

THE USE OF BRAZING FILLERS CONTAINING CADMIUM FOR SAFETY REASONS

(DEROGATION IN PARAGRAPH 9 OF ENTRY 23 OF ANNEX XVII)

REPORT

9 November 2012



1. INTRODUCTION

The use of cadmium in brazing fillers is currently restricted under paragraph 8 of Entry 23 of Annex XVII of REACH, as follows:

`Cadmium shall not be used in brazing fillers in concentration equal to or greater than 0.01% by weight. Brazing fillers shall not be placed on the market if the concentration of cadmium (expressed as Cd metal) is equal to or greater than 0.01% by weight. For the purpose of this paragraph brazing shall mean a joining technique using alloys and undertaken at temperature above 450°C.'

As noted in paragraph 9 of this entry, 'By way of derogation, paragraph 8 shall not apply to brazing fillers used in defence and aerospace applications and to brazing fillers used for safety reasons.'

Following the discussion of this derogation at the REACH Committee meeting in November 2010, and at the request of two Member States (NL, FR), the Commission requested ECHA (May, 2012) to investigate the issue of cadmium in brazing fillers used for safety reasons, with the following objectives:

- (a) To identify any relevant uses to which this derogation might still be applicable;
- (b) For any such uses, to prepare a guideline or a clarification document which would describe the cases in which this derogation could be applied, in order to clarify the provision and help enforcement authorities.

The Commission has clarified that the use of brazing fillers in aerospace and defence applications (also noted in the derogation) is outside the scope of this investigation.

2. METHODOLOGY

For the purposes of this investigation, ECHA has carried out:

- (a) A consultation with Member States and relevant industry stakeholders to obtain any available data of a technical or socio-economic nature on the use of cadmium in brazing fillers intended for safety uses;
- (b) A review of available REACH sources (e.g. registration dossiers) and relevant scientific literature and reports (e.g. consultant reports, EU Risk Assessments).

In the course of this investigation, ECHA has established contacts with:

- (a) Industry stakeholders, including leading EU companies in the brazing fillers market (e.g. Umicore BrazeTec AG & Co., Johnson Matthey Metal Joining) and relevant industry associations (e.g. International Association of Cadmium Manufacturers (ICdA));
- (b) Member States competent authorities via a CIRCABC consultation launched in May 2012.

The consultation posed the following questions (adapted to the nature of the organisation):



- (a) Is there any use of cadmium or its compounds in brazing fillers used for safety reasons, for which the derogation in paragraph 9 of Entry 23 of Annex XVII of REACH could still be applicable?; and, if so,
- (b) Are there any alternatives for cadmium or its compounds available for these uses?; and,
- (c) Are there any socio-economic data that would be relevant to assess the impact of withdrawing this derogation (e.g. potential costs to industry)?

The main findings of the consultation are discussed in section 3.

3. FINDINGS

3.1 Use of cadmium in brazing fillers

According to ISO 857-2, brazing is defined as a 'joining process using filler metal with a fluid temperature above 450 Celsius'; brazing filler metal, or brazing alloy, is defined as 'added metal required for soldered or brazed joints, which can be in the form of wire, inserts, powder, pastes'.

According to a report made by the consultant RPA (2010), the inclusion of cadmium in brazing fillers has three key related advantages: it reduces the brazing temperature; it shortens the duration of the brazing process; and it lowers the cost of brazing. Brazing fillers containing cadmium tend to contain silver, copper and zinc, with the cadmium content generally varying between 10% and 25%. The melting temperature tends to range between 595°C and 795°C, with lower cadmium concentrations being associated with higher melting temperatures. The most commonly used filler uses 25% cadmium and 42% silver (with copper at around 17% and zinc around 16%), as this provides the best combination of the characteristics of melting temperature, speed and cost.

RPA (2010) stated that EU consumption of brazing alloys containing cadmium (for both professional and consumer uses) was 90-140 tonnes in 2010, with a total cadmium content of approximately 22.5-35 tonnes. The main uses of brazing alloys were professional and industrial ones, such as tooling, heat exchangers, refrigeration, plumbing and electrical components. These uses were found to be more widespread in southern European countries such as France, Spain, Italy and Portugal. Following the entry into force (in January 2012) of the REACH Annex XVII restriction on cadmium in brazing fillers (Entry 23), the amount of cadmium used in this application can be expected to fall.

