ECHA
European Chemicals Agency

1July 2010

Background document for Lead chromate molybdate sulfate red (C.I. Pigment Red 104)

Document developed in the context of ECHA's second Recommendation for the inclusion of substances in Annex XIV

1. Identity of the substance

Chemical name:	Lead chromate molybdate sulfate red (C.I. Pigment Red 104)
EC Numbers:	235-759-9
CAS Numbers:	12656-85-8[1]

2. Background information

2.1. Intrinsic properties

Lead chromate molybdate sulfate red was identified as a Substance of Very High Concern (SVHC) according to Article 57(a) and (c) as it is classified according to Annex VI, part 3, Table 3.2 of Regulation (EC) No 1272/2008 as a carcinogen category 2, R45 (may cause cancer), and as toxic to reproduction category 1, R61 (may cause harm to the unborn child)[2], and was therefore included in the candidate list for authorisation on 13 January 2010, following ECHA's decision ED/68/2009.

2.2. Imports, exports, manufacture and uses

2.2.1. Volume(s), imports/exports

Production volumes

According to the association of European Manufacturers of Lead Chromate and Lead Molybdate Pigments (Annex XV dossier, 2009) the volume of lead chromate pigments (C.I. Pigment Yellow 34 plus C.I. Pigment Red 104) produced in Europe in 2008 was 30,000 tons, with 35% representing C.I. Pigment Red 104. However, a non-EU company estimates for the manufacture of the two pigments in Europe a

1 Deleted CAS numbers: 12213-61-5, 8005-36-5, 64523-06-4

2 This corresponds to a classification as carcinogen 1B, H350 (may cause cancer) and as toxic to reproduction 1A, H 360D (may damage the unborn child) in Annex VI, part 3, Table 3.1 of Regulation (EC) No 1272/2008 (List of harmonised classification and labelling of hazardous substances).

maximum of 10,000 t/yr. According to the same source, estimated global production of both pigments is 50,000 t/yr (Consultation with industry, 2010).

Import volumes

Import volume is known only in regard to one non-European manufacturer in 2008 (confidential data), which for C.I. Pigment Red 104 was in the range of 100 - 1,000 t (>80% non-encapsulated ("coated"), <20 % encapsulated, see manufacture process below in section 2.2.2.1) (Annex XV Dossier, 2009). These figures may not cover all imports to the EU.

Volumes used

According to EMLC, use of the two lead chromate pigments (C.I. Pigment Yellow 34 plus C.I. Pigment Red 104) in Europe from European production (confidential data) was much lower in 2008 than the volume manufactured in Europe (range 1,000 – 10,000 t). According to EMLC, all lead chromate pigments placed on the EU market by their members are coated (RCOM). Adding the share of EU manufacture that is used in the EU and the (known) volumes imported, an EU use in the range of > 5,000 to < 10,000 t/yr can be assumed as the minimum for the two lead chromate pigments. According to a main importer of the two lead pigments, about 1/4 of the consumed volumes correspond to C.I. Pigment Red 104.

2.2.2. Manufacture and uses

2.2.2.1. Manufacture and releases from manufacture

Manufacture process

The mixed crystals of C.I. Pigment Red 104 are synthesized by a wet chemical process. According to the Hazardous Substances Data Bank (HSDB)[3] of the National Library of Medicine's - Toxicology Data Network (TOXNET®), C.I. Pigment Red 104 is formed by coprecipitation of lead chromate, lead sulfate and lead molybdate in a reaction solution of sodium (di)chromate, sodium sulfate, sodium molybdate, lead salt (usually lead nitrate), under carefully controlled conditions. The solubility of the reaction product is much lower than the solubility of the starting materials. After the reaction step, the product is dehydrated in chamber filter presses. Numerous shades of C.I. Pigment Red 104 are available on the market, varying to some extent in the exact composition of the crystal. The wet chemical process is used when the raw materials are soluble, which is the case for metal sulfates, chlorides or hydroxides. In the case of oxides, which are sparingly soluble or insoluble, the dry calcination process is used instead (Annex XV Dossier).

