PRTR Estimation Manual

02. Light Metal Products Industry

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- 1. How to Calculate PRTR for Aluminum Surface Treatment Plant
- 1.1 Schematic Process Representation of Aluminum Surface Treatment Plant and Designated Chemical Substances

In order to calculate PRTR, schematic process representation of aluminum surface treatment plant must first be prepared and the Class I Designated Chemical Substances (hereinafter referred as Designated Chemical Substances) and their amounts handled be identified.

Schematic process representation of aluminum surface treatment plant and examples of the Designated Chemical Substances are presented below.

1.1.1 Schematic Representation of Surface Treatment Process for Plant Producing Aluminum Construction Materials



Figure 1 Schematic Representation of Surface Treatment Process for Plant Producing Aluminum Construction Materials

<Examples of chemical substances used in respective steps of this process>

alkalescent washing agent and sodium hydroxide, sodium gluconate sulfuric acid or nitric acid

sulfuric acid or organic acid (sulfonic acids)

- (a) nickel sulfate, boric acid and the like
- (b) Tin(I) sulfate, cresol sulfonicacid and the like
- (c) cupper sulfate, magnesium sulfate and the like
- (d) silver nitrate, magnesium sulfate and the like

solvents such as toluene, xylene, trichloroethylene, dicloromethane and the like

water soluble acrylic coating materials nickel acetate and the like

1.1.2 Schematic Representation of Surface Treatment Process for Plant Producing Aluminum Commodities



Figure 2 Schematic Representation of Surface Treatment Process for Plant Producing Aluminum Commodities

<Examples of chemical substances used in respective steps of this process> alkalescent washing agent and trichloroethylene degreasing fluoric acid, acidic ammonium fluoride or sodium hydroxide nitric acid or sulfuric acid sulfuric acid or oxalic acid nitric acid organic or inorganic dye nickel acetate and the like 1.1.3 Schematic Representation of Surface Treatment Process for Plant Producing Aluminum Decoratives



Figure 3 Schematic Representation of Surface Treatment Process for Plant Producing Aluminum Decoratives

<Examples of chemical substances used in respective steps of this process>

sodium hydroxide

nitric acid and the like

phosphoric acid

fluoric acid, acidic ammonium fluoride and the like

nitric acid

sulfuric acid

nitric acid

organic or inorganic dye

nickel acetate and the like

1.2 Class I Designated Chemical Substances Used in Surface Treatment Process of Aluminum

1.2.1 Class I Designated Chemical Substances

Table 1 shows Class I Designated Chemical Substances (herein after referred as Designated Chemical Substances) generally used in surface treatment process of aluminum.

Cabinet			Specific Class I Designated
Order	CAS No.	Name of substance	Chemical Substances
No.			(Carcinogenic Substances ×)
63	1330-20-7	Xylene	-
68	-	Chromium and trivalent chromates	-
69	-	Hexavalent chromates	×
145	75-09-2	Dichloromethane (also called methylene chloride)	-
207	-	Water-soluble copper salts (excluding complex salts)	-
211	79-01-6	Trichloroethylene	-
227	108-88-3	Toluene	-
231	7440-02-0	Nickel	-
232	-	Nickel compound	×
253	302-01-2	Hydrazine	-
272	117-81-7	Bis(2-ethylhexyl) phthalate	-
283	-	Hydrogen fluoride and its water-soluble salts	-
304	-	Boron and its compounds	-
311	-	Manganese and its compounds	-

 Table 1
 Designated Chemical Substances Used in Surface Treatment Process

1.2.2 Conversion Factor for Converting from Compound to Element

As for the compounds of chromium, copper, nickel, fluorine, boron and manganese in the above table, they need to be converted to respective element weight in order to estimate the amounts handled, released, transferred and shipped. Conversion factors for obtaining the element weight from the compound are shown in Table 2.

Number specified in Cabinet Order	Name of specified substance	CAS No.	Example of individual substance	Composition formula	Molecular weight	Total of atomic weights of metals and the like(M)	Conversion coefficient (M/molecula r weight)	Not applicable (×)	Reason why it is not applicable (water solubility or the like)	Other specified substance
68	Chromium and chromium (III)	7440-47-3	Chromium	Cr	52	52	1			
	compunds	1308-38-9	Chromium oxide (III)	Cr ₂ O ₃	152	104	0.684			
		64093-79-4	Chromium subsulfate (III)	Cr(OH)(SO₄)	165.1	52	0.315			
69	Chromium (IV) compuonds	13530-65-9	Zinc chromate	ZnCrO₄	181.4	52	0.287			Out of object as zinc since this is not wate-soluble
		7789-00-6	Potassium chromate	K₂CrO₄	194.2	52	0.268			
		13765-19-0	Calcium chromate (2 hydrate)	CaCrO₄•2H₂O	192.1	52	0.271			
		7789-06-2	Strontium chromate	SrCrO₄	203.6	52	0.255			
		7758-97-6	Lead chromate	PbCrO₄	323.2	52	0.161			Object as lead
		10294-40-3	Barium chromate	BaCrO₄	253.3	52	0.205			Out of object as barium since this is not wate- soluble
		1333-82-0	Chromium trioxide	CrO ₃	100	52	0.52			
		7778-50-9	Potassium dichromate	K ₂ Cr ₂ O ₇	294.3	104	0.353			
		7789-12-0	Sodium dichromate . (2 hydrate)	Na ₂ Cr ₂ O ₇ • 2H ₂ O	298	104	0.349			
207	Copper salts (water-soluble,	7447-39-4	Copper chloride (II) (anhydride)	CuCl ₂	134.5	63.5	0.473			
	except complex salts)	13933-17-0	Copper chloride (II) (2 hydrate)	CuCl ₂ • 2H ₂ O	170.5	63.5	0.373			
		38465-60-0	Copper fluoborate (II)	Cu(BF₄)₂	237.2	63.5	0.268			Object as boron. Out of object as hydrogen fluoride salts since this is not wate-soluble
		7758-98-7	Copper sulfate (II) (anhydride)	CuSO₄	159.6	63.5	0.398			
		7758-99-8	Copper sulfate (II) (5 hydrate)	CuSO₄∙5H₂O	249.7	63.5	0.255			
		544-92-3	Copper cyanide (I)	CuCN	89.6	63.5	0.709	×	2.6×10 ⁻³ g/L (18)	Object as inorganic scyanides
		12069-69-1	Copper carbonate hydroxide	Cu ₂ (OH) ₂ CO ₃	221.1	127.1	0.575	×	Insoluble	
		1111-67-7	Copper thiocyanate (I)	CuSCN	121.6	63.5	0.522	×	4.4×10 ⁻³ g/L (18)	
		10380-28-6	Oxine copper	C ₁₈ H ₁₂ CuN ₂ O ₂	351.9	-	1	×	insoluble	Object as oxine copper(class 1: 246)

