Cadmium(2+) salts of medium- and long-chain carboxylic acids: Environment tier II assessment

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Preface

This assessment was carried out by staff of the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) using the Inventory Multi-tiered Assessment and Prioritisation (IMAP) framework.

The IMAP framework addresses the human health and environmental impacts of previously unassessed industrial chemicals listed on the Australian Inventory of Chemical Substances (the Inventory).

The framework was developed with significant input from stakeholders and provides a more rapid, flexible and transparent approach for the assessment of chemicals listed on the Inventory.

Stage One of the implementation of this framework, which lasted 4 years from 1 July 2012, examined 3000 chemicals meeting characteristics identified by stakeholders as needing priority assessment. This included chemicals for which NICNAS already held exposure information, chemicals identified as a concern or for which regulatory action had been taken overseas, and chemicals detected in international studies analysing chemicals present in babies' umbilical cord blood.

Stage Two of IMAP began in July 2016. We are continuing to assess chemicals on the Inventory, including chemicals identified as a concern for which action has been taken overseas and chemicals that can be rapidly identified and assessed by using Stage One information. We are also continuing to publish information for chemicals on the Inventory that pose a low risk to human health or the environment or both. This work provides efficiencies and enables us to identify higher risk chemicals requiring assessment.

The IMAP framework is a science and risk-based model designed to align the assessment effort with the human health and environmental impacts of chemicals. It has 3 tiers of assessment, with the assessment effort increasing with each tier. The Tier I assessment is a high throughput approach using tabulated electronic data. The Tier II assessment is an evaluation of risk on a substance-by-substance or chemical category-by-category basis. Tier III assessments are conducted to address specific concerns that could not be resolved during the Tier II assessment.

These assessments are carried out by staff employed by the Australian Government Department of Health and the Australian Government Department of the Environment and Energy. The human health and environment risk assessments are conducted and published separately, using information available at the time, and may be undertaken at different tiers.

This chemical or group of chemicals are being assessed at Tier II because the Tier I assessment indicated that it needed further investigation.

For more detail on this program please visit: www.nicnas.gov.au.

Disclaimer

Acronyms & Abbreviations

Grouping Rationale

This Tier II assessment considers the environmental risks associated with the industrial uses of twenty-five cadmium(2+) salts of medium- and long-chain carboxylic acids. The chemicals in this group are a subset of a large class of industrially important metal-ion salts of aliphatic carboxylic acids which are collectively described as ‘metallic soaps’.

Chemicals in this assessment have primarily been used as stabilisers or lubricants in the manufacture of polyvinyl chloride (PVC) plastics. The toxicity of ionic cadmium has led to the replacement of cadmium soaps in these uses by mixtures of calcium and zinc soaps as well as other stabilisers. The declining industrial uses of cadmium soaps will be used to inform this risk assessment.

Industrial uses of the cadmium salts in this group are a potential source of anthropogenic emissions of cadmium compounds to the Australian environment. Emissions of cadmium compounds to the environment are of concern because they can release bioavailable ionic cadmium which is toxic to wildlife and humans. Ionic cadmium is also of concern in soil because it is taken up rapidly by agricultural crops and can contaminate the human food chain. The environmental fate and effects of ionic cadmium were assessed under the IMAP Framework and the findings are published in the IMAP Environment Tier II Assessment for water soluble cadmium(2+) salts (NICNAS, 2017). This previous assessment should be consulted for details on the environmental hazards associated with ionic cadmium.

The environmental fate and effects of the medium- and long-chain carboxylic acids in this group were also assessed previously under the IMAP Framework and the findings are published elsewhere (NICNAS, 2014a; 2014b; 2014c; 2014d). These acids are generally of low environmental concern and they will not be further considered in this assessment.

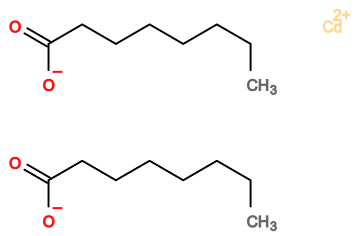
Chemical Identity

The chemicals in this assessment have been categorised into three sub-groups based on similarities in the chemical composition of the sub-group members. The first and largest sub-group includes all cadmium carboxylic acid salts which have a specifically defined chemical composition. Each cadmium salt in this sub-group is a 1:2 stoichiometric compound of cadmium(2+) cations and carboxylate mono-anions of defined chain length.

