

Hexavalent chromium in electroplating:

Prevention and Control of Chromic Acid Mist

Introduction

Soluble hexavalent chromium compounds, and in particular chromic acid (chromium trioxide), are commonly used as electrolytes in electroplating and anodising. In these processes the bursting of small gas bubbles generated by electrolysis causes the formation of mists (fine droplets of electrolyte). These are commonly referred to as chromium plating mists and can be breathed in by platers and other workers.

The amount of mist produced depends on a number of process variables:

- the concentration of chromic acid in solution;
- surface area of the articles treated;
- current density;
- length of time current is passed through the solution.

A breathable mist can also be created through inappropriate use of compressed air, or by pressure washing products to remove plating solution post-plating. (See HSE Research Report RR963 - Exposure to hexavalent chromium, nickel and cadmium compounds in the electroplating industry)

Other substances hazardous to health will be present in plating shops but are not covered in this sheet. Also, inadvertent mixing of incompatible chemicals may lead to hazardous products, for example acid with bisulphite gives sulphur dioxide, acid with hypochlorite gives chlorine, and acid with cyanide produces hydrogen cyanide.

Effects on Health

The main health effects from exposure to chromic acid mist are:

- lung cancer,
- occupational asthma,

Chromic acid (chromium trioxide) has been assigned as a Category 1 (proven human) carcinogen and a Category 2 mutagen (toxic for reproduction).



There is also limited evidence of cancers in the small intestine resulting from inhalation exposure. The risks to severe burns, chrome ulcers and nasal septum perforations, and occupational dermatitis and skin sensitisation are described in Joint SEA/HSE guidance sheet *Hexavalent chromium in electroplating: Prevention and Control of Skin Exposure Risks*.

Prevention and Control of Exposure - What the law says

Registration, Evaluation, Authorisation and restriction of Chemicals (REACH)

REACH is the system for controlling the supply and use of chemicals (including solvents) in Europe. It became law in the UK on 1 June 2007. REACH includes an obligation for substances supplied in quantities of one tonne per year or more to be 'registered' with the European Chemicals Agency (ECHA). REACH also includes an 'authorisation' procedure for substances

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that have been identified as “Substances of Very High Concern” (SVHCs) and included within Annex XIV (which is regularly updated). When a substance has been listed on Annex XIV it will be necessary for companies wishing to supply and use these substances to seek an ‘authorisation’ from the EC unless it meets one of the exemptions in the REACH regulations. Further information can be found in the leaflet REACH Authorisation produced by the UK REACH Competent Authority.

Chromic acid has been added to Annex XIV for substances of very high concern (SVHC’s) which requires ‘authorisation’ in order to continue its supply and use for specific applications. The authorisation process will have wide ranging effects on the use of chromic acid. The SEA’s current opinion (February 2014) is that hexavalent chromium will not be authorised for ‘decorative chrome’ applications and some passivation processes, as trivalent chrome is a viable alternative. The latest application date for authorisation will be 21st March 2016 and the sunset date will be 21st September 2017, after which the supply and use of chromium trioxide will not be allowed unless it is covered by the authorisation.

There will be noticeable changes to the information suppliers provide to the user in the new ‘extended’ safety data sheets (eSDS) (see REACH and safety data sheets), including a move from risk phrases (R) to hazard statements (H) and may include ‘exposure scenarios’. The supplier is required to send the user a new eSDS and also on request by the user at any time.

This information should be used to inform decisions in the COSHH assessment (see below). An exposure scenario describes the operating conditions and risk management measures that have been identified by the supplier as being necessary to use the chemical safely.

REACH requires the user to follow the advice on risk management measures given in the exposure scenario attached to the safety data sheet. However, the user can choose to use different risk management measures to those in the exposure scenario but should then be able to justify why the measures offer an equivalent (or better) level of protection for human health (and the environment). Information in the eSDS will reflect the requirements of the approved authorisation.