 Table2
 Conversion factors for obtaining the element weight from the compound weight

Number specified in Cabinet Order	Name of specified substance	CAS No.	Example of individual substance	Composition formula	Molecular weight	Total of atomic weights of metals and the like(M)	Conversion coefficient (M/molecula r weight)	Not applicable (×)	Reason why it is not applicable (water solubility or the like)	Other specified substance
232	Nickel compounds	6018-89-9	Nickel acetate (4 hydrate)	Ni(CH ₃ COO) ₂ • 4H ₂ O	248.9	58.7	0.236			
		1313-99-1	Nickel (II) oxide	NiO	74.7	58.7	0.786			
		1314-06-3	Nickel (III) oxide	Ni ₂ O ₃	165.4	117.4	0.71			
		13138-45-9	Nickel nitrate (II) (anhydride)	Ni(NO ₃) ₂	182.7	58.7	0.321			
		13478-00-7	Nickel nitrate (II) (6 hydrate)	Ni(NO ₃) ₂ • 6H ₂ O	290.8	58.7	0.202			
		3333-67-3	Nickel carbonate (II) (anhydride)	NiCO ₃	118.7	58.7	0.494			
		101-97-0	Nickel sulfate (II) (6 hydrate)	NiSO₄• 6H₂O	262.5	58.7	0.223			
		10101-98-1	Nickel sulfate (II) (7 hydrate)	NiSO₄• 7H₂O	280.9	58.7	0.209			
		10381-36-9	Nickel phosphate (II)	Ni ₃ (PO ₄) ₂	366.1	176.1	0.481			
283	Hydorogen fluoride and its water-	7664-39-3	Hydrogen fluoride	HF	20	19	0.95			
	soluble saits	7783-82-6	Tungsten hexafluoride	WF ₆	297.8	114	0.383			
		12125-01-8	Ammonium fluoride	NH₄F	37	19	0.513			
		7681-49-4	Sodium fluoride	NaF	42	19	0.452			
		7787-49-7	Beryllium fluoride	BeF ₂	47	38	0.808			Subject as beryllium
		16961-83-4	Silicofluoric acid	H ₂ SiF ₆	144.1	114	0.791	×	Not salt of hydrogen fluoride	
		16893-85-9	Sodium silicofluoride	Na ₂ SiF ₆	188.1	114	0.606	×		
		7783-54-2	Nitrogen trifluoride	NF ₃	71	57	0.803	×		
		7637-07-2	Boron trifluoride	BF ₃	67.8	57	0.841	×	Not salt of hydrogen fluoride	Subject as boron
		7784-18-1	Aluminum fluoride	AIF3	84	57	0.679	×	0.559g in 100mL	
		7787-32-8	Barium fluoride	BaF ₂	175.3	38	0.217	×	1.614g/L(25)	Out of subject as barium since this is not water- soluble.
		7782-41-4	Fluorine	F ₂	38	38	1	×	Not salt of hydrogen fluoride	

Number specified in Cabinet Order	Name of specified substance	CAS No.	Example of individual substance	Composition formula	Molecular weight	Total of atomic weights of metals and the like(M)	Conversion coefficient (M/molecula r weight)	Not applicable (×)	Reason why it is not applicable (water solubility or the like)	Other specified substance
		14075-53-7	Potassium fluoborate	KBF₄	125.9	76	0.604	×	Not salt of hydrogen fluoride	Subject as boron
		16872-11-0	Fluoboric acid	HBF₄	87.8	76	0.865	×		
		13814-97-6	Tin fluoborate (II)	Sn(BF ₄) ₂	292.3	152	0.52	×		
		38465-60-0	Copper fluoborate (II)	Cu(BF ₄) ₂	237.2	152	0.641	×	Not salt of hydrogen fluoride	Subject as boron and copper
		13755-29-8	Sodium fluoborate	NaBF₄	109.8	76	0.692	×	Not salt of hydrogen fluoride	Subject as boron
		-	Sodium fluoborate	NaFO ₃	90	19	0.211	×	Not salt of hydrogen fluoride	
		2551-62-4	Sulfur hexafluoride	SF ₆	146.1	114	0.78	×		
304	Boron and its compounds	7440-42-8	Boron	В	10.8	10.8	1			
		1303-86-2	Boric oxide	B₂O₃	69.6	21.6	0.311			
		7637-07-2	Boron trifluoride	BF ₃	67.8	10.8	0.159			Out of subject as hydrogen fluoride salts since this is not salt of hydrogen fluoride
		10043-35-3	Boric acid	H₃BO₃	61.8	10.8	0.175			
		7632-04-4	Sodium perborate	NaBO ₃	81.8	10.8	0.132			
		10332-33-9	Sodium perborate (1 hydrate)	NaBO₃• H₂O	99.8	10.8	0.108			
		10486-00-7	Sodium perborate (4 hydrate)	NaBO₃• 4H₂O	153.9	10.8	0.07			
		12007-89-5	Ammonium pentaborate	NH₄B₅O ₈	200.1	54.1	0.27			
		1330-43-4	Sodium tetraborate	Na ₂ B ₄ O ₇	201.2	43.2	0.215			
		1303-96-4	Sodium tetraborate (10 hydrate)	Na ₂ B ₄ O ₇ · 10H ₂ O	381.2	43.2	0.113			