Information on use of cadmium has also been gained from a review of the relevant REACH dossiers, as follows:

- (a) Registrations and Downstream User reports: Companies manufacturing or importing cadmium at tonnages of more than one tonne per year had to register this by 1 December 2010. 22 companies (manufacturers, importers and Only Representatives) jointly registered the substance at tonnages above 100 tonnes per year, and two for 10-100 tonnes per year. Uses reported in the registrations dossiers include: PC7 (base metals and alloys); PC38 (welding and soldering products (with flux coatings or fluxes cores), flux products); SU14 (manufacture of basic metals, including alloys); SU0 (other: Nace C25.6.1: treatment and coating of metals);
- (b) Classification and Labelling notifications: 37 Classification and Labelling notifications have been submitted to ECHA for cadmium (REACH-IT search



July/2012, 45 individual notifications and 19 bulk notifications). These companies are manufacturers or importers of cadmium (or of products and mixtures containing it), who place their products on the EU market. The notifications do not contain any information on the uses of the substance on its own or in mixtures;

(c) Registration data: No additional registrations might be expected for the next two registration deadlines. Approximately 500 pre-registrations have been received for all tonnage bands. The information provided in the submitted chemical safety reports refer to small amounts of cadmium metal added to copper-cadmium brazing alloys to improve the mechanical properties (e.g. contact wires in railways, overhead power lines etc). The few other applications of cadmium alloys occur in strictly industrial environments (e.g. as special fusible and joining alloys in nuclear power plants).

3.2 Exposure and risks to human health related to brazing fillers containing cadmium

The EU Risk Assessment Report for cadmium metal and cadmium oxide (2007) concluded that these substances are non-threshold carcinogens and concerns have been identified for both acute respiratory and long-term effects (genotoxicity, carcinogenicity irrespective of the route of exposure). This report covered metallic cadmium and cadmium oxide only, as these substances are mainly converted in the environment into ionic cadmium (Cd²+), which is considered the most toxic form. Prior to REACH entering into force, no EU risk assessments had been made for other compounds of cadmium. The EU Risk Assessment made no quantitative assessment of the exposure on the part of consumers. It does mention, however, that the limited industrial applications (such as in special fusible and joining alloys and nuclear power plants) are expected to generate a potential for consumer exposure which is very low.

RPA (2010) summarised the toxicological profile of cadmium as follows:

'Inhalation exposure to cadmium fumes at comparatively low levels may result in serious - potentially fatal – acute effects in humans. Cadmium also possesses a very high accumulation potential in humans and may cause serious pathophysiological changes under conditions of repeated exposure.'

Due to its physico-chemical properties, the use of cadmium in brazing fillers is of particular relevance in terms of its potential toxicity:

'With a melting point of 321°C, a boiling point of 767°C, and an inherently high vapour pressure, cadmium readily forms metallic fume that reacts with ambient air to form cadmium oxide. Conditions encountered during melting operations, brazing activity and jewellery bench soldering often exceed the boiling point of cadmium, occasionally with inadequate ventilation, greatly enhancing the risk of exposure. Acute exposure to fumes can cause metal fume fever with progression to pulmonary oedema (fluid in the lungs) that can lead to death (RPA, 2010, 2.2.2 Inherent Concerns relating to Cadmium, Summary of the Hazard Profile of Cadmium, p 10).'

Annex 6 of the RPA (2010) report provides information from the relevant literature on levels of exposure to cadmium from brazing, indicating that acute exposure to cadmium oxide fumes can be very significant, especially when little effort is made to control it. On the other hand, long-term effects, especially for consumers, are expected to be limited, predominantly due to the limited quantities used and the short periods spent on brazing activities.



