



Australian Government

Department of Health

Australian Industrial Chemicals Introduction Scheme

Nickel soaps

Evaluation statement

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Draft



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Evaluation statement

Subject of the evaluation

Nickel soaps.

Chemicals in this evaluation

Name	CAS Registry Number
Hexanoic acid, 2-ethyl-, nickel(2+) salt	4454-16-4
Octadecanoic acid, nickel(2+) salt	2223-95-2
9-Octadecenoic acid, nickel(2+) salt, (Z)-	13001-15-5
Octanoic acid, nickel(2+) salt	4995-91-9
Hexanoic acid, 2-ethyl-, nickel salt	7580-31-6

Reason for the evaluation

The Evaluation Selection Analysis indicated a potential risk to the environment.

Parameters of evaluation

The chemicals in this group have been assessed for their risks to the environment according to the following parameters:

- Default domestic introduction of 100 tonnes per annum
- industrial uses listed in the 'Summary of Use' section
- expected release into sewage treatment plants, the water compartment and the soil compartment.

The chemicals have been assessed as a group as they are members of an industrially important class of metal salts known as metallic soaps. They are expected to have similar hazard profiles and use patterns.

Summary of evaluation

Summary of introduction, use and end use

Based on international use information, these substances are expected to be used as additives in:

- lubricant and grease products
- paint and coating products

as well as catalysts, catalyst precursors and process regulators in the manufacture of:

- plastic and polymer products.

There is no information available on the volumes of these chemicals in use in Australia. Data from international jurisdictions indicate that nickel(2+) ethylhexanoate (CAS RN 4454-16-4) is used in the EU at 10–100 tonnes annually, and at up to 454 tonnes annually in the USA. Nickel ethylhexanoate (CAS RN 7580-31-6) has a reported annual use of 340.4 tonnes in the USA.

Environment

Summary of environmental hazard characteristics

The primary environmental effects of the chemicals in this group are expected to be caused by release of nickel(2+) ions, which are very toxic to aquatic organisms. The environmental hazards of nickel(2+) were previously assessed under the Inventory Multi-tiered Assessment and Prioritisation (IMAP) framework established by the National Industrial Chemicals Notification and Assessment Scheme (NICNAS, 2020).

The chemicals in this group are nickel salts of organic acids. A PBT hazard categorisation was not performed for the organic acid components of these chemicals, as they were assessed previously under the IMAP Framework and the findings are published elsewhere (NICNAS, 2014a; 2014b). These organic acids are generally of low environmental concern.

Environmental hazard classification

The chemical satisfies the criteria for classification according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) for environmental hazards as follows. This does not consider classification of physical hazards and health hazards.

Environmental Hazard	Hazard Category	Hazard Statement
Acute Aquatic	Acute aq. – Cat. 1	H400: Very toxic to aquatic life
Chronic Aquatic	Chronic aq. – Cat. 1	H410: Very toxic to aquatic life with long lasting effects

Summary of environmental risk

The principal environmental concern for the chemicals in this group is their potential to release bioavailable forms of ionic nickel into the environment. This poses a concern because bioavailable forms of ionic nickel are very toxic to aquatic organisms.

The nickel soaps in this group are used in a variety of products including lubricants, paints and coatings. These uses may result in diffuse emissions of ionic nickel to water, sediment and soil compartments.

Environmental monitoring of Australian waters and sediments indicates that levels of nickel occasionally exceed recommended guidelines, particularly in the sediment compartment. However, the chemicals in this evaluation are likely to be used in relatively low volumes based on international use volume data. Their contribution to nickel levels in the environment is expected to be small relative to other sources of nickel emissions in Australia, such as

mining and heavy industry. The chemicals are, therefore, not expected to pose a high risk to the environment for the industrial uses identified in this evaluation.

Conclusions

The conclusions of this evaluation are based on the information described in the statement. Obligations to report additional information about hazards under section 100 of the *Industrial Chemicals Act 2019* apply.

The Executive Director is satisfied that the identified environment risks can be managed within existing risk management frameworks. This is provided that all requirements are met under environmental, workplace health and safety and poisons legislation as adopted by the relevant state or territory.