In fact, C.I. Pigment Red 104, in order to be stable under environmental conditions, is normally modified with small amounts oxides of Lanthanides, Al, Ce, Sb, Si, Sn, Ti, Zn, Zr, or Fluorine salts[4]. Various combinations of these stabilising modifiers are used to manufacture different grades of so called "**coated**" crystals (Consultation with

[3] http://toxnet.nlm.nih.gov/cgi-bin/sis/search/r?dbs+hsdb:@term+@na+C.I. PIGMENT YELLOW 34
[4] The Colour Index information for C.I. Pigment Red 104, as updated in November 2009, mentions that the pigment's crystals "may include any one or a combination" of these modifiers (Colour Index International, 2010).

industryC, 2010). Each of these grades shows different thermal, photo-, and/or chemical resistance, fitting to respective industrial applications.

The lead chromate pigments can furthermore be encapsulated in an amorphous glass shell. This process involves bringing the pigment in contact with sodium silicate and sulfuric acid and forms silicic acid layers bound to the particles and aggregations of particles. These silica-**encapsulated** grades possess the highest chemical resistance and thermal stability (Annex XV Dossier, 2009; Consultation with industry, 2010).

Manufacture sites
No information is available on the manufacturing sites of the lead chromate pigments in EU. EMLC has 7 members: 3 in Germany and one each in UK, the Netherlands, Spain, and Austria (one manufacture site for C.I. Pigment Red 104 per member, if any). The HPV (High and low production volume) chemical program of OECD listed the following 7 producers and importers in Europe: 4 in Germany and one each in France, Spain, and Belgium.

Releases from manufacture
During manufacture of lead pigments, there is a potential for exposure to lead pigments, as well as soluble forms of Pb and Cr (VI) used as raw materials in the pigment production. Some studies have shown in the past increased urine and blood chromium levels in lead chromate pigment production workers. Several epidemiological studies are available regarding workers of plants producing either lead or lead and zinc chromates, most of them showing an increased risk of lung cancer. Two studies in plants producing only lead chromate pigments have shown no or slightly increased but not statistically significant risk in respiratory tract tumour (Annex XV Dossier, 2009). There is in general uncertainty on the actual exposure during occupational studies carried out in the past, as well as regarding risk management measures currently implemented at facilities producing the pigments. According to producers, any lung cancer has been attributed over 60 years to exposure to C.I. Pigment Yellow 34 and the observed excess of cancer deaths is more linked to a mixed exposure to soluble zinc, strontium or calcium chromate, which are known carcinogens, than to C.I. Pigment Yellow 34. The manufacturers of lead chromate pigments also underline that exposure of workers to lead chromate pigments is limited to certain steps in the manufacturing process where inhalation is possible, and there exposure is closely monitored and restricted by concentration limits (Eurocolour, 2004 in Annex XV Dossier, 2009; EMLC, 2010).

The pigments' dehydration step during the wet chemical process (after pigments' precipitation) causes a leachate containing some residues of the starting raw materials, by-products of the reaction (mainly salts) and, in some cases, also a dissolved share of the desired pigment product (European Commission, 2007 in Annex XV Dossier, 2009).

2.2.2.2. Uses and releases from uses

Uses
According to information provided by an importer of lead pigments, the uses of pigments CI 34 Yellow and CI 104 Red are mostly industrial, apart from some

coatings used in applications by professionals. There is no use of the pigments in applications for consumers.

In more detail, current uses in the EU include (Annex XV Dossier, 2009):

- Coloration of plastics (~60% of the EU market for the pigments, EMLC 2009 in Annex XV Dossier)

  This use concerns each type of plastic material/composite (polyolefins, polyvinyl chloride and nylon) as well as each process of modelling (injection, extrusion, etc). Applications in this sector include industrial carpet fibres, automotive interiors, non-food packaging, rust resistant furniture and electronic housings. Examples of finished products include trash bags, industrial packaging, piping and tubing, PVC profiles, tarpaulins (DCC in Annex XV dossier, 2009). Nevertheless, DCC (personal communication) declined the use in trash bags for consumer use.
- Coatings (e.g. paints, varnishes) (~40% of the EU market, EMLC 2009)

