# CONVENTION ON THE PROTECTION OF THE MARINE ENVIRONMENT OF THE BALTIC SEA AREA

HELSINKI COMMISSION - Baltic Marine Environment Protection Commission

HELCOM 23/2002 Minutes of the Meeting

23rd Meeting Helsinki, Finland, 5-7 March 2002 Annex 9

### **HELCOM RECOMMENDATION 23/7 \*)**

Adopted 6 March 2002 having regard to Article 20, Paragraph 1 b) of the Helsinki Convention

# REDUCTION OF DISCHARGES AND EMISSIONS FROM THE METAL SURFACE TREATMENT 1)

#### THE COMMISSION,

**RECALLING** Paragraph 1 of Article 6 of the Convention on the Protection of the Marine Environment of the Baltic Sea Area, 1992 (Helsinki Convention), in which the Contracting Parties undertake to prevent and eliminate pollution of the Baltic Sea Area from land -based sources by using , inter alia, Best Environmental Practice for all sources and Best Available Technology for point sources,

**HAVING REGARD** also to Article 3 of the Helsinki Convention, in which the Contracting Parties shall individually or jointly take all appropriate legislative, administrative or other relevant measures to prevent and abate pollution in order to promote the ecological restoration of the Baltic Sea Area.

**RECALLING** Article 5 of the Convention on the Protection of the Marine Environment of the Baltic Sea Area, 1992 (Helsinki Convention), in which the Contracting Parties undertake to prevent and eliminate pollution of the marine environment of the Baltic Sea caused by harmful substances,

**RECALLING ALSO** Annex I, Part 1 of the Convention, according to which the Contracting Parties shall, in their preventive measures, give priority to the groups of substances, including heavy metals, halogenated compounds, cyanides and EDTA listed in Annex I, Part 1 which are generally recognised as harmful substances,

**RECALLING FURTHER** the Ministerial Communiqué 1998, calling to implement the HELCOM Recommendation 19/5 on the HELCOM Objective with regard to Hazardous Substances, which is to prevent pollution of the Convention Area by continuously reducing discharges, emissions and losses of hazardous substances, with the ultimate aim of concentrations in the environment near background values for naturally occurring substances and close to zero for man-made synthetic substances, until 2020,

- \*) Superseding HELCOM Recommendation 16/6
- This Recommendation should apply primarily to plants in which surfaces are plated with metals electrolytically or chemically. This involves the following main operations:
  - pre-treatment (e.g. degreasing/cleaning and pickling);
  - electrolytic or chemical deposition of metals, including intermediate treatment:
  - post-plating treatment (e.g. chromating, dyeing);
  - stripping;
  - phosphating

**RECALLING FURTHER** that the Ministerial Declaration 1988, of the ninth meeting of the Helsinki Commission calls for a considerable reduction of land-based pollution,

**RECOGNIZING** that metal surface treatment is a notable source of discharges of these harmful substances into water and into atmosphere,

**RECOGNIZING** the importance of limiting discharges into water and into atmosphere from the metal surface treatment by application of Best Available Techniques,

**DESIRING** more information about the discharges from the metal surface treatment,

**RECOMMENDS** to the Governments of the Contracting Parties that they apply the precautionary principle, the principle of the Best Available Techniques and the substitution principle, by which is meant substitution of the use of hazardous substances by less hazardous substances or preferably non-hazardous substances where such alternatives are available.

**RECOMMENDS** that the Governments of the Contracting Parties to the Helsinki Convention take the following measures:

- 1. General requirements
- 1.1 if technically possible, substitution of hazardous substances (e.g. cyanide, cadmium, mercury, EDTA and similar sequestering agents, nonylphenol-ethoxylates, chlorinated organics) by substances which are readily biodegradable, non-bioaccumulating and non-mutagenic and have a low toxicity;
- 1.2 substitution of EDTA in degreasing baths, stripping baths and chemical nickel plating baths. Possible substitutes include e.g. citric acid, tartaric acid and gluconic acid;
- 1.3 substitution of processes generating noxious substances wherever possible (e.g. cyanide oxidation with hypochlorite);
- 1.4 treatment of process baths using suitable processes in order to have the longest possible service life. Such processes include, e.g. membrane filtration, ion exchange, electrolysis, thermal processes and evaporation;
- 1.5 retention of bath ingredients by suitable means, such as transporting the goods in such a way that drag-out is minimised; splash guards or optimised bath composition;
- 1.6 multiple use of counter-current rinse waters (at least three rinsing steps should be applied). Suitable techniques to keep more than 90% of the drag-out in a small volume for recovery/recycling are, e.g.:
  - i) static rinse in combination with metal recovery:
  - ii) 2-stage cascade rinsing plus closed cycle rinsing with ion exchange;
  - iii) combined dip/spray/mist rinsing techniques.

If possible these rinsing concentrates should be returned into the process baths, if necessary after specific treatment/concentration. By applying these rinsing techniques process baths can often be operated as closed water/low waste systems;

- 1.7 separation of suitable non-ferrous metal waste water streams to carry out internal recycling (e.g. by electrolysis) or external recovery (e.g. by non-ferrous metal industry);
- 1.8 recovery of EDTA from chemical copper plating baths (e.g. by precipitation as H₄EDTA) and their rinse baths (e.g. by precipitation after a concentration step, e.g. by anion exchange),
- 2. Requirements for the reduction of waste water discharges

The mixing or diluting of different waste waters (i.e. mixing of treated process water with cooling

water) for the purpose of compliance with the limit values established for the effluent should not be allowed. This means that all limit values mentioned below refer to the process waste water.