Supporting information

Rationale

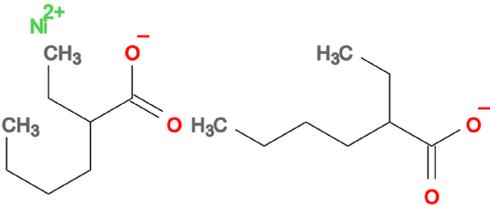
This evaluation considers the environmental risks associated with the industrial uses of five nickel salts of carboxylic acids classed as metallic soaps. This is an industrially important class of metal salts and they are primarily salts of fatty acids (Nora and Koenen, 2012).

The risk assessment of these chemicals has been conducted as a group because all five substances are expected to have generally similar environmental fate and ecotoxicity profiles due to similarities in use pattern and properties. They are used in a variety of products including lubricants, paints and coatings, and polymers. As these salts are soluble in water, they can all potentially release nickel(2+) ions upon dissolution, and these are very toxic to aquatic life.

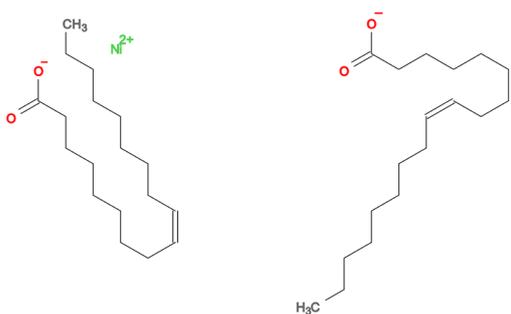
Chemical identity

For four of these substances, the nickel component is specified in the Australian Inventory of Industrial Chemicals (Inventory) name to have a 2+ oxidation state. The Chemical Abstracts Service (CAS) names for these substances specify a 1:2 ratio of nickel(2+) cations to their respective carboxylate mono-anions.

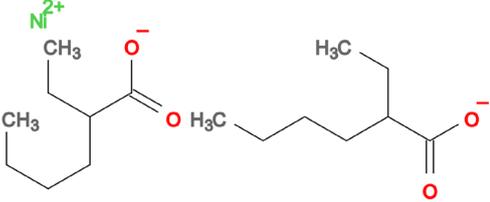
For the fifth substance, nickel ethylhexanoate (CAS RN 7580-31-6), the nickel oxidation state is not defined. For the purposes of this evaluation, it is assumed that this substance predominantly contains nickel in the 2+ oxidation state since it is the most common oxidation state for cationic nickel species (Kerfoot, 2012), and that this salt is composed of a 1:2 ratio of cations to anions.

CAS RN	4454-16-4
Chemical Name	Hexanoic acid, 2-ethyl-, nickel(2+) salt
Synonyms	nickel(2+) ethylhexanoate nickel bis(2-ethylhexanoate) 2-ethylhexanoic acid, nickel salt nickel(2+) 2-ethylhexanoate nickel 2-ethylhexanoate nickel 2-ethylhexoate nickel isoctanoate
Structural formula	
Molecular formula	C ₁₆ H ₃₀ NiO ₄
Molecular weight (g/mol)	345.1
SMILES	O=C([O-])C(CC)CCCC.O=C([O-])C(CC)CCCC.[Ni++]
Chemical description	-

CAS RN	2223-95-2
Chemical Name	Octadecanoic acid, nickel(2+) salt
Synonyms	nickel(2+) stearate nickel stearate stearic acid, nickel(2+) salt nickel distearate nickel(2+) octadecanoate
Structural formula	
Molecular formula	$C_{36}H_{70}NiO_4$
Molecular weight (g/mol)	625.6
SMILES	<chem>O=C([O-])CCCCCCCCCCCCCCCCCC.O=C([O-])CCCCCCCCCCCCCCCCCC.[Ni++]</chem>
Chemical description	-

CAS RN	13001-15-5
Chemical Name	9-Octadecenoic acid, nickel(2+) salt, (Z)-
Synonyms	nickel(2+) oleate nickel oleate oleic acid, nickel(2+) salt nickel bis(oleate) nickel dioleate
Structural formula	
Molecular formula	$C_{36}H_{66}NiO_4$
Molecular weight (g/mol)	621.6
SMILES	<chem>C(C/C=C\CCCCCCCC)CCCCC([O-])=O.C(C/C=C\CCCCCCCC)CCCCC([O-])=O.[Ni++]</chem>
Chemical description	-

