THIS DOCUMENT HAS BEEN PREPARED ACCORDING TO THE PROVISIONS OF ARTICLE 136(3) “TRANSITIONAL MEASURES REGARDING EXISTING SUBSTANCES” OF REACH (REGULATION (EC) 1907/2006). IT IS NOT A PROPOSAL FOR A RESTRICTION ALTHOUGH THE FORMAT IS THE SAME

# Annex XV dossier

# Transitional Dossier

| | |
|---|---|
| **Substance Name:** | **Trisodium hexafluoroaluminate** |
| **EC Number:** | 237-410-6 |
| **CAS Number:** | 13775-53-6 |

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# RESTRICTION PROPOSAL

| | |
|---|---|
| **Substance Name:** | **Trisodium hexafluoroaluminate** |
| **EC Number:** | 237-410-6 |
| **CAS number:** | 13775-53-6 |

**Restriction proposal:** None

Other Risk reduction measures see attached Risk Reduction Strategy.

# INFORMATION ON HAZARD AND RISKS

## 1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

Trisodium hexafluoroaluminate herein after referred to as cryolite is a mineral of very limited natural distribution. It was only found in large quantities on the west coast of Greenland, USA Canada and in the Urals. The composition is: 12.95 % aluminium, 54.29 % fluorine and 32.86 % sodium (Ullmann, 1988). Natural cryolite has the CAS-number 15096-52-3.

Today cryolite is produced synthetically. Synthetic cryolite has the CAS-number 13775-53-6.

Cryolite is the main constituent of the electrolytic bath in the production of aluminium (bath material) and is formed as a by-product during the electrolytic process containing 50 – 85 % cryolite. This by-product is listed as a UVCB-substance in EINECS with the CAS number 91696-24-1. It does not have same characteristics as CAS number 13775-53-6.

### 1.1 Name and other identifiers of the substance

| | |
|---|---|
| Chemical Name: | Trisodium hexafluoroaluminate |
| EC Name: | 237-410-6 |
| CAS Number: | 13775-53-6 |
| IUPAC Name: | Trisodium hexafluoroaluminate |

### 1.2 Composition of the substance

Natural cryolite has a purity of 75 to 95 %. The principal impurity is siderite (< 20 %). Quartz occurs in quantities of < 5 %. Other impurities are galena, zincblende, pyrite, chalcopyrite and fluorine minerals in small quantitites (Roholm, 1937).

Synthetic cryolite has a purity of >95 %. Impurities are aluminium oxide, aluminium fluoride, lithium fluoride, magnesium fluoride, calcium fluoride (each ≤ 5 %), quartz (≤ 0.2 %), diiron trioxide (≤ 0.1 %). In Table 1.1 a short summary about the composition of the three forms of cryolite is given.

**Table 1.1: Overview of the composition**

| Name | Natural cryolite | Synthetic cryolite | Flux remnant from the aluminium production |
|---|---|---|---|
| CAS number | 15096-52-3 | 13775-53-6 | 91696-24-1 |
| purity (%) | 75-95 | > 95 | 50 - 85 |
| impurity (%) | siderite < 20<br>quartz < 5<br>galena, zinc blende, pyrite, chalcopyrite, fluorine minerals: each in small amounts | diiron trioxide (CAS no. 1309-37-1) ≤ 0.1<br>quartz ≤ 0.2<br>aluminium oxide (CAS-no. 1344-28-1), aluminium fluoride (CAS-no. 7784-18-1), magnesium fluoride (CAS-no. 7783-40-6), calcium fluoride (CAS-no. 7789-75-5): each < 5 % | n.n. |