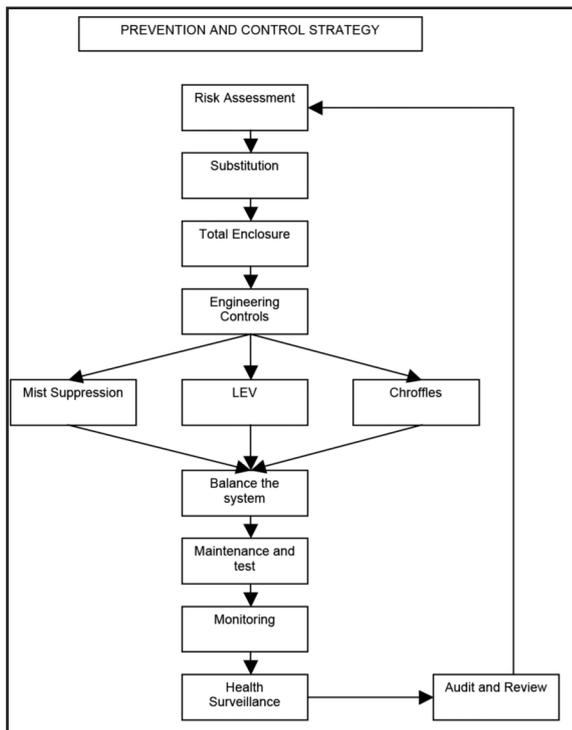
Current users of chromic acid (chromium trioxide) should discuss the implications of REACH with their chemical and equipment suppliers as a matter of priority.

Further information on REACH can be obtained from HSE’s REACH web pages.

Substitution and Control of exposure

The Control of Substances Hazardous to Health (COSHH) Regulations requires that exposure to hazardous substances is prevented, or where this is not reasonably practicable, adequate control is achieved. For a carcinogen/asthmagen like chromic acid, adequate control means reducing exposure to as low a level as is reasonably practicable (ALARP) below the present Workplace Exposure Limit (WEL). The WEL for hexavalent chromium is 0.05 mg/m³ (8 hour time weighted average as chromium) as specified in HSE Guidance note EH40 Workplace exposure limits.

COSHH requires employers to carry out an assessment of risks to health arising from a work activity such as electroplating. The information below will inform the COSHH assessment process.



There are additional specific requirements for control of carcinogens in Regulation 7(5) of COSHH which are in addition to applying all the “principles of good practice for the control of exposure to substances hazardous to health” contained in Schedule 2A of COSHH. These control measures need not be applied if you can maintain these compounds in a non-inhalable form, ie additional controls are not necessary if the mist does not contain hexavalent chromium compounds.

COSHH first requires that consideration is given to substituting hexavalent chromium for a less hazardous material. As trivalent chromium chemistry is commonly used for decorative chrome finishes and for passivation processes substitution would be expected. You should keep aware of research into new plating technologies as this will enable considered and timely substitution decisions.

Where an employer can demonstrate that substitution is not an option (possibly hard chrome for safety critical products), adequate

control of chromic acid mist must be achieved by other means as outlined below.

For more information on COSHH see Approved Code of Practice and guidance

Engineering Controls

Total enclosure of the process and handling systems should be the first option to be considered. This is how Europe approaches exposure control and should similarly be used in the UK. Total enclosure is likely to be reasonably practicable for new installations. For existing systems there may be scope for total or partial enclosure by the greater use of removable lids or other means. Lids should always be fitted and used where longer plating times are used.

Mist Suppressants

If total enclosure is not reasonably practicable then to achieve adequate control the electrolyte (plating solution) should be treated with a mist suppressant to limit the emission of mist into the workplace. Due to the cancer risk from inhaling hexavalent chromium mist and ALARP requirements, the mist should be prevented from forming (rather than capturing it after it has formed).

Fluorinated surfactants (eg based on PFOS) provide the best protection because they are more stable than other types. PFOS (and its derivatives), however, is due to be removed from the market in July 2015 because it can build up in the environment. Alternative surfactants have been available for some time, although many have similar chemistries and are likely to have similar environmental effects. Newer alternative mist suppressants are available which are also effective in

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limiting mist production. They are more expensive to purchase (as a raw material) and are more difficult to operate in terms of maintaining their efficacy, however, they should still be used to meet ALARP requirements.