CAS RN	4995-91-9
Chemical Name	Octanoic acid, nickel(2+) salt
Synonyms	nickel(2+) octanoate nickel octanoate nickel(2+) octoate nickel dioctanoate nickel octoate nickel octylate nickel(2+) caprylate
Structural formula	
Molecular formula	$C_{16}H_{30}NiO_4$
Molecular weight (g/mol)	345.1
SMILES	<chem>O=C([O-])CCCCCCC.O=C([O-])CCCCCCC.[Ni++]</chem>
Chemical description	-

CAS RN	7580-31-6
Chemical Name	Hexanoic acid, 2-ethyl-, nickel salt
Synonyms	nickel ethylhexanoate nickel 2-ethylhexanoate
Representative structural formula	
Representative molecular formula	$C_{16}H_{30}NiO_4$
Representative molecular weight (g/mol)	345.1
Representative SMILES	<chem>O=C([O-])C(CC)CCCC.O=C([O-])C(CC)CCCC.[Ni++]</chem>
Chemical description	A salt of nickel and 2-ethylhexanoic acid with undefined stoichiometry. For the purposes of this evaluation, it is assumed that the nickel is predominantly in the 2+ oxidation state, and that the substance composition is therefore a 1:2 ratio of nickel(2+) cations to 2-ethylhexanoate mono-anions.

Relevant physical and chemical properties

Nickel(2+) ethylhexanoate and nickel(2+) oleate have been described as green or greenish pastes for which no definitive melting points have been reported (Nora and Koenen, 2012; REACH, 2017). Nickel(2+) stearate is described as a bright green powder with a melting range of 80–86°C (Nora and Koenen, 2012).

Studies of the solubility of various divalent metallic soaps show that nickel(2+) soaps typically dissociate in water to release nickel(2+) ions and carboxylate mono-anions (Hunter and Liss, 1976; Mauchauffee, et al., 2008). These studies also show that the water solubility of metallic soaps of straight-chain fatty acids decreases as chain length increases.

Water solubility data for two chemicals in this group and one analogue chemical are presented in the table below. Water solubility data for nickel(2+) ethylhexanoate was taken from the REACH dossier for the compound (REACH, 2017). The measured nickel(2+) ion concentration at saturation of nickel(2+) octanoate has been reported in the scientific literature (Mauchauffee, et al., 2008). Solubility data for an analogue chemical, nickel(2+) palmitate (CAS RN 13654-40-5), was calculated from the solubility product (K_{sp}) determined for this chemical (Hunter and Liss, 1976). The solubility product of this chemical is a quantitative measure of the position of the solubility equilibrium and was obtained at an ionic strength of 0.1 M NaCl. The nickel(2+) ion concentration was calculated from this value using an activity coefficient of 0.586:

Chemical	Nickel(2+) ethylhexanoate	Nickel(2+) octanoate	Nickel(2+) palmitate
Water solubility	110 mg/L at 30°C	3030 mg/L (calc.)	2.26 mg/L (calc.)
K_{sp}	-	-	5.01×10^{-17} at 25°C
Ni(2+) concentration at saturation	18.7 mg Ni/L (calc.)	515 mg Ni/L at 20°C	0.233 mg Ni/L (calc.)

Nickel(2+) palmitate is the nickel salt of a C₁₆ carboxylic acid. The solubility data for this chemical is taken to conservatively represent the solubilities of nickel(2+) stearate and nickel(2+) oleate, two nickel salts of longer-chain C₁₈ carboxylic acids. Assuming the same molar solubilities for all three chemicals, water solubilities of 2.48 and 2.46 mg/L, respectively, were calculated for nickel(2+) stearate and nickel(2+) oleate, based on their molar mass.

Introduction and use

Australia

No specific Australian use, import or manufacturing data have been identified for the chemicals in this group.