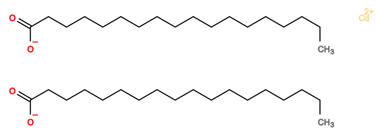
The other two chemically distinct sub-groups are composed of cadmium salts that are expected to dissociate and hydrolyse in water to release identical chemical species to those released by dissolution of chemicals in the stoichiometric cadmium carboxylic acid salts sub-group. The second sub-group includes basic cadmium salts of carboxylic acids with a defined chain length. The third sub-group consists of two cadmium salts which are in the category of unknown or variable composition, complex reaction products or biological materials (UVCBs). Both UVCBs are cadmium salts of mixtures of fatty acids.

Structural formulae for two 1:2 cadmium carboxylic acid salts in this group are provided below for illustrative purposes:

1:2 Cadmium Carboxylic Acid Salts

CAS RN	2191-10-8
Chemical Name	Octanoic acid, cadmium salt
Synonyms	cadmium dioctanoate cadmium octanoate
Structural Formula	
Molecular Formula	$Cd(C_8H_{15}O_2)_2$
Molecular Weight (g/mol)	398.81
SMILES	[Cd++].CCCCCCCC(=O)[O-].CCCCCCCC(=O)[O-].

CAS RN	2223-93-0
Chemical Name	Octadecanoic acid, cadmium salt
Synonyms	cadmium distearate cadmium dioctadecanoate cadmium stearate

Structural Formula	
Molecular Formula	$Cd(C_{18}H_{35}O_2)_2$
Molecular Weight (g/mol)	679.33
SMILES	[Cd++].CCCCCCCCCCCCCCCCCC(=O)[O-].CCCCCCCCCCCCCCCCCC(=O)[O-].

CAS RN	2420-98-6
Chemical Name	Hexanoic acid, 2-ethyl-, cadmium salt
Synonyms	cadmium bis(2-ethylhexanoate) cadmium 2-ethylhexanoate
Molecular Formula	$Cd(C_8H_{15}O_2)_2$
Molecular Weight (g/mol)	398.81

CAS RN	30304-32-6
Chemical Name	Isooctanoic acid, cadmium salt
Synonyms	cadmium isooctanoate
Molecular Formula	$Cd(C_8H_{15}O_2)_2$

Molecular Weight (g/mol)	398.81

CAS RN	5112-16-3
Chemical Name	Nonanoic acid, cadmium salt
Synonyms	cadmium nonan-1-oate cadmium dinonanoate
Molecular Formula	$Cd(C_9H_{17}O_2)_2$
Molecular Weight (g/mol)	426.88

CAS RN	93686-40-9
Chemical Name	Nonanoic acid, branched, cadmium salt

CAS RN	2847-16-7
Chemical Name	Decanoic acid, cadmium salt
Synonyms	cadmium didecanoate
Molecular Formula	$Cd(C_{10}H_{19}O_2)_2$
Molecular Weight (g/mol)	454.93

CAS RN	93965-24-3
Chemical Name	Isodecanoic acid, cadmium salt

Molecular Formula	$Cd(C_{10}H_{19}O_2)_2$
Molecular Weight (g/mol)	454.93

CAS RN	61951-96-0
Chemical Name	Neodecanoic acid, cadmium salt
Synonyms	cadmium neodecanoate
Molecular Formula	$Cd(C_{10}H_{19}O_2)_2$
Molecular Weight (g/mol)	454.91

CAS RN	93965-30-1
Chemical Name	Isoundecanoic acid, cadmium salt
Synonyms	cadmium bis(isoundecanoate)
Molecular Formula	$Cd(C_{11}H_{21}O_2)_2$
Molecular Weight (g/mol)	482.98

CAS RN	2605-44-9
Chemical Name	Dodecanoic acid, cadmium salt
Synonyms	cadmium dilaurate

	cadmium dodecanoate
Molecular Formula	$Cd(C_{12}H_{23}O_2)_2$
Molecular Weight (g/mol)	511.04