- 2.1 waste water streams should be separated according to the kind of necessary treatment and to achieve a sludge composition such that the metals can be recovered. The treatment should be carried out in batch reactors:
- 2.2 cadmium and mercury containing water streams should be treated and monitored separately with the following maximum concentrations:

Cadmium - 0.20 mg/l;

Mercury - 0.05 mg/l;

2.3 before discharging into sewers or surface waters the treatment should be provided so that the concentrations of the following substances do not exceed the following levels:

Substance Concentration	mg/l
Chromium (total) (Cr-tot)	0.7
Chromium (VI) (Cr-VI)	0.2
Copper (Cu)	0.5
Lead (Pb)	0.5
Nickel (Ni)	1.0
Silver (Ag)	0.2
Zinc (Zn)	2.0
Unbound cyanide	0.2
Volatile organic halogens (VOX)	0.1

Plants discharging small loads of metals (defined as sum of total chromium, copper, lead, nickel and zinc less than 200 g/day prior to end-of-pipe treatment) may be subject to limit values up to maximum four times higher for total chromium, copper, lead and nickel. Maximum concentration of zinc shall not exceed 4 mg/l;

- 2.4 in some cases organic substances could be present in the waste water. Thus, if possible and considered suitable, such waste water from the metal surface treatment should undergo biological treatment. This includes treatment in a municipal sewage treatment plant,
- 3. Requirements to avoid as far as possible the use of chlorinated solvents:

They should be replaced by water-based systems or non-halogenated organic solvents. In specific cases, where it is proven that substitution is technically not possible, the following requirements should be met

- 3.1 In operating surface treatment plants, the only volatile chlorinated hydrocarbons, which should be used for degreasing, are commercial-grade tetrachloroethene, trichloroethene or dichloromethane. The use of other halogenated solvents is not necessary for technical reasons. Substances widely acknowledged as carcinogenic should not be contained as additives in, nor be added to, the halogenated hydrocarbons;
- 3.2 Surface treatment plants should be established and operated in such a way that goods to be processed should be treated in an enclosure in the cases where volatile solvents are used. This enclosed plant, except for the openings for venting the waste gases, is sealed on all sides;
- 3.3 Vented waste gas should be led to a separator, which is used to ensure that the emissions of

volatile halogenated hydrocarbons do not exceed a mass concentration of 20 mg/m³. As a variation from this: if the solvent contains more than 50% of dichloromethane in the volative halogenated hydrocarbons, the emission, may not exceed a mass concentration of 50 mg/m³. These concentrations should not be achieved by diluting the waste gas with air. The separated volatile halogenated hydrocarbons should be recovered;

- 3.4 Halogenated solvents or residues containing halogenated solvents should be stored, transported and handled in closed vessels:
- 3.5 The waste water from processes in which volatile halogenated hydrocarbons are used (e.g. greasing, degreasing) should be treated separately and should comply with the following limit value:

Sum of trichloroethene, tetrachloroethene and dichloromethane: less than 0.1 mg/l (expressed as chlorine in a representative sample),

### 4. Analysing methods

Internationally accepted standardized sampling, analysing and quality assurance methods (e.g. CEN-standards, ISO-standards and OECD-Guidelines) should be used whenever available,

**RECOMMENDS FURTHER** that the Contracting Parties re-evaluate in three years the limit values of this Recommendation and reconsider them as appropriate,

**RECOMMENDS FURTHER** that the Contracting Parties report to the Commission every three years starting from 2006.

# REPORTING FORMAT FOR HELCOM RECOMMENDATION 23/7 CONCERNING REDUCTION OF DISCHARGES AND EMISSIONS FROM THE METAL SURFACE TREATMENT

Lead Co	untry
Country:	•
Year.	

- 1. Number and type of plants discharging directly into surface waters and number and type of plants discharging to municipal sewers.
- 2. Summarised description of the sector 1) including:
- efforts to reduce the volume of waste water discharged and its pollutant load as specified in paragraph 1 of the Recommendation;
- efforts to avoid and substitute the use of chlorinated solvents as specified in paragraph 3 of the Recommendation;
- actions taken to reduce discharges and emissions during the last 3 years.
- 3. Information on waste water discharges for plants discharging directly to surface waters.
  - 3.1 Waste water volume, concentration of heavy metals and other substances as specified in paragraph 2 of the Recommendation (preferably plant by plant).

Plant	Waste water volume	Concentration, mg/l										
		Cd	Hg	Cr-tot	Cr- VI	Cu	Pb	Ni	Ag	Zn	Unbound cyanide	VOX

- 3.2 Sum of trichloroethene, tetrachloroethene and dichloromethane in mg/l (expressed as chlorine in a representative sample).
- 4. VOC emission data to the air.
- 5. Summarized data on plants discharging directly to municipal sewers including:
- number or percentage of plants which comply with the different requirements of the Recommendation (Please specify e.g. which parameters / requirements cause problems for compliance).
- 6. Summary of evaluation of compliance with the requirements of the Recommendation including:
- problems encountered in the implementation of the requirements and the foreseen development of the situation.

Applies primarily to plants in which surfaces are plated with metals electrolytically or chemically. This involves the following main operations: pre-treatment (e.g. degreasing/cleaning and pickling); electrolytic or chemical deposition of metals, including intermediate treatment; postplating treatment (e.g. chromating, dyeing); stripping and phosphating.

- 7. Specify means used when nationally putting into force the Recommendation
- via general reference in the national legislation via a specific adoption of an amendment to existing national legislation via administrative or other means, please specify.

Possible problems identified when putting into force nationally the Recommendation.