  These pigments are used in a variety of industrial coatings. Applications in this sector include:
  - Vehicles not covered by the end of live vehicles directive (trucks, buses, commercial vehicles, vintage cars)
  - Agricultural equipment
  - Civil engineering material
  - Boats / Ships
  - Road sign and road painting / Thermoplastic road marking / Airport horizontal painting
  - General industrial: skips, plant and machinery; industrial doors, pumps, machinery; large steel structures; gas cylinders; off shore steel structures (e.g. drilling rigs)
  - Camouflage / ammunition, interior coatings for military equipment
  - Aeronautics
  - Coil coating
  - Coating of plastic material (PVC, PP, ABS edge bands)
  - GRP constructions (boats, auto parts, silos)
  - Coatings that can be applied to industrial surfaces by printing, such as decals (e.g. used for commercial identification)
  - Thermochromic paint

Additionally, C.I. Pigment Red 104 was identified as constituent of a product used in dentistry at a concentration of 5-10% (Technical report, 2010). The product is used as protection for defined parts of surfaces to prevent them of covering with metal during galvanisation processes.

The use of C.I. Pigment Red 104 in manufacturing of primary anti-corrosive and hanging-up paints in the Defence sector could not be verified (Annex XV Dossier).

According to EMLC, no new uses outside from the established ones in plastics and coatings are foreseen (RCOM). Other uses mentioned in the literature, which could not be confirmed, include textile printing, leather finishing, printing inks (e.g. outer surface of food packaging), tattoo inks, artists' paints, mastics, paper, linoleum / flooring compounds, colouring of rubber, and wall covering.

Uses of regular grades of lead chromate pigments are confined to processes taking place at temperatures up to approximately 260°C. Silica-encapsulated pigments can be used in plastics or coatings applications at temperatures of up to approximately 300°C, with the majority (>90%) used for coatings (e.g. coil coatings and signage).

Releases from uses

There is a potential exposure of workers during formulation of paints and colour master batches (emptying pigment bags into the formulation matrix), as well as during industrial end uses (application of paint, manufacture of plastics). According to industry, appropriate Risk Management Measures (RMM) are available / in place to control exposure in these areas (Consultation with industry, 2010).

It is not clear which RMMs are in place/observed to prevent exposure during professional applications (e.g. coating but as well repair manipulation of coated surfaces (exposure to dust from sanding, high pressure particle-blasting of surfaces).

Releases from coloured or coated articles during service life may be low, but there may be releases from the waste phase or during recycling (no separate collection or particular treatment of lead chromate pigment treated items according to an exporter of lead pigments to EU; waste containing lead chromate can not be recycled, but must be disposed of as a special waste in accordance with local regulations, according to EMLC, 2010), although dispersion of the pigments in the matrix of paints and plastics tends to render them less available. According to Environment Canada, specific applications and/or the post-application phase are expected to make the greatest contribution to environmental releases of C.I. Pigment Red 104 (Annex XV Dossier). Incineration of pigmented articles is expected to lead to transformation of the lead chromate pigments. Modern flue gas treatment facilities remove more than 99.5% of the mobilized lead (BASF, 2005), to which anyway the contribution of lead pigments in plastics in the municipal waste stream is expected to be very low (Nakamura et al, 1996 as cited in Consultation with Industry, 2010).

Some studies have shown decreased bioavailability of the encapsulated forms of the pigments, nevertheless there are also some uncertainties on this issue. For example, uncertainties relate to the degree to which encapsulation moderates absorption by the organism (for each route of exposure), the dependence of bioavailability on the degree of encapsulation, or the extent to which partial solubility in gastric acid could lead to effects after long-term ingestion of lead chromate pigments. Moreover, it cannot be excluded that in highly weathered pigments encapsulation may fail.

2.2.2.3. Geographical distribution and conclusions in terms of (organisation and communication in) supply chains

The supply chains seem to contain a medium number of EU manufacturers and importers. As the pigments are used in many industrial sectors in the application areas of coatings / paints and plastics, a high number of downstream users is envisaged, including formulators and industrial users. Furthermore, a medium number of professional users are anticipated to involve in the supply chains.

The involved actors in EU are probably widespread all over EU.