CAS RN	10196-67-5
Chemical Name	Tetradecanoic acid, cadmium salt
Synonyms	cadmium myristate cadmium tetradecanoate
Molecular Formula	$Cd(C_{14}H_{27}O_2)_2$
Molecular Weight (g/mol)	567.15

CAS RN	6427-86-7
Chemical Name	Hexadecanoic acid, cadmium salt
Synonyms	cadmium dipalmitate cadmium hexadecanoate
Molecular Formula	$Cd(C_{16}H_{31}O_2)_2$
Molecular Weight (g/mol)	623.25

CAS RN	84878-36-4

Chemical Name	Isooctadecanoic acid, cadmium salt
Synonyms	cadmium isooctadecanoate
Molecular Formula	$Cd(C_{18}H_{35}O_2)_2$
Molecular Weight (g/mol)	679.33

CAS RN	10468-30-1
Chemical Name	9-Octadecenoic acid, cadmium salt, (*Z*)-
Synonyms	cadmium dioleate 9-octadecenoic acid (9*Z*)-, cadmium salt
Molecular Formula	$Cd(C_{18}H_{33}O_2)_2$
Molecular Weight (g/mol)	675.33

CAS RN	13832-25-2
Chemical Name	9-Octadecenoic acid, 12-hydroxy-, cadmium salt (2:1), [R-(*Z*)]-
Synonyms	cadmium diricinoleate
Molecular Formula	$Cd(C_{18}H_{33}O_3)_2$
Molecular Weight (g/mol)	707.33

CAS RN	69121-20-6

Chemical Name	Octadecanoic acid, 12-hydroxy-, cadmium salt (2:1)
Synonyms	cadmium 12-hydroxyoctadecanoate cadmium bis(12-hydroxyoctadecanoate)
Molecular Formula	$Cd(C_{18}H_{35}O_3)_2$
Molecular Weight (g/mol)	711.32

CAS RN	14923-81-0
Chemical Name	Eicosanoic acid, cadmium salt
Synonyms	cadmium diicosanoate
Molecular Formula	$Cd(C_{20}H_{39}O_2)_2$
Molecular Weight (g/mol)	735.47

CAS RN	34303-23-6
Chemical Name	Docosanoic acid, cadmium salt
Synonyms	cadmium behenate cadmium didocosanoate
Molecular Formula	$Cd(C_{22}H_{43}O_2)_2$
Molecular Weight (g/mol)	791.58

Basic Cadmium Carboxylic Acid Salts

'Basic' cadmium carboxylic acid salts are produced using an excess of cadmium oxide (CAS RN 1306-19-0). These salts are mixtures of cadmium oxide and a stoichiometric cadmium carboxylic acid salt wherein the ratio of oxide to salt is in a range between 1:1 and 2:1 (Hirsch and Fleischer, 1988; Nora and Koenen, 2012):

CAS RN	90411-62-4
Chemical Name	Hexanoic acid, 2-ethyl-, cadmium salt, basic

CAS RN	101012-89-9
Chemical Name	Dodecanoic acid, cadmium salt, basic

CAS RN	101012-93-5
Chemical Name	Octadecanoic acid, cadmium salt, basic

CAS RN	101012-94-6
Chemical Name	Octadecanoic acid, 12-hydroxy-, cadmium salt, basic

Cadmium Salts of Hydrogenated Fatty Acids

The carboxylate counter ions in the two UVCB cadmium salts of this group are hydrogenated fatty acids derived from animal fats (tallow) or vegetable oils (castor oil). Fatty acids have an even number of carbon atoms in their chain as their biosynthesis occurs mainly through addition of two carbon units in the form of acetyl-CoA (Voet and Voet, 1990). The UVCB, hydrogenated tallow fatty acids is primarily composed of hexadecanoic acid (CAS RN 57-10-3; palmitic acid) and octadecanoic acid (CAS RN 57-11-4; stearic acid), which are linear long-chain carboxylic acids that are represented in the stoichiometric cadmium carboxylic acid salts of this group assessment (i.e., CAS RNs 6427-86-7 and 2223-93-0) (Gunstone, et al., 1995):