Number specified in Cabinet Order	Name of specified substance	CAS No.	Example of individual substance	Composition formula	Molecular weight	Total of atomic weights of metals and the like(M)	Conversion coefficient (M/molecula r weight)	Not applecable (×)	Reason why it is not applicable (water solubility or the like)	Other specified substance
		14075-53-7	Potassium fluoborate	KBF₄	125.9	10.8	0.086			Out of subject as hydrogen fluoride salts since this is not salt of hydrogen fluoride
		16872-11-0	Fluoborate acid	HBF₄	87.8	10.8	0.123			
		13814-97-6	Tin fluoborate (II)	Sn(BF ₄) ₂	292.3	21.6	0.074			
		38465-60-0	Copper fluoborate (II)	Cu(BF ₄) ₂	237.2	21.6	0.091			
		13755-29-8	Sodium fluoborate	NaBF₄	109.8	10.8	0.098			
311	Manganse and its compounds	7439-96-5	Manganse	Mn	54.9	54.9	1			
		13446-34-9	Manganous chloride (II) (4 hydrate)	MnCl ₂ •4H ₂ O	197.9	54.9	0.278			
		7722-64-7	Potassium permanganate	KMnO₄	158	54.9	0.348			
		638-38-0	Manganse (II) acetate	Mn(CH₃COO)₂	173	54.9	0.318			
		6156-78-1	Manganse (II) acetate (4 hydrate)	Mn(CH ₃ COO) ₂ •4H ₂ O	245.1	54.9	0.224			
		1313-13-9	Manganse dioxide	MnO ₂	86.9	54.9	0.632			
		10377-66-9	Manganse nitrate (II)	Mn(NO ₃) ₂	178.9	54.9	0.307			
		598-62-9	Manganse carbonate (II)	MnCO ₃	114.9	54.9	0.478			
		10034-99-8	Manganse sulfate (II) (7 hydrate)	MnSO₄•7H₂O	277.1	54.9	0.198			
		10124-54-6	Manganse phosphate	MnxPO ₄ (Calculated as Mn ₃ (PO ₄) ₂)	354.8	164.8	0.465			

- 2. Estimation Method of PRTR Amounts for Aluminum Surface Treatment Plant
- 2.1 Primary substances Handled and their Release Points in Aluminum Surface Treatment Process
- 2.1.1 Primary substances Handled and their Release Points in Alumite and Mixed Coating Treatment Processes
- 1) Identify Designated Chemical Substances and their Release Points by means of process flow sheets

As for the primary substances and their release points in alumite treatment process, construct the detailed flow sheets of the treatment process such as shown in Figures 5 to 6 and identify the Designated Chemical Substances and their release points

2) Specify the Release Points

Specify the release points according to the flow sheet of the treatment process, as shown in Figure 4.



Figure 4 Schematic Diagram of Release Points (alumite and mixed coating treatment processes)



Figure 5: Example of Designated Chemical Substances and Release Points in the process flow sheet of almite and mixed coating treatment line



Figure 6: Example of Designated Chemical Substances and Release Points in the process flow sheet of decorative alumite line

Estimation Procedure 1: for Alumite and Mixed Coating Treatment Processes Wherein Nickel etc. are Involved



- Note: 1) The Manual prepared by the government office suggests firstly to estimate "the maximum possible amount released to the environment". Instead, however, this manual has chosen to estimate the actual amounts rather than the maximum possible amounts, and the maximum possible amount released was not estimated.
- Note 2) Sludge A is the by-product, aluminum hydroxide.

Estimation Procedure 2: for Alumite and Mixed Coating Treatment Processes Wherein Boron etc. are Involved



2.2 Primary substances Handled and their Release Points in Coating Process

2.2.1 Identify Released Substances and their Release Points by means of Flow Sheet of Coating-Surface Preparation Treatment Process

As for the primary substances handled and their release points in coating-surface preparation treatment process, construct the detailed flow sheets of the treatment process as shown in Figure 8 and identify the designated chemical substances and their release points.

2.2.2 Specify the Release Points

Specify the release points according to the flow sheet of the treatment process, as shown in Figure 7.



Figure 7 Schematic Diagram of Release Points (coating-surface preparation treatment process)



Figure 8: Example of Designated Chemical Substances and their release points in the flow sheet of chromate-coating treatment line in coating-surface preparation treatment process

Estimation Procedure 3: for Coating-surface Preparation Treatment Process Wherein Chromium Recovered Completely and None Released to Water Bodies



*: In case sold to regeneration dealer as valuables, no notification is required.

2.2.3 Identify Designated Chemical Substances and their Release Points according to the Coating Process Flow Sheet

As for the primary substances handled and their release points in coating process, construct the detailed flow sheets of the process as shown in Figure 9 and identify the designated chemical substances and their release points.