## 1.3 Physico-chemical properties

### 1.3.1 Physico-chemical properties for natural cryolite

| **REACH ref Annex, §** | **Property** | **IUCLID section** | **Value** | **[enter comment/reference or delete column]** |
|---|---|---|---|---|
| VII, 7.1 | Physical state at 20°C and 101.3 KPa | 3.1 | clear or white to yellowish, sometimes reddish or black solid<br>monoclinic cube-like crystals | Roholm (1937) |
| VII, 7.2 | Melting/freezing point | 3.2 | 1009 – 1012 °C | Ullmann (1988) |
| VII, 7.3 | Boiling point | 3.3 | no information available | |
| VII, 7.4 | Relative density | 3.4 density | 2.97 at 29 °C | Ullmann (1988) |
| VII, 7.5 | Vapour pressure | 3.6 | 253 Pa at 1009 °C | Ullmann (1988) |
| VII, 7.6 | Surface tension | 3.10 | not determined (inorganic complex salt) | |
| VII, 7.7 | Water solubility | 3.8 | 0.39 g/l at 25 °C (pH unknown)<br>0.9 g/l at 20 °C (pH 4 – 7) [1)]<br>ca. 400-500 mg/l at 20 °C (pH 8)<br>ca. 100-200 mg/l at 20 °C (pH 8.5)<br>ca. 20-40 mg/l at 20 °C (pH 10)<br>144 mg/l at 20 °C (pH 7.7-7.9) | Roholm (1937)<br>Sjöberg (2002) [2)]<br>Sjöberg (2002) [2)]<br>Sjöberg (2002) [2)]<br>Sjöberg (2002) [2)]<br>IWL (1998) [2)]; after 24 h stirring; test medium of *Daphnia* ecotoxicity test (see section 3.2.1.1.2) |
| VII, 7.8 | Partition coefficient n-octanol/water (log value) | 3.7 partition coefficient | not applicable (inorganic complex salt) | |
| VII, 7.9 | Flash point | 3.11 | not conducted (solid) | |
| VII, 7.10 | Flammability | 3.13 | not determined (inorganic complex salt) | |
| VII, 7.11 | Explosive properties | 3.14 | not determined (inorganic complex salt) | |
| VII, 7.12 | Self-ignition temperature | | | |
| VII, 7.13 | Oxidising properties | 3.15 | not determined (inorganic complex salt) | |
| VII, 7.14 | Granulometry | 3.5 | | |
| XI, 7.15 | Stability in organic solvents and identity of relevant degradation products | 3.17 | | |
| XI, 7.16 | Dissociation constant | 3.21 | | |
| XI, 7.17, | Viscosity | 3.22 | | |

| | | | | |
|---|---|---|---|---|
| | Auto flammability | 3.12 | not determined (inorganic complex salt) | |
| | Reactivity towards container material | 3.18 | | |
| | Thermal stability | 3.19 | | |

1) Sjöberg calculated in his report the water solubility of cryolite as a function of the pH. The solubility is approximately constant in the pH range 4 – 7 and results to 4.5 mMol. This value based on cryolite forming about 25 % $AlF_3$, 55 % $AlF_4^-$ and 19 % $AlF_5^{2-}$ in water. In the acidic range the solubility increases due to the extensive formation of HF. With pH > 7.5 the solubility decreases due to the formation of $Al(OH)_3$. It is noted, that water solubility as calculated by Sjöberg is a theoretical maximum solubility. In figure 1.1 the predominance area diagram of the speciation as a function of pH and the free fluoride concentration as $\log[F^-]$ is visualised in an aquatic solution containing F and Al.

2) Water solubility is not specified for natural or synthetic cryolite.