International

The class of chemicals known as nickel soaps are known to be used as oxidation catalysts to accelerate drying, for example, in the film formation of paints based on drying oils. They are also used as oil-soluble hydrogenation catalysts, and as additives in lubricating oils for preventing undesirable reactions (Nora and Koenen, 2012).

Nickel(2+) ethylhexanoate and nickel ethylhexanoate have reported uses as process regulators in rubber products and catalysts in the manufacture of polymers in the United States, Europe and the Nordic countries (REACH, 2017; SPIN, 2021; US EPA, 2016). In the United States they also have reported use as additives in lubricants, wood coatings and paints (NCBI, 2021).

In the European Union, the nickel(2+) salt of 2-ethylhexanoic acid (CAS RN 4454-16-4) is registered at 10–100 tonnes annual use (REACH, 2017), with all other members of this group not registered. In the United States, nickel(2+) ethylhexanoate (CAS RN 4454-16-4) and nickel ethylhexanoate (CAS RN 7580-31-6) are registered at < 453.6 and 340.4 tonnes annual use, respectively (US EPA, 2016). No international use volume data were identified for the remaining three substances in this group.

There is some indication that chemicals in this group are or have been used in pesticides (as an inert component) (NCBI, 2021). However, such use is beyond the scope of this assessment, as it is not considered an industrial use under the *Industrial Chemicals Act 2019*.

Existing Australian regulatory controls

Environment

Nickel and nickel compounds are subject to reporting under the Australian National Pollutant Inventory. Contaminant guidelines for nickel are discussed in the IMAP Environment Tier II assessment of water soluble nickel(2+) salts (NICNAS, 2020).

Default guideline values have been published for nickel in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZG, 2000; 2018a). For slightly-moderately disturbed freshwater ecosystems, a high reliability guideline value has been determined to be 11 micrograms of nickel per litre ($\mu\text{g Ni/L}$) (95% species protection). The equivalent recommended values for marine and sediment ecosystems are 7 $\mu\text{g Ni/L}$ (99% species protection) and 21 milligrams of nickel per kilogram (mg Ni/kg) dry weight (dw), respectively.

International regulatory status

United Nations

The chemicals in this group are not currently identified as Persistent Organic Pollutants (UNEP, 2001), ozone depleting substances (UNEP, 1987), or hazardous substances for the purpose of international trade (UNEP & FAO, 1998).

European Union

All substances in this evaluation are on the Restriction list (Annex XVII) as members of the group 'Nickel and its compounds', which restricts their use in items that have direct, prolonged contact with skin such as piercings, jewellery and garment fasteners (ECHA, 2021).

Environmental exposure

The nickel soaps in this group are used in a variety of products including lubricants, paints and coatings, and polymers. These uses may result in diffuse emissions of ionic nickel to water, sediment and soil compartments.

Based on the available use pattern information, nickel soaps are expected to be used primarily in lubricants, paints and coatings. Diffuse emissions of nickel compounds to the environment can occur as result of use in such products. Depending on the use of the lubricant, release to the environment can occur as the result of spills, leakage and, in the case of automotive lubricants, exhaust emissions (OECD, 2004). Uses in surface coatings may result in release to the environment through flaking, chipping and weathering (OECD, 2009). Such release may contribute to pollutants in urban runoff, which has been shown to be a significant source of nickel contamination in urban wastewater, waterways and groundwater in Europe (ICON, 2001). Paints and pigments have also been identified as a domestic source of nickel in urban wastewater (ICON, 2001). Polymer products that were manufactured using nickel soaps as catalysts may retain small amount of these chemicals in the final product. However, emission of nickel compounds from such products would be expected to be minor compared to those from products in which they are intentionally incorporated and present in larger amounts.

The Australian National Pollutant Inventory requires reporting of all emissions of nickel and nickel compounds from facilities that use more than 10 tonnes per year of these substances (NPI, 2019). Emissions from diffuse sources are estimated taking into account studies of emissions from small industrial facilities and commercial and domestic activities in all major urban and some regional areas (NPI, 2014). According to NPI data (NPI, 2021), approximately 540 tonnes of nickel were released to the Australian environment in 2019/2020. Of this, the majority is attributed to emissions from industrial processes such as metal ore mining, coal mining, and non-ferrous metal manufacture (446 tonnes, 82% of total). Another significant source was diffuse emissions from paved and unpaved roads (38 tonnes, 7% of total), which is expected to originate from nickel in clutch and brake linings and chrome plating (ICON, 2001). Other sources of diffuse emissions of nickel include windblown dust, which are fine particles from eroded or bare land surfaces, and fuel combustion.