2.2.4 Schematic Representation of Release Points for Coating Process

Specify the release points according to the flow sheet of the treatment process, as $\frac{1}{2}$



Figure 9 Schematic Diagram of Release Points (coating process)



Figure 10 Examples of the designated chemical substances and their emission points as seen in process flow sheet of coating of aluminum

Estimation Procedure 4: for Coating Process Wherein Toluene, Xylene, etc. are Involved



2.3 Examples of Estimating Released and Transferred Amounts of Designated Substances in Aluminum Surface Treatment Process

2.3.1 Fundamental Items on Estimation Methods of Amounts Released and Transferred

(1) Regarding how to figure out annual handled amounts of designated chemical substances

In estimating the amounts released and transferred, the calculation method of the annual handled amount of the designated chemical substances may differ from plant to plant, and it should be recognized that the method that can calculate it most accurately must be adopted.

Therefore, it is important for each plant to keep the record and accurately calculate the amounts of the annual amount purchased, the inventory amount at year end, the inventory amount at year beginning, and the amount used.

(2) Regarding how to estimate amounts released and transferred

Although the amount released to air, water body, soil, etc. as well as the amount transferred can be estimated from the amount handled and from the routine measurements of the concentrations, it can also be determined by taking material balance.

In aluminum surface treatment plants, the emission to the environment such as air, water body, soil etc., and the transfer while contained in the wastes are envisaged. The amount released to environment and the amount transferred can be calculated by the following methods.

Amount released to water body

Amount released to water body can be estimated from analysis result of the concentration in discharged water \times discharged amount, and also by taking a material balance (Note 3).

Note 3: Calculations are made based on the values from the water meters and telemeters, and if such measuring instruments are not in place, calculations can be made by using the values from city-water meters and industrial-water meters.

Amount released to air

Amount released to air can be estimated from analysis results of concentration of the designated substances \times exhausted gas volume, and also by taking a material balance (Note 4).

Note 4: This can be determined by calculating exhausted gas volume from the projected values contained in the facility notification, or from the amount of fuel used, and multiplying it by the value of concentration analysis result of the designated chemical substances in the exhaust gas.

Amount released to soil

Amount released to soil can be estimated from analysis result of concentration in the release \times amount released, and also by taking a material balance, similarly to the amount released to water body. However, at present, it is considered none. Amount shipped as product

The term "amount shipped" is defined as the amount taken out of plant while contained in or accompanying with the product, and for the case of aluminum surface treatment plants it is often difficult to estimate the amount shipped as product and therefore it is suggested to estimate it by taking a material balance as described below (Note 5).

Note 5: Among the alumite and mixed-coating treated products, those to which electro deposition was applied contain nickel compounds in the alumite coating film, which are specific class I designated chemical substance (carcinogenic substance), and they are brought out of plants as product. Their amounts, however, differ depending on the color tone, coating thickness and the like, and if an analysis on the amount of nickel deposited is tried, the variation will be too great to make accurate estimation from the actual products. Thus it is suggested to make the estimation by taking a material balance, which comprise first estimating the amount of the others released and transferred which can actually be estimated, and then subtracting it from the total. Amount removed by decomposition removal process

This is the case where the designated substances are removed by a method such as decomposition process, and the amount can be estimated using a decomposition removal efficiency and the like.

Transferred amount while contained in wastes

For alumite processes, it is suggested to perform the estimation by the formula :

analysis result of concentration of the designated chemical substances in a luminum sludge \times amount of a luminum sludge.

Amount recycled

For cases where they are removed by a recovery process and the like and reused as the raw material or the material source, the estimation can be made using the formula:

amount recycled (kg/year) = amount handed over to recycle dealer (kg/year) \times content in the solution (%).

2.3.2 Estimation Examples in Alumite and Mixed-coating Treatments

- Example of Calculating Nickel From Nickel Compound (e.g., Nickel Sulfate and Nickel Acetate) in Processes of Electro-deposition and Cavity-Seal Treatment (Hereinafter, values are hypothetical)
 - (1) Calculate the amount of nickel handled for the nickel sulfate hexa-hydrate $(NiSO_4-6H_2O)$ used in electro-deposition process from sources such as monthly records on use (Note 6).

 $50,000(kg/year) \times 0.223(conversion factor)$

= 11,150(kg/year) (A)

Note 6: A conversion factor for converting nickel sulfate hexa-hydrate to element nickel (atomic weight of Ni / formula weight of NiSO₄- $6H_2O$) is to be used

(2) Calculate the amount of nickel handled for the nickel acetate $(Ni[CH_3COO]_2-4H_2O)$ used in cavity-seal treatment process from sources such as monthly records (Note 7).

 $7,000(kg/year) \times 0.24(Content in cavity sealant: 24\%)$

 $\times 0.236$ (conversion factor)

= 396(kg/year) (B)

Note 7: Nickel acetate content in the cavity sealant, and the conversion factor are to be used.

(3) Calculate the total amount of nickel handled.

Total amount of nickel handled = (A) + (B) = 11,150 + 396= 11,546(kg/year) (C)

(4) According to "Calculation Manual" prepared by the government office, "maximum potential amount released to the environment" is to be calculated here.

Maximum potential releases

= amount handled - {transfers + amount shipped as product}

However, it is extremely difficult to calculate the amount of nickel shipped as product, in the alumite treatment process.

Therefore this manual does not use the concept of maximum potential releases.

(Nor the maximum potential releases are calculated for other calculation examples either, as they are not needed in the calculation.)

(5) Calculate the transferred amount being contained in waste (amount handed over).

Nickel will co-precipitate during the treatment of discharged water and will be included in the precipitate which is aluminum hydroxide (aluminum sludge). This amount will be the amount transferred being contained in waste.

Nickel concentration in B sludge: 3(g/kg; analyzed value of content in dry sludge)

(a) B sludge				
To Company A:	1,500,000			
To Company B:	250,000			
To Controlled disposal:	50,000			
Total:	1,800,000(kg/year)	-	water	content:
75%				

(b) Conversion to solid content:

 $1,800,000(\text{kg/year}) \times (1 - 0.75)$ (Note 8) = 450,000(kg/year)

Note 8: It is necessary to take the water content into consideration in the calculation.