3.3 Alternatives to brazing fillers containing cadmium

RPA (2010) summarises the types of cadmium-free fillers that can be used to replace cadmium-bearing alloys for various applications. They are based on silver, copper and zinc alloys. For specific applications, additions of nickel and manganese, or tin and/or silicon may occur. Most alloy manufacturers currently offer (sometimes exclusively) cadmium-free alternatives besides cadmium-based alloys (RPA, 2010; Weldmax, 2012).

During the consultation, Umicore BrazeTec and ICdA claimed that brazing filler metals containing cadmium can be replaced by cadmium-free alternatives in more than 99 per cent of cases. Cadmium-free brazing alloys start with brazing temperature of 650°C, but, for brazing temperatures in the range of 610–650°C, no cadmium-free alternative is available. More information about the (non-)feasibility of alternatives to cadmium for brazing fillers used for safety reason is given in the next section.

3.4 Applications of brazing fillers containing cadmium for safety reasons

During the consultation ECHA received responses from 10 Member State competent authorities, but none identified uses of brazing fillers containing cadmium which were within the scope of ECHA's investigation. The consultation with industry stakeholders identified a number of applications for which brazing alloys are said to require the use of cadmium for safety reasons, as follows.

3.4.1 Turbine wheels used in power plant technology

Umicore BrazeTec is the EU market leader for silver brazing alloys, with production facilities in China, US and Brazil. They provided information about a customer company which uses cadmium-based brazing fillers in turbine wheels. These turbine wheels are parts of drives for gas compressors and boiler feed pumps used in power plant technology. Cadmium-based brazing fillers are said to be required in this application because, at the higher brazing temperatures of cadmium-free alternatives, the strength of the parent material of the turbine wheels is reduced.

This company, which is the only manufacturer of this kind of brazed turbine wheels used in facilities for energy supply, provided ECHA with more information on this application (further details in the annex, A-1). The brazing method based on fillers containing cadmium is used on special turbine wheels in the high power range where the use of bolts is not possible due to high mechanical stress load in the part. The safety aspect of this application relates to the fact that any failure of the turbine wheel due to a bad brazing could lead to the turbine wheel failing catastrophically. This could result in serious injuries for workers and others in the vicinity of the wheel from parts and shrapnel which could be expelled through the wheel housing due to the high rotational speed. It could also lead to major failure of the complete machine which then results in a sudden complete shut down of the power plant, the compressor station of a gas pipeline, or of a refinery, with potential knock-on impacts on economic activity. The company informed that typically the turbine wheel does not need to be changed during the whole life time. In addition, it clarified that the detection of a upcoming failure is not easy as it happens suddenly if the brazing is not good enough.

The company noted that turbine wheels they produce using cadmium-based brazing fillers are used only in industrial installations (e.g. in processing) and not in devices to be used by consumers. Within the EU, the company manufactures 100 turbine wheels



per year using this brazing method. The turbine wheel is installed inside a closed housing and has a mass of approximately 100kg, for which less than 100g of brazing filler is needed. This suggests that approximately 2kg of cadmium is consumed per year in the EU for this brazing application in turbine wheels (100 turbine wheels \times 0.1kg brazing filler \times 20% Cd by weight (source: Brazetec) = 2kg).

In response to the suggestion that this application might be more readily classed as a reliability issue rather than a safety one, the company agreed that this use has a significant reliability aspect (the potential failure of the turbine wheel), but reasserted that in the worst case (damage of the outer housing) there could also be a serious safety issue. Most specifically, they claimed that there could be direct violation by ejection of pieces through the housing or some major incident (fire, explosion) in hazard (explosive) areas which are typically present when a unit is driving gas compressors.

3.4.2 Production of high pressure acetylene systems

Johnson Matthey Metal Joining is a global supplier of brazing and soldering filler metals to approximately 50 countries worldwide, having a significant market share in the UK and Republic of Ireland and exporting from the UK to the rest of Europe. They drew attention to an application where cadmium is still being used by two UK companies in brazing filler metals with the claim that this is for safety reasons, in the production of high pressure acetylene systems.