CAS RN	68953-39-9
Chemical Name	Fatty acids, tallow, hydrogenated, cadmium salts

The UVCB, castor oil fatty acids is composed of greater than 90% ricinoleic acid (CAS RN 141-22-0), which when hydrogenated forms octadecanoic acid, 12-hydroxy- (CAS RN 106-14-9) (Patel, et al., 2016). This UVCB substance is therefore predominantly octadecanoic acid, 12-hydroxy-, cadmium salt (2:1) (CAS RN 69121-20-6):

CAS RN	91697-35-7
Chemical Name	Fatty acids, castor oil, hydrogenated, cadmium salts

Physical and Chemical Properties

Cadmium distearate (CAS RN 2223-93-0) is a white powder with a melting point of 105–115°C (Nora and Koenen, 2012). Limited information is available on the physical properties of the other chemicals in this group.

The metallic soaps of divalent metal ions are typically made using aliphatic carboxylic acids with eight to twenty-two carbon atoms (C_8 to C_{22}) (Nora and Koenen, 2012). Studies of the water solubility of cadmium soaps indicate that they dissociate in water to release cadmium(2+) ions and carboxylate mono-anions. These studies also show that the solubilities of cadmium carboxylic acid salts decrease as the length of the carbon atom chain increases (Hunter and Liss, 1976; Mauchauffee, et al., 2008).

Solubility products (K_{sp}), which are a quantitative measure of the position of the solubility equilibrium, have been determined for cadmium dioctanoate (CAS RN 2191-10-8) and cadmium distearate (Hunter and Liss, 1976; Mauchauffee, et al., 2008). The cadmium ion concentration at saturation for each salt was estimated from the respective K_{sp} values using an activity coefficient of 0.586 as used in (Hunter and Liss, 1976):

Chemical	cadmium dioctanoate	cadmium distearate
K_{sp}	6.46×10^{-9}	6.92×10^{-21}
Cadmium(2+) Concentration at Saturation	225 mg Cd/L	0.02 mg Cd/L

K_{sp} values obtained from the literature were determined for stoichiometric cadmium salts of linear carboxylic acids (Hunter and Liss, 1976; Mauchauffee, et al., 2008). The water solubility of cadmium salts of carboxylic acids with branched, unsaturated and/or hydroxylated carbon chains in this group is not expected to be less than the solubility of cadmium salts of linear saturated carboxylic acids with the same number of carbon atoms.

The basic cadmium carboxylic acid salts in this group are expected to contain quantities of cadmium oxide. A transformation/dissolution test has been performed on powdered cadmium oxide at pH 8 (EU RAR, 2007). The solubility of cadmium oxide under the conditions of this test is in the range of 0.1–0.23 milligrams dissolved cadmium per litre. This water solubility value has been taken to provide an indication of the minimum water solubility of the basic cadmium carboxylic acid salts considered in this assessment.

Import, Manufacture and Use

Australia

Cadmium soaps have been used in Australia as stabilizers in the manufacture of PVC. However, this use pattern has been in long-term decline (Coghlan, 2001). Cadmium soap stabilisers have largely been replaced by zinc and calcium soaps (Tjadraatmadja and Diaper, 2006). Use of cadmium soap stabilisers has not been reported by signatories to the Vinyl Council of Australia’s Product Stewardship Program since 2004 (Vinyl Council Australia, 2017).

The only chemical in this group with specific Australian use information is cadmium dioleate (CAS RN 10468-30-1), which was reported to be used as a PVC stabiliser under previous mandatory and/or voluntary calls for information (NICNAS, 2013).

International

The primary use of chemicals in this group is as stabilisers and lubricants in PVC manufacturing (Nora and Koenen, 2012; NTP RoC, 1999). Cadmium carboxylic acid stabilisers react with hydrochloric acid released during polymer degradation to form cadmium chloride and the conjugate carboxylic acid (Anderson and McKenzie, 1970). The products of this reaction are present both on the surface of PVC articles and within the plastic matrix (Tjadraatmadja and Diaper, 2006).

Cadmium stabilisers improve the stability of PVC during manufacturing and increase resistance to ultra-violet (UV) and thermally initiated degradation in the final manufactured article. These properties are functional requirements for the use of PVC in water and drain pipes as well as in other construction materials. Cadmium stabilisers are typically present in PVC articles at 0.5–2.5% by weight (European Commission, 2000; NTP RoC, 1999).