(So applies to the rest entirely.)

(c) Nickel contained in B sludge = $450,000(kg/year) \times 3(g/kg)$

= 1,350(kg/year) (D)

Other sludge / To Company C: 360,000(kg/year) / water content: 80%

(a) Conversion to solid:

 $360,000(kg/year) \times (1 - 0.80) = 72,000(kg/year)$

(b) Nickel contained in it = $72,000(kg/year) \times 3(g/kg)$

= 216(kg/year) (E)

Total transfers being contained in waste

= transfers being contained in B sludge (D)

- + transfers being contained in other sludge (E)
- = 1,350 + 216
- = 1,566(kg/year) (F)

(6) Calculate the amount released (releases) to air as follows:

The release to air can be estimated by first analyzing the concentrations at outlets and then using the concentrations as shown below:

In case where there is no measurements made on your facilities, use the average concentration of nickel sulfate of 10 member companies (an actual value measured during the voluntary management of toxic air pollutant in 1999) and the calculation can be made based on the exhaust gas volumes of your facilities.

Average of 10 companies: $1.49(\mu g/m^3)$

Exhaust gas volume: $100(m^3/minute)$; operating condition: 300 days / year and 24 hours / day

Amount of nickel sulfate released to air

 $= 0.00149(\text{mg/m}^3) \times 100(\text{m}^3/\text{minute}) \times 60(\text{minutes}) \times 24(\text{hours})$

 \times 300(days/year)

= 0.064(kg/year)

Since the above released value is the amount as nickel sulfate, convert to an amount as element nickel.

Amount released to air as element nickel:

 $= 0.064(kg/year) \times 0.223(conversion factor)$

= 0.014(kg/year)

Values like this, in general (unless there is any special circumstance in which high concentrations of nickel are being released), lead to a judgment that the amount released to air can be regarded as zero as it being less than the unit base value. (0.1)

Amount released to air = 0 (G)

(7) Calculate releases to water bodies as follows:

Since all of the wastewater in alumite treatment process are gathered, and they undergo treatments of neutralization, coagulation, and precipitation, and then are discharged, it is necessary to analyze its concentration at the discharge outlets about once a month to identify the average concentration. Conditions assumed

Average of nickel concentration analyzed = 3(mg/l)

Total amount of wastewater = $3,000(m^3/day)$

Operating days = $30(\text{days/month}) \times 12(\text{months/year})$

Estimate the amount of nickel released in wastewater

Amount of nickel released in wastewater

 $= 3(mg/l) \times 3,000(m^{3}/day) \times 30(days/month) \times 12(months/year)$

= 3,240(kg/year) (H)

(8) Estimate the amount shipped as product as follows by taking mass balance (Note 10):

The amount shipped as products

= amount of nickel handled (C) - {transfers being contained in waste (F)

+ releases to air (G) + releases to water bodies (H)}

$$= 11,546(kg/year) - \{1,566(kg/year) + 0(kg/year) + 3,240(kg/year)\}$$

= 6,740(kg/year) (I)

Note 10: The method like this is known as a method by taking material balance.

(9) Confirm if the total amount released, transferred and shipped corresponds to the amount of nickel handled (C).

Total amount

= releases to air (G) + releases to water bodies (H)

- + transfers being contained in waste (F) + amount shipped as product (I)
- = 0(kg/year) + 3,240(kg/year) + 1,566(kg/year) + 6,740(kg/year)

= 11,546(kg/year)

As seen, this value agrees with the previously calculated value of the amount handled (C).

As shown above, the amount of nickel released to water bodies, transferred being contained in wastes, and shipped as product can be determined.

(10)For the purpose of reference now, the amounts released, transferred, and shipped that resulted respectively from nickel sulfate and nickel acetate are determined as follows.

It can be assumed that the amounts of nickel shipped as product are derived only from nickel sulfate.

Assume that the amounts released to the waste water and the sludge are equally discharged and they can be calculated from the amounts of nickel sulfate and nickel sulfate handled by applying proportional allotment.

Amount of nickel derived from nickel sulfate :

= (A)-(I)

= 11,150(kg/year) - 6,740(kg/year)

 $= 4,410(kg/year) \dots (J)$

Amounts of nickel derived from both nickel sulfate and nickel acetate:

= (J) + (B)

= 4,410(kg/year) + 396(kg/year)= 4,806(kg/year)Percent of the amount of nickel derived from nickel sulfate: $= (4,410/4,806) \times 100 = 91.8\%$ (Percent of the amount of nickel derived from nickel acetate: = 100 - 91.8 = 8.2%) Amount released to waste water = $3,240 \times 0.918 = 2,974$ (kg/year).....from nickel sulfate 3,240 - 2,974 = 266(kg/year)...from nickel acetate Amount transferred being contained in sludge: • B sludge: $1,350 \times 0.918 = 1,239$ (kg/year)....from nickel sulfate 1,350 - 1,239 = 111(kg/year)...from nickel acetate • Other sludge: $216 \times 0.918 = 198(\text{kg/year})$from nickel sulfate 216 - 198 = 18(kg/year).....from nickel acetate (11)Breakdown of the amount of nickel released and transferred (unit: kg/year) Amount of nickel handled = 11.546Amount released to water bodies = 3,2402,974(portion derived from nickel sulfate) 266(portion derived from nickel acetate) Amount released to air = 0Amount transferred being contained in waste (B sludge) = 1,3501,239(portion derived from nickel sulfate) 111(portion derived from nickel acetate) Amount transferred being contained in waste (Other sludge) = 216198(portion derived from nickel sulfate) 18(portion derived from nickel acetate) Amount shipped as product (portion derived from nickel sulfate) = 6,740Total amount of nickel released and transferred = 11,546

- 2) Calculation Example of Amount of "Boron" in Electro Coloring Treatment
 - (1) Calculate the amount of boric acid handled from sources like monthly inventory reports, and convert them to the amount of element boron.