Comparatively, nickel emissions from some of the industrial uses for nickel soaps identified in this evaluation appear to be low. For example, estimated combined annual nickel emissions from basic polymer manufacture and polymer product manufacture were 13.5 kg in 2019/2020 (NPI, 2021).

Environmental fate and effects

The chemicals in this group are expected to be released into the terrestrial and aquatic environment where they will dissociate into the corresponding acids and ionic nickel.

The environmental fate and effects of the conjugate acids of the organic carboxylate anions of the chemicals in this group were assessed previously under the IMAP Framework and the findings are published elsewhere (NICNAS, 2014a; 2014b). These acids are generally of low environmental concern and they will not be further considered in this assessment.

A detailed account of the environmental fate and effects of ionic nickel is available in the IMAP Environment Tier II assessment of water soluble nickel(2+) salts (NICNAS, 2020). In summary, the behaviour of the nickel(2+) ion is strongly dependent on the chemistry of the environmental compartment into which it is released, and nickel is not expected to bioaccumulate to a significant extent in aquatic or terrestrial organisms, apart from in certain hyperaccumulator plants.

Bioavailable forms of nickel(2+) are highly toxic to aquatic life, toxic to terrestrial organisms and can have some toxic effects on sediment-dwelling organisms. The toxicity of ionic nickel to aquatic organisms varies considerably between species and is strongly influenced by water chemistry. In general, nickel toxicity is greatest in waters with alkaline pH, low water hardness and a low concentration of dissolved organic carbon (DOC) (NICNAS, 2020). The toxicity of bioavailable forms of nickel(2+) to terrestrial and sediment-dwelling life are influenced by physico-chemical properties such as the cation exchange capacity (CEC) in the case of soils, and total organic carbon (TOC) and concentration of acid-volatile sulfide (AVS) for sediments.

Predicted environmental concentration (PEC)

A PEC was not calculated for the chemicals addressed in this assessment or their ionic components.

Monitoring studies have found moderate to high concentrations of nickel in sediments from Australian rivers, urban harbours and industrial ports. In areas impacted by mining or sediment dredging, average nickel concentrations from multiple samples exceed the

Australian and New Zealand Guidelines for Fresh and Marine Water Quality default guideline value of 21 mg Ni/kg dw in sediment, while some of the highest recorded concentrations exceed the upper guideline value (GV-high) of 52 mg Ni/kg dw. Average nickel sediment concentrations from urban harbours are lower than the guideline values, though some high maximum concentrations have been recorded.

The highest sediment concentration of 118 mg Ni/kg dw was measured in Sydney harbour (Birch, et al., 2020). Mean measured sediment values from Sydney harbour were lower, at 15 mg/kg dw. In the same study, maximum and mean concentrations found in samples from Darwin harbour were 27 mg/kg dw and 8.8 mg/kg dw, respectively.

Mean sediment concentrations found in the Pilbara region in Western Australia ranged from 8.4 mg/kg dw in reference areas where there is relatively low anthropogenic impact, to 19.8 mg/kg dw in harbours impacted by dredging activity (Stoddart, et al., 2019). Maximum concentrations of 22 mg/kg dw and 58 mg/kg dw were found in reference and impacted areas, respectively.

Sediment concentrations in 12 samples taken in Tasmania were in the range of 3–117 mg/kg dw (Mehler, et al., 2019). Concentrations in six samples were above the default guideline value, of which two were above the 'upper' guideline value. However, many of the sampling sites were likely impacted by mining emissions. A reference sample taken from the Melbourne area returned a concentration of 8 mg/kg dw.