## 1.3.2 Physico-chemical properties for synthetic cryolite

| **REACH ref Annex, §** | **Property** | **IUCLID section** | **Value** | **[enter comment/reference or delete column]** |
|---|---|---|---|---|
| VII, 7.1 | Physical state at 20°C and 101.3 KPa | 3.1 | white crystalline solid | |
| VII, 7.2 | Melting/freezing point | 3.2 | 1027 °C | Solvay (1997) 1) |
| VII, 7.3 | Boiling point | 3.3 | no information available | |
| VII, 7.4 | Relative density | 3.4 density | 2.95 at 20 °C | Solvay (1997) |
| VII, 7.5 | Vapour pressure | 3.6 | 2.5 mbar (= 250 Pa) at 1027 °C | Solvay (1997) |
| VII, 7.6 | Surface tension | 3.10 | not determined (inorganic complex salt) | |
| VII, 7.7 | Water solubility | 3.8 | 0.41 g/l at 25 °C (pH unknown)<br>0.9 g/l at 20 °C (pH 4 – 7) 1 in table 1.1<br>See table 1.1 for other values | Rethmann (1996)<br>Sjöberg (2002) |
| VII, 7.8 | Partition coefficient n-octanol/water (log value) | 3.7 partition coefficient | not applicable (inorganic complex salt) | |
| VII, 7.9 | Flash point | 3.11 | not conducted (solid) | |
| VII, 7.10 | Flammability | 3.13 | not determined (inorganic complex salt) | |
| VII, 7.11 | Explosive properties | 3.14 | not determined (inorganic complex salt) | |
| VII, 7.12 | Self-ignition temperature | | | |
| VII, 7.13 | Oxidising properties | 3.15 | not determined (inorganic complex salt) | |
| VII, 7.14 | Granulometry | 3.5 | | |
| XI, 7.15 | Stability in organic solvents and identity of relevant degradation products | 3.17 | | |
| XI, 7.16 | Dissociation constant | 3.21 | | |
| XI, 7.17, | Viscosity | 3.22 | 6.7 mPa.s | Solvay (1997) |
| | Auto flammability | 3.12 | not determined (inorganic complex salt) | |
| | Reactivity towards container material | 3.18 | | |
| | Thermal stability | 3.19 | | |

1) For the melting point, relative density and vapour pressure only data of a safety data sheet are available. In comparison with the data for natural cryolite and under consideration of the purity these values are acceptable.

**Table 2.2: Summary of physico- chemical properties**

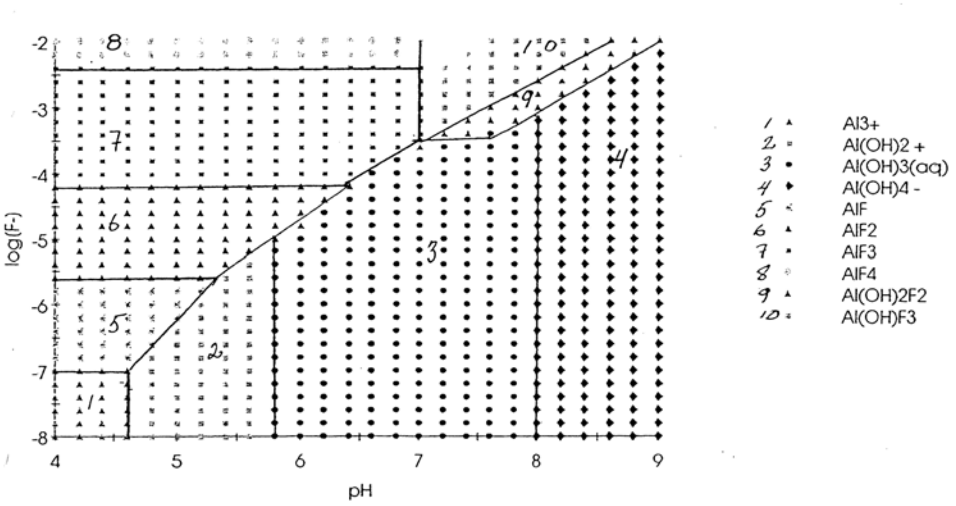

**Figure 1: Predominance area diagram of the Al3+-F-.OH- system (Sjöberg, 2002)**

# 2 MANUFACTURE AND USES

See Risk Assessment Report

# 3 CLASSIFICATION AND LABELLING

## 3.1 Classification in Annex I of Directive 67/548/EEC

*This should include the classification (including specific concentration limits) listed in Annex I of Directive 67/548/EEC (including the Index Number)*

### 3.1.1 Current classification

Classification according to Annex I of Directive 67/548/EEC:

T Toxic

| | |
|---|---|
| R48/23/25 | Toxic: danger of serious damage to health by prolonged exposure through inhalation and if swallowed |

Xn Harmful

| | |
|---|---|
| R20/22 | Harmful by inhalation and if swallowed |

N Dangerous for the environment

| | |
|---|---|
| R51-53 | Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment |

### 3.1.2 Proposed classification

T Toxic

| | |
|---|---|
| R48/23/25 | Toxic: danger of serious damage to health by prolonged exposure through inhalation and if swallowed |

On the basis of the data submitted, the current classification of cryolite is confirmed. The corroboration for classification is based on the hazard identification determined by the selected inhalation studies (90-day study and 5-months study, both in rats) according to the lowest concentration causing serious health effects. The toxic profile of cryolite is dominated by its systemic toxicity. The critical adverse effects for serious damage to health after prolonged inhalation or the oral route of exposure are distinct toxic effects on the bones and teeth. In a 5-month inhalation study with rats toxic effects on the bones and teeth were observed at ≥ 1 $mg/m^3$ cryolite (6h/d, 6d/week, whole body exposure (Plotko et al., 1973)). Local effect in rats after subchronic inhalation of predominantly respirable cryolite dust was lung toxicity seen as interstitial pneumonia at a low concentration of 1.04 $mg/m^3$ (0.001 mg/l) cryolite (90-day inhalation study, 6h/d, 5d/week (BG Chemie, unpublished report, 1997)).

These identified concentrations are far below the cut-off value for attributing R48/20 (0.25 mg/l) in a 90-day inhalation study. The observed critical effect levels presented in experimental animals are comparable in magnitude to the effect dose concentrations described in man occupationally exposed to cryolite dust. In male pot room workers employed in aluminium plants skeletal fluorosis was observed at average fluoride concentrations of 2.4 to 6.0 mg/m$^3$ (on average 8h/d, with 36-50 % content gaseous fluoride) (Kaltreiter et al., 1972). In humans skeletal fluorosis was observed at 6 mg/m$^3$ and increased bone density was noted in workers of a phosphate fertilizer manufacturing plant exposed to concentrations of about 3.38 mg/m$^3$ fluorides in the form of dusts and gases over a period ranging from 4.5 to 29.9 years with an average of 14.1 years (Derryberry et al., 1963). In a more recent study skeletal changes were determined in workers employed at an aluminium plant in Poland exposed to hydrogen fluoride concentrations of 0.5 mg/m$^3$ (Czerwinski et al., 1988).

The critical effect following repeated dietary exposure to cryolite in experimental animals was fluoride accumulation and the appearance of its consequence: non-neoplastic bone disease - skeletal fluorosis - was observed in rats (males/females) from the lowest dose tested of 3.8/4.5 mg/kg bw/d and in dogs from 17 mg/kg bw/d upward, respectively (90-day studies, EPA 1996). Toxic effects on the bones and teeth were also reported in early repeated dose toxicity studies in rats. Findings on the teeth were noted at 1 mg/kg bw/d, and development of abnormally structured osseous tissue and renal effects at 5 mg/kg bw/d (Roholm, 1937a,b). These identified dose levels are far below the cut-off value for attributing R48/22 (50 mg/kg bw/d) in a 90-day study. Comparable effect dose levels were also described in man. In occupationally exposed workers 20-80 mg of fluoride per day caused skeletal effects (Roholm, 1937 a,b). Long-term intake of fluoride in water and foodstuffs is the primary causative factor for endemic skeletal fluorosis in humans. Very high intakes have been observed in areas world-wide in which the environment is rich in fluoride and where humans consume groundwater containing high concentrations of fluoride. There is clear evidence from India and China that significant skeletal effects are seen at a total intake of 14 mg fluoride/day, equivalent to about 0.2 mg/kg bw/d calculated on a assumed body weight of 70 kg person (WHO 2002).

Thus, classification and labelling with T, Toxic, R48/23/25 (Toxic: danger of serious damage to health by prolonged exposure through inhalation and if swallowed) is confirmed.

Xn Harmful

R20 Harmful by inhalation

After inhalation of cryolite an acute $LC_{50}$ of 4470 µg/l was estimated in rats (4-h exposure). Therefore, a classification as harmful and labelling with R20 is appropriate.

Based on the results of available tests on acute oral toxicity, cryolite shows no relevant acute oral toxicity with LD50 values for rats > 5000 mg/kg bw. Therefore, labelling with R22 is not appropriate.