Amount of boron handled

= amount of boric acid handled $40,000(kg/year) \times 0.175(conversion factor)$

= 7,000(kg/year)(A)

(2) In case of boron, since it will hardly be released to air nor be shipped as product, it need not be calculated. Therefore there will be only the amount released to water bodies and the amount transferred being contained in waste.

(3) Amount released to water bodies can be calculated from the analyzed value of boron concentration in waste water 4.0(mg/L) as shown below.

Analyzed value of boron concentration in waste water 4.0(mg/L) = 0.004(g/L)

 $= 0.004 (kg/m^3)$

Amount released to water bodies

= (volume of discharged water) × (boron concentration)

 $= 3,000(\text{m}^3/\text{day}) \times 30(\text{day/month}) \times 12(\text{months/year}) \times 0.004(\text{kg/m}^3)$

= 4,320(kg/year)(B)

(4) Amount transferred being contained in waste (sludge) can be calculated by taking mass balance.

Amount transferred being contained in sludge:

= amount handled (A) - amount released to water bodies (B)

= 7,000(kg/year) - 4,320(kg/year)

- = 2,680(kg/year)(C)
- (5) Confirm if the total amount released, transferred, and shipped agree with the amount handled.

Total amount

= amount released to water bodies (B)

+ amount transferred being contained in waste (C)

= 4,320(kg/year) + 2,680(kg/year)

= 7,000(kg/year)

which agrees with the amount handled (A).

(6) Breakdown of the amount of boron released and transferred (unit: kg/year)

Amount of boron handled = 7,000(kg/year)

Amount released to air = 0

Amount released to water bodies = 4,320

Amount transferred being contained in waste = 2,680

Total amount of boron released, transferred, and shipped = 7,000

2.3.3 Calculation Example of Amount Released and Transferred in Coloring Process

Acidic metal-complex-salt containing compounds are used as the dye in the coloring process of alumite treatment, and if aniline, phenylenediamine, diphenylamine, or chromium compound and fluorine compound, or the like are contained in them, they come under the subject of PRTR law.

However, although the substance to be concerned with respect to the acidic metal-complex-salt containing dye used in alumite coloring process is the trivalent chromium, its content in the dye is no more than 5% and also because it was revealed by a survey that no facilities use it more than 1 ton,, the calculation example of amount released and transferred in coloring process is omitted.

- 2.3.4 Calculation Example of Amount of the Designated Chemical Substances in Coating Surface Preparation and Coating Processes.
- 1) Calculation Example of Chromium Released and Transferred in the Process of Coating Surface Preparation
 - (1) Conditions Assumed

All of the hexavalent chromium is recovered by ion-exchange resin and is not to be released to water bodies. (The entire amount of chromium in the regular wastewater from the treatment basins, primary wastewater, and water from the washing process is adsorbed and removed by means of ion-exchange treatment, and the recovered water is reused in the water washing processes.)

Production amount: 200,000(m²/year)

Amount of chromium coated on the products: $100(mg/m^2)$

Form of chemicals used: solution in water

Content of anhydrous chromic acid in the chemicals used: 12% (according to MSDS)

(2) Calculation of amount of hexavalent chromium handled

The amount of hexavalent chromium handled is calculated from sources such as monthly report, etc.

Annual amount of treatment chemicals handled: 1,400(liters/year); amount of chromic acid: 120(g/liter)

Amount of anhydrous chromic acid handled = $1,400(\text{liters/year}) \times 120(\text{g/liter})$

= 168,000(g/year) = 168(kg/year)

Amount of hexavalent chromium handled = $168(kg/year) \times 0.52(conversion factor) = 87(kg/year)$ (A)

Note 21 In this case, the calculation result of hexavalent chromium handled is 87 kg, which is less than negligible line (0.5 ton/year), thus is not required to be reported. Respective estimation methods are shown below for reference.

(3) From the results above, it will be recognized that there is no release to air or water bodies or transfer being contained in the waste (sludge). Therefore, the releases and transfers thereof need not be calculated.

Thus, what is to be calculated here is only the amounts shipped as products and transferred being contained in the ion-exchange resins.

- (4) The amount shipped as products is calculated as follows (Note 11):
 - Annual production amount: 200,000(m²/year)

Amount adhering to products (per unit area) = $100(mg/m^2) = 0.0001(kg/m^2)$ Amount shipped as products

 $= 0.0001 (\text{kg/m}^2) \times 200,000 (\text{m}^2)$

$$= 20(kg/year)$$
 (B)

(5) Transfers being contained in ion-exchange resin (amount handed over to

recycle dealers *) are calculated by taking material balance (Note 11).

Transfers being contained in ion-exchange resin

= Amount handled (A) - amount shipped as products (B)

= 87(kg/year) - 20(kg/year)

= 67(kg/year) (C)

(Note 11) In the above (4) and (5), the amount shipped as products was first calculated from the amount adhering to products, and then the transfers being contained in ion-exchange resin was calculated by taking mass balance. On the other hand, it is possible to first calculate the transfers being contained in ion-exchange resin (amount handed over to recycle dealers) and then to calculate the amount shipped as products by taking material balance.

In this case, the following is an example of how to calculate the transfers being contained in ion-exchange resin.