Based on the available information, it is assumed that the supply chains of this substance contain many levels and a high number of actors, with the types of industry branches involved producing a large number of different products. Industry has though stated that in general the supply chain is getting simpler with direct purchase of Lead chromates from manufacturers, while the number of manufacturers is decreasing (Consultation with industry, 2010). In conclusion, according to the available information, the supply chains for lead chromate molybdate sulfate red are rather complex. The level of communication within the supply chains is unknown.

2.3. Availability of information on alternatives[5]

According to EMLC, as well as a non-EU manufacturer exporting the lead pigments in EU,, there are potential alternatives, but not direct substitutes for C.I. Pigment Yellow 34 and C.I. Pigment Red 104. Application requirements, such as weather resistance, light fastness, opaqueness capacity and others are not met. Moreover, the technical implementation of substitutes is difficult and often inefficient (lack of stability, etc.). Furthermore, costs for such alternatives are four to ten times the price.

Substitution may be applied for some specific uses but nor for all (Annex XV Dossier, 2009).

2.4. Existing specific Community legislation relevant for possible exemption

No data available.

2.5. Any other relevant information (e.g. for priority setting)

No data available.

3. Conclusions and justification

3.1. Prioritisation

Verbal-argumentative approach

Lead chromate molybdate sulfate red is used in high volumes and at a high number of sites and may be released (presumably in relatively low amounts) at very many sites

[5] Please note that this information was not used for prioritisation.

from articles during service life or (in potentially higher but unknown and uncontrolled amounts) after the end of the service life in the waste state or during recycling. Releases to the working environment and worker exposure during formulation and coating steps appear to be controlled, but there is potentially uncontrolled exposure during repair/refurbishing of coated surfaces (e.g.sanding / high pressure blasting etc.). At least widespread and in some applications wide dispersive use can be concluded.

On the basis of the prioritisation criteria, lead chromate molybdate sulfate red qualifies for prioritisation.

Scoring approach

Score			Total Score (= IP + V + WDU)
Inherent properties (IP)	Volume (V)	Uses - wide dispersiveness (WDU)	
1 Carcinogen, cat. 2; Toxic to reproduction, cat. 1	7 (high volumes)	Overall score: 3 * 3 = 9 Site-#: 3 (Use at a high # of sites) Release: 3 (Uncontrolled releases) (Environmental releases diffuse and for some uses uncontrolled occupational exposure cannot be excluded whereas for other uses occupational exposures seem to be controlled)	17

Conclusion, taking regulatory effectiveness considerations into account

On the basis of the prioritisation criteria, lead chromate molybdate sulfate red qualifies for prioritisation. No regulatory effectiveness considerations have been identified that would suggest to refrain from prioritisation.

Therefore, it is suggested to prioritise lead chromate molybdate sulfate red for inclusion in Annex XIV.

4. References

Annex XV Dossier (2009): Annex XV dossier for the proposal for identification of Lead chromate molybdate sulfate red as a CMR CAT 1 or 2, PBT, vPvB or a substance of an equivalent level of concern. Submitted by France. http://echa.europa.eu/doc/consultations/svhc/svhc_axvrep_france_cmr_lead_chromate_sulfate_red_20090831.pdf

BASF (2005): Data sheet on product safety Sicomin Red L 3035 S (August 2005).

Colour Index International (2010): C.I. Constitution Number C.I. 77600 (also 77603). http://www.colour-index.org/

Consultation with industry (2010): Personal communication and letters to ECHA, April-May 2010.

EMLC (2010): Letter to ECHA, 17 May 2010, on behalf of seven members of the Lead Chromate Consortium.

Nakamura et al. (1996): Waste Management, Vol.16, No 5/6, pp. 509-517.

RCOM: “Responses to comments” document compiled from the commenting period on the identification of Lead chromate molybdate sulfate red as SVHC (31.08-15.10.2009). http://echa.europa.eu/doc/about/organisation/msc/msc_rcoms2009/rcom_lead_chromate_molybdate_sulfate_red/svhc_rcom_final_CC017228-63_lead_chromate_molybdate_sulfate_red_20091116%20.pdf

Technical report (2010): Data on the European Market, Uses and Releases/Exposures for Lead Chromate prepared for ECHA by DHI in co-operation with Risk & Policy Analysts Limited and TNO (Contract ECHA/2008/2/SR25), 11.June 2010.