Acetylene is known to form explosive compounds with copper and silver as well as a number of other materials (both pure elements, alloys, compounds and certain chemicals). Copper acetylide and silver acetylide are very reactive, and their formation can result in an explosive hazard. For this reason, acetylene must not be transferred through copper or high-alloyed copper pipe, or come into contact with silver-brazed joints in tubes or pipes transporting acetylene. The hazard does not seem to occur as long as the copper and silver content of brazing filler metals is kept below a certain percentage of the brazing filler metal. In silver brazing filler metals, cadmium and/or zinc are included in the alloy system to lower melting temperature. However in the case of brazing filler metals for acetylene systems, the addition of cadmium and/or zinc to a filler metal also has the desirable side effect of reducing the overall percentage of copper and silver in the filler metal.

Earlier standards governing high-pressure acetylene systems (e.g. BS 5741:1979, 'Specification for pressure regulators used in welding, cutting and related processes') set limits on silver and copper content which effectively precluded the use of cadmium-free brazing fillers, which are likely to contain relatively high proportions of these metals. However, as the health risks of cadmium have become better understood, standards have been revised to allow higher silver and copper levels, thereby making the use of cadmium-free fillers more feasible. For instance, BS EN ISO 9539:2010 'Gas welding equipment. Materials for equipment used in gas welding, cutting and allied processes' (and previous BS EN 29539:1992/ISO 9539:1988) sets limits of 46 per cent silver and 37 per cent copper, when the most likely cadmium-free filler metal, due to its brazing characteristics, would be Ag 145 (according to ISO 17672: 2010 'Brazing-Filler metals'), with 45 per cent silver and 27 per cent copper.

The British Compressed Gases Association (BCGA) reported (email communication of 18 July 2012) that their Code of Practice 5 ('The Design and Construction of Manifolds using Acetylene Gas from 1.5bar to a Maximum Working Pressure of 17bar (246.5 lbf/in²)') provides information on the type of materials that may or may not be allowed



when being used for the distribution of acetylene gas. In the section on materials 'not allowed or recommended only under certain conditions', it is stated that 'silver alloys [are] suitable for brazing provided that the silver content does not exceed 43% and the copper content does not exceed 21% and that the gap between the two parts to be brazed does not exceed 0.3mm'. It recommends that special care be taken to minimise the area of filler metal exposed to acetylene and to remove as far as practical all traces of flux.

In response to a request for confirmation that these guidelines are still relevant, BCGA advised (email of 15 October 2012) that the use of fillers containing cadmium is essential and is still strongly recommended in the UK (under their Code of Practice 5 for industrial applications) for the production of high pressure acetylene systems. Lack of cadmium would result in lower quality joints and would subsequently increase the risk of explosion. Details of BCGA's response, following the recent discussion of their Technical Committee on Code of Practice 5, are given in Annex A-2.

3.4.3 'Own specification' and other applications

Umicore BrazeTec has suggested that there could be a number of proprietary applications which exist for historical reasons with specifications which require the use of cadmium-based brazing fillers. Switching to cadmium-free fillers could entail significant costs due to the need to re-engineer associated processes. Furthermore, specifications of components produced outside Europe might require a specific brazing alloy containing cadmium in order to achieve certification, which can be an important reason for non-substitution (ICdA). According to the industry, a further restriction on the use of cadmium in these bearing alloys would result in a loss of these customers (and a subsequent loss of competitiveness in these areas that could have some impact in employment).

It should be noted, however, that examples of new specifications for cadmium-free alloys are available on the internet (e.g. Silvallloy, 2012, Electrobraze, 2012). This has been confirmed as part of this consultation by ICdA, which indicated that brazing fillers which do not contain cadmium are now most commonly used in the EU. However, brazing fillers which contain cadmium are still used in the aerospace and military sectors, and in high-speed trains, where safety and security are said to be the main drivers for non-substitution, with the quantity of cadmium involved being less than 25 tonnes per year in Europe. In relation to the identified use in high-speed trains, ICdA noted that cadmium is used in the realisation of 'aluminium cooling systems' for electrical equipment. However, it seems that this application is more relevant to soldering (<450°C) rather than brazing, and therefore would be considered as falling out of the scope of this investigation.