(4')The transfer being contained in the ion exchange resins (the amount handed over to recycle dealers) is calculated as follows:

Conditions assumed

- (a) Amount of ion-exchange resins handed over to recycle dealers = 1,300(liters/year)
- (b) The volume of the ion-exchange resin per unit tower is 350(liters) which can ion-exchange 35 kg of anhydrous chromic acid (Minichro-pack CR350 type is presumably used)

Equivalence ratio of hexavalent chromium to anhydrous chromic acid

= 52/100 = 0.52

Amount of chromium removed per tower

 $= 35(kg) \times 0.52 = 18.2(kg/350 \text{ liters})$

Transfers being contained in ion-exchange resin

 $= 1,300(liters/year) \times 18.2(kg) / 350(liters)$

= 67(kg/year) (B')

(5')The amount shipped as product is calculated by taking material balance.

Amount shipped as product

= Amount handled (A)

- amount transferred being contained in ion exchange resin (B')
- = 87(kg/year) 67(kg/year)

= 20(kg/year) (C')

(6) Confirm if the total of the shipped and transferred agrees with the amount handled (A).

The total amount = Amount shipped as product (B)

+ Amount transferred being contained in waste ion exchange resins (C)

= 20(kg/year) + 67(kg/year)

= 87(kg/year),

which agrees with the amount handled (A).

(7) Breakdown of the amount of hexavalent chromium released and transferred (unit: kg/year)

Amount of chromium handled = 87

Amount released to air = 0

Amount released to water bodies = 0

Amount shipped as product = 20

Amount transferred being contained in waste = 0

Amount transferred being contained in ion exchange resins = 67

Total amount of chromium released, transferred and shipped = 87

- 2) Calculation Example of the Releases and Transferres in the Coating Process
 - (1) Find out the types of the coating materials and thinners, and the compounding compositions, from MSDS.

Mostly, the coating materials used in the surface treatment of aluminum are the following types.

Coating material: acrylic urethane type coating material (for coloring)

Fluorinated coating material

Acrylic coating material

Solvent	: Thinner for acrylic urethane type coating material
	Thinner for fluorinated coating material

(2) Find out the amount of the designated substances handled for each coating materials and thinners.

Find out t	the	types	of	coating	materials	and	thinners	as	well	as	their	amount
handled.												

- (a) Acrylic urethane coating material amount handled 12,000(kg/year)
- (b) Fluorinated coating material amount handled 20,000(kg/year)
- (c) Thinner for acrylic urethane type coating material amount

4,200(kg/year)

handled

(d) Thinner for fluorinated coating material amount handled 3,000(kg/year)

Find out the amounts of toluene and xylene in the coating materials and the thinners from MSDS.

- (a) Calculate the amount of toluene (content 25%) and xylene (content 20%) contained in the acrylic urethane coating material: 12,000(kg/year). Amount of toluene handled: 12,000(kg/year) × 0.25 = 3,000(kg/year) Amount of xylene handled : 12,000(kg/year) × 0.20 = 2,400(kg/year)
- (b) Calculate the amount of toluene (content 20%) and xylene (content 15%)

contained in the fluorinated coating material: 20,000(kg/year). Amount of toluene handled: $20,000(kg/year) \times 0.20 = 4,000(kg/year)$ Amount of xylene handled : $20,000(kg/year) \times 0.15 = 3,000(kg/year)$

(c) Calculate the amount of toluene (content 35%) and xylene (content 30%) contained in the thinner for acrylic urethane type coating material: 4,200 (kg/year).

Amount of toluene handled: $4,200(kg/year) \times 0.35 = 1,470(kg/year)$ Amount of xylene handled : $4,200(kg/year) \times 0.30 = 1,260(kg/year)$

(d) Calculate the amount of toluene (content 15%) and xylene (content 30%) contained in the thinner for fluorinated coating material: 3,000(kg/year) Amount of toluene handled: 3,000(kg/year) \times 0.15 = 450(kg/year) Amount of xylene handled : 3,000(kg/year) \times 0.30 = 900(kg/year)

Calculate the total amount of toluene and xylene.

Total amount of toluene handled = 3,000 + 4,000 + 1,470 + 450= 8,920(kg/year) (A) Total amount of xylene handled = 2,400 + 3,000 + 1,260 + 900= 7,560(kg/year) (B)

(3) Calculation Example Wherein Toluene and Xylene are Removed by Catalytic Combustion Decomposition (Case [1] in Figure 10)

As there is no toluene nor xylene shipped as product, no calculation is necessary.

Calculation of the amount transferred being contained in waste

Assuming the annual amounts of waste of the coating materials containing toluene and xylene are each 200 kg for both the acrylic urethane and the fluorinated coating materials, the transferred amount can be calculated from their contents as follows.

- Acrylic urethane coating material Toluene: $200 \times 0.25 = 50(kg/year)$ Xylene : $200 \times 0.20 = 40(kg/year)$ - Fluorinated coating material Toluene: $200 \times 0.20 = 40(kg/year)$ Xylene : $200 \times 0.15 = 30(kg/year)$ - Amount transferred being contained in waste Toluene: 50 + 40 = 90(kg/year) (C) Xylene : 40 + 30 = 70(kg/year) (D)

Calculation of the amount released to water bodies

If the coating booth is a type of water washing booth, toluene and xylene are released to water bodies and this amount need to be calculated.

Assuming the waste water discharge from the wet booth = $1 \text{ m}^3/\text{day}$ and the operating days = 200 days/year, the amount released to water bodies can be calculated from the solubility data for toluene, i.e. $570(\text{mg/liter}) = 0.57(\text{kg/m}^3)$ as follows.

- Amount of toluene released to water bodies

 $= 0.57 (\text{kg/m}^3) \times 1 (\text{m}^3/\text{day}) \times 200 (\text{days/year})$

= 114(kg/year)

- Amount of xylene released to water bodies is calculated in the same way.

= 26(kg/year)

(Note 12) As xylene dissolves 0.13g/l in water.