Xi Irritating

R36 Irritating to eyes

Scarce data on eye irritation indicate a moderate potential of cryolite to induce eye irritation, but due to a low quality of available data, a final assessment is not possible. In order to avoid additional animal testing, a precautionary classification with R36 is proposed.

Xn; Repr.Cat.3; R63 Possible risks of harms to the unborn child

On the basis of the data submitted (two-generation reproduction toxicity study with rats) cryolite needs to be classified and labelled as a reproductive toxicant. The critical adverse effects that had been revealed were impairment of postnatal growth evidenced by significantly decreased pup body weights during lactation as well as gross pathological changes in several organs (kidney, liver, heart) of the pups resulting from dose levels without any significant systemic toxicity.

Cryolite is at the present included in Annex I of Directive 67/548/EEC with a classification N; R51-53 for the environment.

The present classification is according to ECB (ECB/61/95-Add 22) based on a $LC_{50}$(98h) of 47.0 mg/l for rainbow trout (Johnson and Finley, 1980), EC50(48h) of 5 mg/l for *Daphnia pulex* (Sanders and Cope, 1966) and NOEC(96h) of > 5000 mg/l for algae (Bayer AG data; as cited in ECB/61/95-Add 22). First two of these values have been assigned by the Rapporteur a reliability grade of 4 (not assignable; see section 3.2) and for the third value no documentation at all has been available to the Rapporteur.

Reliable acute ecotoxicity test results are available for algae ($EC_{\mu 50}$ = 8.8 mg $l^{-1}$)(Solvay Pharmaceuticals, 2008b), invertebrates ($EC_{50}$ = 156 mg $l^{-1}$)(IWL, 1998) and fish ($LC_{50}$ > 100 mg $l^{-1}$) (Solvay Pharmaceuticals, 2008a). Due to the sensitivity of algae, the present classification R51/53 is confirmed.

### 3.2 Self classification(s)

*This should include the classification, the labelling and the specific concentrations limits. The reason and justification for no classification should be reported here.*

*It should be stated whether the classification is made according to Directive 67/548/EEC criteria or according to GHS criteria.*

## 4 ENVIRONMENTAL FATE PROPERTIES

See Risk Assessment Report Draft of November 2008.

## 5 HUMAN HEALTH HAZARD ASSESSMENT

See Risk Assessment Report Draft of November 2008.

## 6 HUMAN HEALTH HAZARD ASSESSMENT OF PHYSICO-CHEMICAL PROPERTIES

See Risk Assessment Report Draft of November 2008.

# 7 ENVIRONMENTAL HAZARD ASSESSMENT

# 8 PBT AND VPVB ASSESSMENT

# 9 EXPOSURE ASSESSMENT

# 10 RISK CHARACTERISATION

# INFORMATION ON ALTERNATIVES

## 11 INFORMATION ON THE RISKS TO HUMAN HEALTH AND THE ENVIRONMENT RELATED TO THE MANUFACTURE OF USE OF THE ALTERNATIVES

## 12 AVAILABILITY OF ALTERNATIVE, INCLUDING THE TIME SCALE

## 13 TECHNICAL AND ECONOMICAL FEASIBILITY

# JUSTIFICATION FOR RESTRICTION AT COMMUNITY LEVEL

## 14 JUSTIFICATION THAT ACTION IS REQUIRED ON THE COMMUNITY-WIDE BASIS

None

Other measures see Risk Reduction Strategy.

## 15 JUSTIFICATION FOR THE PROPOSES RESTRICTION

### 15.1 Effectiveness

### 15.2 Practicality

### 15.3 Monitorability

# SOCIO ECONOMIC ASSESSMENT

# OTHER INFORMATION

*It is suggested to include here information on any consultation which took place during the development of the dossier. This could indicate who was consulted and by what means, what comments (if any) were received and how these were dealt with. The data sources (e.g registration dossiers, other published sources) used for the dossier could also be indicated here.*

# REFERENCES

See Risk Assessment Report.

## ANNEX

Risk Assessment Report

Risk Reduction Strategy