The mean concentrations of dissolved nickel in seawater from six NSW ports, which ranged from < 1 to 1.6 µg Ni/L (Jahan and Strezov, 2017), were within guideline values for marine water (7 µg/L for *slightly to moderately disturbed* marine systems at the 99% protection level) (ANZG, 2018b). Although one measured maximum value of 9 µg/L exceeded the guideline value, all other maximum concentrations of nickel were below 1 µg/L.

The IMAP Environment Tier II assessment of water soluble nickel(2+) salts (NICNAS, 2020) addresses chemicals most likely to be emitted from use in nickel plating operations, and therefore discusses concentrations of nickel in Australian soils (1.4 to 55 mg Ni/kg), wastewater entering STPs (4 to 11 µg Ni/L), and biosolids (average of 32 mg Ni/kg).

Relevant monitoring data for nickel levels in freshwater were not identified.

GHS classification of environmental hazard

The classification of the nickel soaps in this evaluation is based on the available acute ecotoxicity values for the nickel(2+) ion as identified in the IMAP Environment Tier II assessment of water soluble nickel(2+) salts (NICNAS, 2020), in accordance with the classification procedure for metals and metal compounds under the GHS (UNECE, 2017).

The aquatic hazards associated with the chemicals in this group are dependent on their capacity to release ionic nickel at concentrations that exceed identified acute toxicity thresholds for ionic nickel. Nickel(2+) ethylhexanoate, nickel ethylhexanoate, and nickel(2+) octanoate are classified as Acute and Chronic Aquatic Category 1 as their calculated or measured maximum ionic nickel concentrations at saturation exceed the most sensitive acute toxicity values for ionic nickel.

Nickel(2+) oleate and nickel(2+) stearate are classified as Acute and Chronic Aquatic Category 1 as their estimated maximum ionic nickel concentration at saturation, based on read-across from nickel(2+) palmitate, exceed the most sensitive acute toxicity values for ionic nickel.

It is preferable to classify the hazard posed by metals and metal compounds using the findings of a study conducted in accordance with the OECD Transformation and Dissolution protocol (UNECE, 2017). Therefore, should a study conducted in accordance with this protocol suggest a lower hazard classification is warranted, these chemicals may be reclassified as appropriate.

Environmental risk characterisation

The chemicals in this group contain nickel(2+) ions which can be released to the environment from their main industrial uses in products such as lubricants, paints and coatings. Anthropogenic emissions of nickel to the environment are of concern both domestically and internationally due to the toxicity of bioavailable forms of ionic nickel.

The environmental compartment most impacted by nickel in Australia appears to be the sediment compartment. The areas consistently exceeding default guideline values are typically impacted by point-emission sources associated with mining and heavy industry. This is consistent with NPI data indicating that the major sources of reported anthropogenic emissions of nickel to the environment in Australia are associated with large-scale industrial processes such as mining.

The release of nickel to the Australian environment from industrial uses of chemicals in this group is expected to be limited in volume and diffuse in nature. Nickel soaps are a minor source of diffuse emissions of nickel to the environment compared with sources such as nickel metal and alloys, fuel combustion and natural erosion. Furthermore, available information indicates that the global volume of use of the chemicals in this group is relatively low. The default assumed introduction volume of 100 tonnes per annum of each chemical in this group into Australia is therefore likely to be an overestimate.

Therefore, although some recorded environmental levels of nickel do exceed environmental guidelines for nickel in marine sediments, it is unlikely that the use of the nickel soaps considered in this evaluation significantly contributes to those exceedances.

Uncertainty

This evaluation was conducted based on a set of information that may be incomplete or limited in scope. Some relatively common data limitations can be addressed through use of conservative assumptions (OECD, 2019) or quantitative adjustments such as assessment factors (OECD, 1995). Others must be addressed qualitatively, or on a case-by-case basis (OECD, 2019).

The most consequential areas of uncertainty for this evaluation are:

- No Australian volume of use data is available for the chemicals in this group
- Should information become available to indicate that the chemicals in this group are used in high volumes or they are released directly to the environment, the outcome of this evaluation may change
- There are no domestic monitoring data for nickel in the freshwater compartment. The risk profile of these chemicals may change should monitoring data become available to indicate that nickel is present in Australian freshwater at levels that exceed water quality guideline values.

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