Of the toluene and xylene in the exhausts from the coating booth and baking furnace, the amount removed by catalytic combustion decomposition process is calculated as follows.

If the percent decomposition removal rate of the catalytic combustion decomposition process = 96%,

Amount removed by catalytic combustion decomposition process

= {amount handled - (amount transferred being contained in waste + amount released to water bodies from coating booth)} \times percent removal rate of the catalytic combustion process

- Amount of toluene removed = (A) - $\{(C) + (E)\} \times 0.96$

 $= [8,920(kg/year) - \{90(kg/year) + 114(kg/year)\}] \times 0.96$

= 8,367(kg/year)(G)

- Amount of xylene removed = (B) - $\{(D) + (F)\} \times 0.96$

 $= [7,560(kg/year) - {70(kg/year) + 26(kg/year)}] \times 0.96$

= 7,165(kg/year)(H)

Amount of toluene and xylene released to air

= amount handled - {amount transferred being contained in industrial disposal

+ amount released to water bodies from coating booth

+ amount removed by catalytic combustion decomposition process}

- Amount of toluene released to air

 $= (A) - \{(C) + (E) + (G)\}$

 $= 8,920(kg/year) - \{90(kg/year) + 114(kg/year) + 8,367(kg/year)\}$

= 349(kg/year)(I)

- Amount of xylene released to air

 $= (B) - {(D) + (F) + (H)}$

 $=7,560(kg/year) - {70(kg/year) + 26(kg/year) + 7,165 (kg/year)}$

= 299(kg/year)(J)

Confirm if the total amount released, removed and transferred agrees with the amount handled $\{(A) \text{ or } (B)\}$.

The total amount = Amount released to air + Amount released to water bodies

+ Amount removed + Amount transferred being contained in waste - Total amount of toluene = (I) + (E) + (G) + (C)

= 349 + 114 + 8,367 + 90= 8,920(kg/year),which agrees with the amount handled (A). - Total amount of xylene = (J) + (F) + (H) + (D)= 299 + 26 + 7.165 + 70= 7,560(kg/year),which agrees with the amount handled (B). Breakdown of the amount of toluene and xylene released and transferred (unit: kg/year) Amount of handled Toluene = 8,920Xylene = 7,560Amount released to water bodies Toluene = 114Xylene = 26Amount released to air Toluene = 349Xylene = 299Amount removed by catalytic combustion process Toluene = 8,367Xylene = 7,165Amount transferred being contained in waste Toluene = 90Xylene = 70Amount shipped as product Toluene = 0Xylene = 0

Total amount of toluene released, transferred, removed and shipped = 8920 Total amount of xylene released, transferred, removed and shipped =

7,560

(4) Calculation Example Wherein Toluene and Xylene are not Treated for Removal (by Catalytic Combustion Decomposition Process) (Case [2] in Figure 10)

Calculation of the transfer contained in the waste (Similarly to that for catalytic combustion decomposition removal process)

Toluene: 50 + 40 = 90(kg/year)(C) Xylene: 40 + 30 = 70(kg/year)(D)

Calculation of the release to water bodies (Similarly to that for catalytic

combustion decomposition removal process)

Assuming the waste water discharge from the wet booth

 $= 1(m^3/day),$

and the operating days

= 200(days/year),

the amount released to water bodies can be calculated from the solubility data for toluene, i.e. 570(mg/liter)

 $= 0.57 (\text{kg/m}^3)$ as follows.

- Amount of toluene released to water bodies

 $= 0.57 (\text{kg/m}^3) \times 1 (\text{m}^3/\text{day}) \times 200 (\text{days/year})$

= 114(kg/year)(E)

- Amount of xylene released to water bodies

 $= 26(kg/year) \dots (F)$

Calculate the amount released to air.

Amount released to air

- = amount handled {amount transferred being contained in waste
- + amount released to water bodies}
- Amount of toluene released to air
- $= (A) {(C) + (E)}$
- $= 8,920(kg/year) \{114(kg/year) + 90(kg/year)\}$
- = 8,716(kg/year)(I)'

- Amount of xylene released to air

 $= (B) - {(D) + (F)}$

 $= 7,560(kg/year) - \{70(kg/year) + 26(kg/year)\}$

= 7,464(kg/year)(J)'

Confirm if the total amount released and transferred agrees with the amount handled $\{(A) \text{ or } (B)\}$.

The total amount = Amount released to air + Amount released to water bodies

+ Amount transferred being contained in waste

- Total amount of toluene = (I)' + (E) + (C)

- = 8,716 + 114 + 90
- = 8,920(kg/year),

which agrees with the amount handled (A).

- Total amount of xylene = (J)' + (F) + (D)

=7,464+26+70

= 7,560(kg/year),

which agrees with the amount handled (B).

Breakdown of the amount of toluene and xylene released and transferred (unit: kg/year)

Amount of handled

```
Toluene = 8,920

Xylene = 7,560

Amount released to water bodies

Toluene = 114

Xylene = 26

Amount released to air

Toluene = 8,716

Xylene = 7,464

Amount transferred being contained in waste

Toluene = 90

Xylene = 70

Amount shipped as product

Toluene = 0

Xylene = 0
```

Total amount of toluene released, transferred, and shipped = 8,920Total amount of xylene released, transferred, and shipped = 7,560

3) Calculation example of the amount of pigment's component released and transferred in coating preesses

Some coating materials may contain metal compounds such as chromium, zinc, cadmium, or lead compound, as the pigment's components, and if they fall under the subject of the designated chemical substances, their amounts released and transferred must be calculated and notified.

However, upon survey, it has become clear that no pigments contained in the coating materials used for aluminum fall under the subject of the class I designated substances. Therefore the calculation examples of the releases and transfers for the pigment's components contained in the coating materials were omitted from this manual.