3.4.4 Socio-economic information on the impacts on industry of a potential restriction on the identified safety uses

(a) Turbine wheels: As well as the technical limitations relating to brazing temperatures, the cost of alternatives appears to be one of the key considerations for professional users of these alloys. According to Umicore BrazeTec, one of the main issues for downstream users of brazing fillers is the higher silver content of the cadmium-free alternatives, which leads to a significant increase in cost. BrazeTec claimed that a change in silver content from 1% to 22% by weight leads to a change in cost from $\mathfrak{C}7.16$ to $\mathfrak{C}157.30$ per kg of silver brazing alloy for the same or even higher (and hence higher cost) brazing temperature.



The higher cost of silver-based alloys is confirmed by RPA (2010), which found that costs increased by £3.20-3.50 (€3.70-4.00) per kg of filler for each additional 1% of silver. During the RPA consultation, one brazing filler supplier reported significant reluctance on the part of some customers, in particular SMEs, to move to the more expensive cadmium-free brazing fillers.

In response to this ECHA consultation, Umicore BrazeTec stated that the recent restriction imposed on cadmium alloys has already adversely impacted producers in Europe by limiting their sales of alloys containing cadmium to countries outside Europe. This has an effect on their sales to countries in northern Africa, countries in Eastern Europe not belonging to the EU and some Asian countries. According to BrazeTec, further restriction of cadmium-based brazing alloys in the currently exempted safety uses could further negatively affect their exports outside the EU.

(b) High pressure acetylene systems: Johnson Matthey Metal Joining estimated that a move to cadmium-free alternatives in high pressure acetylene systems would mean an increase in silver content from 40% to 45%. At current silver prices, this might be expected to add £30-40 to the cost of 1kg of brazing filler. If the UK companies reported as still using these filler metals consume around 100-150 kg of brazing filler metal per annum, this would increase their costs by around £3-6k per year. There would also be additional cost arising from the longer heating time and greater use of energy in heating.

4. CONCLUSIONS

ECHA's consultation with Member States and industry has suggested that, although the use of cadmium had been declining for several years, a small number of continued uses of cadmium in brazing fillers still exist in the EU. These applications seem to relate to the need to achieve a specific operating temperature range at which, in the absence of cadmium, there would be a risk of explosion or catastrophic failure. ECHA received indication that other specialised, proprietary uses of cadmium in brazing fillers might exist but no further information to identify the existence and nature of these uses.

These features imply that amending or removing the derogation concerning brazing fillers provided in paragraph 8 of Entry 23 could have significant costs for the industrial sectors concerned and/or occupational safety while the reduction in risks from cadmium if the derogation was removed would seem be very small as far as safety applications are concerned. It is concluded that the derogation on brazing fillers for safety applications is still relevant and applicable.

It is proposed that ECHA prepare a new entry in the Questions & Answers for restrictions relevant to Annex XVII of REACH. This entry would explain the conditions under which the derogation might apply. This would improve clarity of the scope of the derogation and help Member State Competent Authorities with enforcement.

It cannot be excluded, however, that there might be additional applications of relevance which have not been identified in the course of this ECHA consultation. In this case, the list of uses in a new Questions & Answers entry for restriction of Annex XVII of REACH would represent an indicative, rather than comprehensive, list of applications using brazing fillers containing cadmium for safety reasons.



REFERENCES

- Electrobraze 2012, available on http://www.electrobraze.com/index.php?p=2_19_Cadmium-Free-Pin-Brazing, searched July 2012.
- EU RAR (2007) European Union Risk Assessment Report: Cadmium oxide and cadmium metal. Part I Environment. 3rd Priority List, Volume 72, EUR 22919 EN, European Chemicals Bureau.
- RPA 2010, Socio-Economic Impact of a Potential Update of the Restrictions on the Marketing and Use of Cadmium, Revised Final Report Prepared for European Commission Directorate-General Enterprise and Industry, RPA, April 2010.
- Silvalloy 2012, available on http://www.silvaloy.com/cadmium.php, searched July 2012.