The use of cadmium stabilisers in plastics manufacturing declined in many countries between 1980 and 2010 (International Cadmium Association, 2019; Schulte-Schrepping and Piscator, 2012; UNEP, 2010).

Environmental Regulatory Status

Australia

A detailed discussion of the regulatory status of cadmium in Australia has been published elsewhere (NICNAS, 2017).

United Nations

The United Nations Environment Programme (UNEP) received a mandate to address the environmental and health risks of cadmium in 2001 (UNEP, 2019). UNEP published a review of scientific information on cadmium including sources of emissions and the effects of cadmium on human health and the environment which was last updated in 2010 (UNEP, 2010).

OECD

No chemicals in this group have been sponsored for assessment under the Cooperative Chemicals Assessment Programme (CoCAP) (OECD, 2013).

Canada

Chemicals containing cadmium are listed as a broad class of compounds (‘Inorganic cadmium compounds’) under Schedule 1 (the Toxic Substances List) of the *Canadian Environmental Protection Act 1999* (CEPA) (Government of Canada, 2013).

European Union

All chemicals in this group are regulated as containing cadmium and are listed in Annex XVII (Restriction) under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation as a broad class of compounds (‘Cadmium and its compounds') (ECHA, 2019a). The restrictions relate to the use of these chemicals in polymers (plastic material), plastic articles, paints, painted articles, articles containing recovered PVC, cadmium metal plating, cadmium plated articles, brazing fillers and jewellery. All chemicals in this group have been pre-registered under REACH (ECHA, 2019b).

United States of America

Twelve of the chemicals in this group are listed on the United States Environmental Protection Agency (US EPA) Chemical Substances Inventory, established under the Toxic Substances Control Act 1976 (TSCA) (US EPA, 2019). Cadmium dioleate, cadmium distearate, cadmium bis(2-ethylhexanoate) (CAS RN 2420-98-6), and cadmium dilaurate (CAS RN 2605-44-9) are all registered as 'active', which indicates that they have recently been manufactured, imported or processed by industry in the USA.

Cadmium and cadmium compounds are listed on the 2014 Update to the TSCA Work Plan list of existing chemicals for assessment (US EPA, 2014).

Environmental Exposure

Diffuse emissions of cadmium compounds to the environment can occur as a result of the use of cadmium soaps as stabilisers in PVC articles. The introduction of cadmium soaps into Australia is no longer expected to contribute to this emission pathway as a result of changes in the way PVC is manufactured domestically. However, the chemicals in this group may be used as stabilisers in PVC manufactured overseas and imported into Australia.

The only known environmental exposure pathway for ionic cadmium from uses of chemicals in this group is as a result of leaching from PVC articles during use and after disposal in waste management facilities. Available information indicates that the cadmium stabilisers present on the surface of PVC articles are rapidly removed with initial use. Leaching experiments typically indicate that cadmium based stabilisers are not readily released from the PVC matrix in simulated landfill conditions (European Commission, 2000; Tjadraatmadja and Diaper, 2006).

Programs and policies on the end-of-life management of PVC articles may need to consider the hazards associated with the presence of cadmium based stabilisers (GBCA, 2010). Cadmium stabilisers may present a hazard during recycling or where waste streams are incinerated as a means of disposal or for power generation (Coghlan, 2001; European Commission, 2000). The environmental risks arising from recycling or incineration of PVC articles is beyond the scope of this assessment.

The principal manufacturers of PVC in Australia now use less hazardous zinc and calcium soaps as stabilisers (Coghlan, 2001; Vinyl Council Australia, 2017). The introduction of cadmium soaps for use as stabilisers in the manufacture of PVC is, therefore, considered to be unlikely. The major emissions of cadmium compounds to the Australian environment are primarily associated with point-source emissions from industrial processes, such as non-ferrous metal refining (Department of the Environment, 2019). Diffuse emissions of cadmium from ongoing uses of cadmium carboxylic acid salts as stabilisers in PVC are expected to constitute a very small proportion of the total anthropogenic emissions in Australia.