Local Exhaust Ventilation (LEV)

LEV should always be provided to capture the chromic acid mist where mist suppressants are not used. The performance of existing LEV must be reviewed to ensure that any mist is effectively captured. Where LEV is used in combination with PFOS the withdrawal of PFOS will have an effect on the performance criteria required to ensure effective capture and the performance of the LEV will need review. Newly designed LEV should be properly commissioned to ensure its initial effectiveness. Regular maintenance and ongoing performance checks will need to be carried out in line with the Joint SEA/HSE guidance sheet - Monitoring for exposure to Chromium (VI) arising from Electrolytic Hexavalent Chromium Processes

LEV will usually be lip extraction or push-pull systems. Issues that should be considered to ensure this is effective include:

- ensuring that the minimum freeboard (distance between plating solution surface and the top of the plating tank) is at least 150mm on existing tanks (300mm or more is preferred),
 - the 300mm standard should apply to all new installations,
 - the freeboard on existing tanks can be increased by building up the sides (increasing the freeboard and reducing the LEV flow rate can give substantial savings),

- maintaining the required freeboard using an alarm, automatic dosing, or a level indicator on the side wall of the tank
- lids for existing plating tanks especially if longer plating times are worked (enabling cost savings to be achieved from turning down the LEV and reduced heat loss).
- lids should always be provided on new equipment.

Even when the process can be enclosed (or lids provided for partial enclosure), extract ventilation should still be provided at the enclosure opening (to prevent build up of explosive gases). The extraction should be sufficient to ensure that air is drawn into the access points within the enclosure when they are opened, so preventing emission of chromic acid mist into the workroom atmosphere.

For further information see the HSE publication HSG258 Controlling airborne contaminants at work - A guide to local exhaust ventilation and COSHH essentials guidance sheet G406 New and existing engineering control systems covering LEV systems.

Chroffles

Chroffles appear similar to ping-pong balls and form a floating layer on the surface of the electrolyte. Their primary purpose is to reduce heat loss from the tank. There is some evidence that mist levels are reduced when chroffles are used and therefore, this can be considered as a control measure to reduce mist levels. [See HSE research report RR963 Exposure to hexavalent chromium, nickel and cadmium compounds in the electroplating industry.]



Setting up the control systems

The exposure control system should be set up to ensure that adequate protection is given under worst-case conditions, when there is the:

- greatest electrolyte displacement (least freeboard),
- highest current density,
- greatest chromic acid concentrate
- longest plating time.

The surface tension (mN/m, previously dynes/cm), freeboard distance (measured between the level of electrolyte and the top of the tank), and average capture velocity (from a representative sample of measurements taken at the duct opening in the lip extraction) need to be recorded. Surface tension should be measured using a tensiometer and must not exceed the upper limit specified by the supplier of the mist suppressant.

A sufficient number of air samples should be taken to establish a reliable benchmark of exposure under these conditions. If the amount of mist emitted from the tank is below the WEL of 0.05 mg/m³ (8 hour time weighted average), it is likely that adequate inhalation

control is being achieved at the time of the test. Experience has shown that exposure levels of persons working adjacent to the tank are approximately one tenth of the WEL when mist measurements taken above the tank are at the WEL.

Maintenance of equipment

Chromic acid mist is extremely corrosive and all LEV should be constructed of corrosion resistant materials.

The LEV should be visually checked on a regular basis, usually once a week including:

- checking for corrosion damage
- checking manometers or gauges weekly to ensure that they give acceptable readings (refer to the user's manual),
- supplementing the weekly checks with monthly visual observation of smoke patterns from a smoke generator,
- keeping a record of all the checks,

LEV operation should be monitored, for example by measuring the duct velocity using a pitot tube and comparing against the standard specified by the plant manufacturer. These checks should be carried out as recommended in the LEV operation manual to ensure its ongoing performance. Any trends of decreasing flow rates should be investigated and remedial measures taken to achieve and maintain the original specification. A record should be kept.

The LEV must be thoroughly examined and tested by a competent LEV examiner at least once every 14 months and a record is kept for at least five years (COSHH Regulation 9(2)).