Weldmaxx 2012, available on www.udomsawat.com, searched February 2012.



ANNEX

A-1 Technical information on use of Cd containing brazing fillers in turbine wheels used in power plant technology

According to Umicore BrazeTec (statement of July 2012), the standardized Cd-free brazing alloys start with brazing temperature of 650°C. This company has been engaged for years in the research and development of cadmium-free brazing material, offering adequate alternatives to Cd bearing brazing fillers to their customer (such as alloys with a brazing temperature at 630°C). However, alternatives do not work efficiently in the application of the turbine wheels.

More clarifications on the safety aspect of the "turbinewheel" application and the essential use of cadmium have been provided by a customer of Brazetec. They explained that they are suppliers of variable speed drives (hydrodynamic fluid couplings, torque converters). The torque converter has a power range from 200 kW up to 65000 kW, with a rotational speed at approx. 1000 rpm up to 20000 rpm. Their variable speed drives are installed between a driving machine (typical E-motor) with a constant speed and a driven machine (e.g. boiler feed pumps in power plants, gas compressors in refineries, pipeline compressors and off-shore oil and gas applications) which need variable speed.

The company noted that only one single part in the torque converter, the turbine wheel, is using the brazing process and provided more information to clarify this application. A Variable Speed Drive in the power range of 15000 kW has a mass of approximately 25 tons, while the turbine wheel (installed inside of a closed housing) has a mass of approx. 100 kg. In one year, they are manufacturing about 100 turbine wheels using the brazing method and for the brazing of each one 100g of brazing filler is needed (10 kg per year).

The brazing method is only used on special turbine wheels in the high power range where the use of bolts is not possible due to high mechanical stress load in the part. The company highlighted that all these turbine wheels are only used in industrial installations (e.g. in the processing) and not in devices to be used by consumers. They are not used as single parts and they are always installed in a closed housing.

A-2 BGCA input on cadmium containing fillers in the production of high pressure acetylene systems

British Compressed Gases Association (BCGA) has recently informed ECHA (15 October 2012) that they publish a series of Codes of Practice, Guidance Notes and Technical Reports, prepared in the knowledge and with the co-operation of the Health and Safety Executive and other regulatory bodies in the UK.

Following discussions within their relevant Technical Committee (1st August 2012), BCGA arrived at the following conclusions concerning the BCGA Code of Practice 5 (The design and construction of manifolds using acetylene gas from 1.5 bar to a maximum working pressure of 17 bar (246.5 lbf/in²). Currently Revision 2: 2010).



BCGA Code of Practice 5 provides information on the type of materials that may or may not be allowed when being used for the distribution of acetylene gas. Within the section on materials not allowed or recommended only under certain conditions BCGA refers to – Silver Alloys - Suitable for brazing provided that the silver content does not exceed 43% and the copper content does not exceed 21% and that the gap between the two parts to be brazed does not exceed 0.3 mm. Special care shall be taken to minimise the area of filler metal exposed to acetylene and to remove as far as practical all traces of flux.

The BCGA's specification is itself not concerned with Cadmium but by definition, constituent elements of Silver Content ≤43 % and Copper ≤21 % require Cadmium to produce a viable product.

The BCGA's code was produced for two main reasons:

- To give manufacturers the best guidance towards an optimum joint. As the joints form part of a pressurised system; properly containing Acetylene is critical due to many risks associated with its escape. Cadmium facilitates the capillary action and solder penetration hence providing a good quality joint of high integrity. It also allows a lower Copper content (see next point).
- To provide the best guidance on material compatibility. Both Copper and Silver can form compounds with Acetylene, which can explode when subjected to friction or shock, introducing the possibility of Acetylene decomposition. By limiting the proportions of Copper and Silver this risk is mitigated.

Taking account of the points above the following can be concluded.

Cadmium free solders contain higher proportions of Copper. No studies exist within the BCGA membership that can safely justify this increase.

The safety of equipment produced is dependent upon the mechanical strength and leak tightness of its joints. Again, no studies exist which can justify the reliability of a Cadmium free solder. Solder penetration could well be inferior without further study.