Environmental Effects

The critical environmental effects of the chemicals in this group are those of the dissolved cadmium ions. A detailed account of the ecotoxicity of ionic cadmium is available in the IMAP Environment Tier II Assessment for water soluble cadmium(2+) salts (NICNAS, 2017). In summary, cadmium bioaccumulates in terrestrial and aquatic organisms and bioavailable forms of ionic cadmium are highly toxic to aquatic life. In the aquatic compartment, fish and invertebrates are more sensitive to ionic cadmium than algae; however, considerable variation is observed even in closely related species (Mebane, 2010; NICNAS, 2017).

Risk Characterisation

The chemicals in this group contain cadmium(2+) ions which can be released to the environment from their main industrial use as stabilisers in PVC. Anthropogenic emissions of cadmium to the environment are of concern both domestically and internationally due to the toxic and bioaccumulative properties of bioavailable forms of ionic cadmium.

The release of cadmium to the Australian environment from industrial uses of chemicals in this group is expected to be limited in volume and diffuse in nature. Available information indicates that current uses of cadmium stabilisers in PVC are small and declining. The substitution of cadmium stabilisers by less hazardous alternatives in PVC manufacturing has significantly reduced consumption of these substances.

The importation of PVC articles which contain cadmium stabilisers and PVC articles still in use which contain cadmium stabilisers are a consideration for recycling and waste management activities in Australia. Cadmium stabilisers present in PVC disposed of in landfill are expected to be immobilised. However, there is the potential that cadmium contained in these articles may be released by recycling or waste management processes that deteriorate the PVC matrix.

Key Findings

The chemicals in this group have had historical use as stabilisers in polyvinyl chloride plastics. National and international reports indicate that cadmium soaps have largely been replaced by less hazardous alternatives for this use.

The principal environmental concern for industrial uses of cadmium soaps is the potential to release soluble forms of ionic cadmium. This poses a concern as ionic cadmium is considered to be a highly significant environmental contaminant. Based on current use patterns the chemicals in this group are expected to pose a low and declining risk to the environment.

The volume of cadmium based stabilisers introduced to Australia in imported PVC articles is not known. This may be a consideration for waste management activities which involve the recycling of PVC articles, or their destruction in waste-to-energy conversion processes.

Recommendations

The chemicals in this group are not priorities for further evaluation.

Environmental Hazard Classification

The classification of the environmental hazards for all of the chemicals in this group according to the third edition of the United Nations' Globally Harmonised System of Classification and Labelling of Chemicals (GHS) (UNECE, 2009) is presented below:

Hazard	GHS Classification (Code)	Hazard Statement
Acute Aquatic	Category 1 (H400)	Very toxic to aquatic life
Chronic Aquatic	Category 1 (H410)	Very toxic to aquatic life with long lasting effects

The aquatic hazards of the chemicals in this group have been classified based on the available acute and chronic toxicity values for ionic cadmium in accordance with the classification procedure for metals and metal compounds under the GHS (UNECE, 2007).

The aquatic hazards associated with the chemicals in this group is dependent on their capacity to release ionic cadmium at concentrations that exceed identified acute and chronic toxicity thresholds for the soluble cadmium ion. The chemicals in this group with up to eighteen carbon atoms in the carboxylate anion are classified as Acute and Chronic Aquatic Category 1 as their calculated maximum ionic cadmium concentrations at saturation exceed the most sensitive acute and chronic toxicity values for ionic cadmium.

Based on the observed trend in water solubility for stoichiometric cadmium carboxylic acid salts, eicosanoic acid, cadmium salt and docosanoic acid, cadmium salt are both expected to have solubilities in excess of the relevant acute and chronic toxicity end points. These chemicals have, therefore also been classified as Acute and Chronic Aquatic Category 1.

The minimum water solubility of the basic cadmium carboxylic acid salts in this group was estimated based on the solubility of cadmium oxide as determined using the OECD transformation and dissolution protocol (UNECE, 2007). As the dissolved cadmium concentration for cadmium oxide measured using this protocol exceeds the relevant toxicity endpoints for ionic cadmium all of these salts have also been classified as Acute and Chronic Aquatic Category 1.

The two UVCB cadmium salts of hydrogenated fatty acids are primarily composed of cadmium salts of carboxylic acids that have eighteen carbon atoms in the carboxylate anion. Cadmium distearate has, therefore, been used to indicate the minimum water solubility of these substances. Hence, both cadmium UVCBs in this group are categorised as Acute and Chronic Aquatic Category 1.

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