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Maintenance of solutions

Freeboard levels should be constantly maintained through a combination of visual indicators (eg high level mark inside the tank), alarms and automatic dosing. The level of electrolyte should not be allowed to rise above the levels set.

Where spray/mist suppressants are used to control chromic acid mist emissions the electrolyte solution should be checked and maintained in accordance with the supplier's instructions. Surface tension should not be allowed to rise above the level specified by the supplier and must be monitored using a tensiometer at regular intervals, initially every 4 hours of use. When the characteristics of the process are understood the frequency of testing can be adjusted as appropriate but should not exceed 40 hours of tank operation.

A record should be kept showing surfactant additions together with a graph of surface tension.

Exposure Monitoring

Exposure monitoring for inhalation (and dermatitis) risks including air sampling and biological monitoring is a complex area which requires further detailed guidance. See SEA/HSE guidance sheet - Monitoring for exposure to Chromium (VI) arising from Electrolytic Hexavalent Chromium Processes.

Health Surveillance

Exposure to hexavalent chromium compounds can cause a number of occupationally-related diseases (eg. occupational asthma or dermatitis). Health surveillance should be considered wherever exposure is considered significant for respiratory or skin risks. Health surveillance is not capable of being used to detect the early signs of cancer.

All employees whose exposure is considered significant to inhalable hexavalent chromium (i.e. mist) should be under suitable health surveillance for occupational asthma. This applies to any mist exposures at any level, whether or not a mist suppressant or LEV is provided. An occupational health professional needs to be involved in preparing a health surveillance programme. If the symptoms of occupational asthma are detected early enough and steps are taken to manage employee exposure, this will minimise the long-term health consequences. Information from suitable health surveillance will also contribute to the assessment of the effectiveness of the workplace controls.

A responsible person should be appointed to complete respiratory questionnaires of employees exposed to hexavalent chromium. An occupational doctor or nurse should train the responsible person. Questionnaires should be completed pre-employment, after six weeks, after six months, and then annually. Examples of initial and follow-up questionnaires are provided in the Appendix.

For more information see COSHH essentials sheet G402 Health surveillance for occupational asthma

For health surveillance requirements for skin issues see Joint SEA/HSE guidance sheet - *Prevention and Control of Skin Exposure Risks from Chromic Acid*.

Reporting adverse health conditions

Besides referring skin or respiratory problems for medical opinion, there is a separate legal requirement under the Reporting of Injuries, Diseases and Dangerous Occurrences (RIDDOR) Regulations 2013 to report to HSE any cases of:

- Occupational cancer where this relates to workplace exposure to a known carcinogen;
- Occupational asthma;
- Occupational dermatitis;

which are related to exposure to hexavalent chromium compounds. Chrome ulceration of the nose or throat, or to the skin of the hands or forearm are no longer required to be reported following the introduction of the 2013 RIDDOR Regulations.

To report a case of occupational disease you should complete the Form F2508A- Case of ill health notification online.

Further Information

1 HSE Research Report RR963

Exposure to hexavalent chromium, nickel and cadmium compounds in the electroplating industry

2 HSE leaflet Chromium and You INDG346

Working with chromium- Are you at risk?

3 HSE website

Health and safety in surface engineering

4 Joint SEA/HSE guidance sheet

Monitoring for exposure to Chromium (VI) arising from Electrolytic Hexavalent Chromium Processes

5 Joint SEA/HSE guidance sheet

Prevention and Control of Skin Exposure Risks from Chromic Acid in the Electroplating industry

6 Joint SEA/HSE guidance sheet

Nickel and Nickel Alloy Plating Operations: Controlling the Risk of Inhaling Mist Containing Nickel

7 HSE Research Report RR963

Nickel and Nickel Alloy Plating Operations: Controlling the Risk of Skin Exposure

8 EN15154

Safety Showers

9 COSHH Approved Code of Practice and Guidance L5

COSHH ACOP and guidance

10 HSE Guidance Note

EH40/2005 Workplace exposure limits

11 HSE publication HSG258

Controlling airborne contaminants at work A guide to local exhaust ventilation,

12 COSHH essentials sheet G402

Health surveillance for occupational asthma

13 COSHH essentials guidance sheet G406

New and existing engineering control systems covering LEV systems



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