appliances
- Tin-Cobalt-Alloy allows barrel plating of small articles e.g. for the sanitary-industry.

The electrochemical coating process for these surfaces has the following features:

- A low process temperature that enables universal application of a very wide range of different substrates
- Reversible application process
- Suitable for both small and large components
- Cost-effective coating, in particular with an eye on upstream and downstream processes
- Process capable and easy to automate
- Manufacturing processes are, to a large extent, closed-loop processes.

In summary, it is possible to say that there are many contexts in daily life that make use of the technical advantages afforded by technical and decorative cobalt and/or cobalt-alloy-coatings. By using this coating method, it is possible to protect components against wear and corrosion, which increases their lifetime and effective usage time dramatically. In this way, technical and/or bright cobalt and/or cobalt-alloy plating makes a considerable contribution to the efficient use of resources.

Bright cobalt-alloys are an integral part of the state-of-the-art manufacture of consumer goods. In many key products, cobalt or cobalt-alloy has no economical or technical alternative - and this applies both within Europe and outside it.

Restricting the use of solutions containing cobalt(II)-sulphate, cobalt(II)-nitrate, cobalt(II)-chloride, cobalt(II)-acetate and/or cobalt(II)-carbonate for technical or bright cobalt plating will lead to a considerable relocation of manufacturing facilities away from the European Economic Area.

Environmental and personal safety aspects

Closed-loop manufacturing

The cobalt-salts used in electrochemical cobalt and cobalt-alloy plating processes are subject to the following reactions and processes:

- Reduction to metallic cobalt as an intentional reaction
- Drag-out from the process tanks to the rinsing baths
- Drag-out from the process tanks in exhaust air and air scrubbers
- Regeneration or material recovery

To reduce losses and prevent environmental damage, the drag-out of cobalt-salts in rinsing water is returned to the cobalt plating stage to compensate for evaporation loss of the electrolyte. With most cases of technical and decorative cobalt or cobalt-alloy plating, it is possible to recover almost all the materials. If it is not possible, the first rinse (economic rinse) can be filtrated for regenerate the metals by ion exchange or electrolyse.

Personal protection and hygiene in handling cobalt compounds

When metallic cobalt is deposited electrochemically from aqueous solutions, aerosol mists are generated which have to be extracted using suitable, state-of-the-art extractors and scrubbing systems to produce scrubbed waste air.

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 examination of the efficiency and functions of the air extractors
- 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.

Applying these rules consistently results in a situation in which neither the staff nor the environment come into contact with the cobalt(II)-sulphate, cobalt(II)-nitrate, cobalt(II)-chloride, cobalt(II)-acetate and/or cobalt(II)-carbonate. This safely ensures that people and the environment are free of contamination.

In addition, the use of suitable wetting agents in open tanks causes the surface tension to be reduced and this minimises the generation of mist.

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.

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.

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.

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.

Environmental protection when using solutions containing cobalt

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.

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.

Economic importance of electrochemical cobalt plating from solutions containing cobalt(II)-salts

General

Industrially manufactured articles made from iron, non-ferrous metals or plastics often do not have the required functional or decorative characteristics for a particular application as a result of the inherent materials. This can apply, for example, to the hardness, chemical resistance, appearance, feel or brightness.

It is not until they are treated with a coating that they attain a form suitable for functional or decorative use.

One such coating method is electrochemical cobalt or cobalt-alloy deposition which generates layers that are both fully functioning and appealingly decorative. As a result of its solderability in gold alloys, electrochemically deposited metallic cobalt increases the resistance of decorative surfaces to wear, at the same time considerably improves the article's resistance to corrosion and thus increases the part's lifetime.

Cobalt and cobalt-alloy plating

Cobalt and cobalt-alloy plating is considered to be the most desirable final finish for a majority of electroplated consumer goods and electronic equipment. Other surfaces cannot provide the same levels of quality and economy. The economic advantage is in the attractive appearance of the surface and the high degree of hardness in different alloys, chemical resistance and toxicological harmlessness, achieved with very little effort. Products plated in this way can be expected to have a long service lifetime. To cite just one example, consider the decorative cobalt-tin or cobalt-gold alloy plating of taps and fittings in sanitary installations. Even where they are subjected to tough professional use and cleaned with abrasive cleaners, these cobalt included surfaces will provide decades of protection on high-grade taps and similar parts. The technical and decorative cobalt alloy surface is thus a contribution to careful use of natural resources.

In combination with the cobalt-alloy-plating it is to be feared that the related manufacturing steps within the production line would be transfered to regions with less restrictions. This process will be supported by the fact that there are noch import restrictions due to toxicological aspects of the metallic cobalt or cobalt alloy layers. As a consequence, high-quality and harmless surfaces would be imported from the non-european areas.

Broad spectrum of industrial sectors

Decorative and technical cobalt or cobalt alloy plating is a manufacturing technique applied in many fields of industry. It is for this reason that the trade is not seen to be an independent industrial sector. Decorative and technical cobalt or cobalt alloy plating is an irreplaceable component of many industrial fields, such as the electronic industry, and, as yet, there are no alternatives available.

Electronic industry:

- Solderability
- Wear resistant
- Anti-corrosion

Sanitary installations:

- Taps and fittings
- Wire baskets
- Soap dispensers
- Towel rails and hooks

- Door openers.

Consumer articles:

- Small electrical appliances
- Household goods
- Home entertainment products

Furniture-making industry:

- Fittings
- Tubular constructions for seating
- Light bulbs
- Reflectors
- Shop-fitting.

Additional fields of industry:

Jewellery, watches and clocks, medical implements, music instruments industry and defence industry are further important users of functional or decorative cobalt or cobalt alloy surfaces.

What alternatives are available

Zinc-Copper (brass):

- Low hardness and wear-resistance
- Low solderability
- Complex process control
- Lack of a conversion coating on uncoated areas
- No aceptance in the electronic industry

Paint:

- Low hardness and wear-resistance
- No electrical conductivity
- No shielding properties
- Low quality appeal
- Low acceptance by consumers
- Corrosion protection depends on coating thickness and layer combination
- Low solvent resistance
- Lack of a conversion coating on uncoated areas

Conclusions

Metallic layers with a cobalt or cobalt alloy surface are well established and widely used in the market place. The tendency in the electronic industry and other industrial sectors continues to emphasise the look and technical advantages cobalt or cobalt alloys while taking into account the existing quality standards.

Long-term studies of the alternatives demonstrate the irreplaceability of cobalt or cobalt alloy surfaces made using electrolytes containing cobalt(II)-sulphate, cobalt(II)-nitrate, cobalt(II)-chloride, cobalt(II)-acetate and cobalt(II)-carbonate for most applications.

The finish color, corrosion protection and solderability offered by layers made using cobalt or cobalt alloy electrolytes is noticeably poorer, which has a negative effect on the lifetime of the products to which the process is applied. This necessitates increased use of raw materials which is contrary to achieving sustainability targets set by European programmes.

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

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