Specific Environmental Release Categories (SPERCs) for Industrial Use of Coatings in Installations with Wet Scrubber for Collection of Overspray (intermittent release to water due to replacement of scrubber content maximum twice per year)

Background Document

Edited by ACEA (official approval pending)
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SPERCs are specific environmental release categories and are meant to specify broad emission scenario information (ERCs) as suggested for the use of substances throughout their life cycles (Reihlen et al., 2016). Although specific, SPERCs still reflect emissions of a broad application area of a substance within an industry sector. For their purpose, SPERCs are conservative and, therefore, their emission estimates are not intended to reflect all regulatory requirements that may relate to environmental emissions.

1 Purpose statement

ECHA Guidance R.16 provides one set of release factors each for the industrial use of a substance as a processing aid (ERC4) or resulting in inclusion of a substance into a matrix (ERC5). This document provides background information to the SPERC factsheet(s) for the industrial use of liquid spray coatings in installations with wet scrubber for collection of overspray, considering as additional operational condition the intermittent release to water due to replacement of scrubber content maximum twice per year. As the use of a wet scrubber stands for a process integrated risk management measure with impact on the fate of volatile and non-volatile compounds, this SPERC/these SPERCs are referring to ERC 4 and 5. Specific information is provided on product application (ch.2), exposure relevant operational use conditions (ch. 3), on risk management measures (ch. 4), and on the information sources (ch. 5) including the derivation method and justification of use rates and release factors.

The SPERC Factsheets covered in this document comprises a number of subSPERCs:

<table>
<thead>
<tr>
<th>ACEA SPERC Code</th>
<th>Type of ingredient</th>
<th>Application area</th>
</tr>
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<tbody>
<tr>
<td>ACEA SPERC 4/5_1SB</td>
<td></td>
<td>Application of solvent-borne/liquid spray coatings</td>
</tr>
<tr>
<td>subSPERC 4.1.a</td>
<td>volatile ingredients</td>
<td>Volatile substances with water solubility &gt; 10 mg/l</td>
</tr>
<tr>
<td>subSPERC 4.1.b</td>
<td>volatile ingredients</td>
<td>Volatile substances with water solubility &lt; 10 mg/l</td>
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<tr>
<td>subSPERC 5.1.a</td>
<td>non-volatile ingredients</td>
<td>Non-volatile substances with water solubility &lt; 10 mg/l</td>
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<tr>
<td>ACEA SPERC 4/5_1WB</td>
<td></td>
<td>Application of water-borne spray coatings</td>
</tr>
<tr>
<td>subSPERC 4.1.c</td>
<td>volatile ingredients</td>
<td>Volatile substances with water solubility &gt; 10 mg/l</td>
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<tr>
<td>subSPERC 5.1.a</td>
<td>non-volatile ingredients</td>
<td>Non-volatile substances with water solubility &lt; 10 mg/l</td>
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</table>

For non-volatile substances with water solubility > 10 mg/l, no release factor has been derived due to lack of measured data. Typical pigments, extenders and additives in coatings do not have such high solubility, dyes (i.e. water soluble compounds) are rarely used. Based on the model assumptions, a linear relation between water solubility and a release factor may be supposed.

2 Scope

The SPERC of this application area is valid for refinement of release factors for substances used in an industrial setting in liquid spray coatings, comprising solvent-borne, water- borne and liquid solvent-free mixtures. Due to the specific relevance of water solubility for transfer rates and release factors, a presentation with inclusion of sub-SPERCs is preferred.
2.1 Uses of liquid spray coatings: Ingredients and product types

Liquid spray coatings are used, when complex three-dimensional objects need to be coated with a protective, functional or decorative layer and when other coating technologies (e.g. pre-coated substrates, dipping, rolling, brushing, pouring, in-mould coating, powder coatings, adhesive films) are not suitable for technical or economic reasons.

Spray coating of liquid materials is linked to limited transfer efficiency of atomization techniques. The part of spray aerosols, which is not deposited on coated substrates is known as overspray. Retention of overspray by process-integrated risk management measures is standard. This is achieved by either dry filtering systems, dry precipitation systems or by wet scrubbers. Only the wet scrubber case is described here as the potential transfer to a waste water stream is only linked to this technology. Sophisticated wet scrubbers with intermittent release to water due to replacement of scrubber content maximum twice a year are widely used in large installations (automotive OEM, plastic parts) as they fit well into processes with continuous sludge removal and limited need of line stops for maintenance (exchange of filters). A more general description of overspray collection by wet scrubbers is provided in corresponding CEPE SPERCs. This SPERC does not cover use of dry filters or other dry techniques for the collection of overspray. For the use of dry techniques all releases would be allocated to air.

The liquid products may be solvent-borne (up to 95 % volatile content), water-borne (up to 85 % volatile content including between 5 and 25 % organic solvents) or with only minor content of volatiles (e.g. UV curing materials).

The major constituents of coatings are binders, activators, pigments, extenders, and solvents including water. In addition, additives such as catalysts, initiators, UV absorbers, neutralizing compounds and sagging control agents are used as typical minor ingredients.

Many volatile compounds have moderate or good solubility in water (low boiling alcohols, glycols, ketones, esters, lactams) whereas others have low or almost negligible solubility (aliphatic and cycloaliphatic hydrocarbons, aromatic hydrocarbons, terpenes, high boiling alcohols). Only a small number of compounds are assigned to a hazard for the aquatic environment (e.g. high-boiling alcohols, aromatic hydrocarbon blends, heptane, ethyl benzene, terpenes). By now (2016), environmental assessments are only available for aromatic hydrocarbon blends (with no PNEC values derived) and some high boiling alcohols (assigned to very low PNEC values surface water). Mixture effects need to be considered.

Resins, additives, pigments and extenders have low or almost negligible solubility in water and can be extracted mechanically from circulating water after coagulation. Only a small number of compounds are assigned to a hazard for the aquatic environment (e.g. zinc compounds, catalysts, UV absorbers, very few pigments). By now (2016), environmental assessments are only available for zinc compounds (assigned to low PNEC values surface water).

Solvent-borne coatings do not need biocidal control agents at any manufacturing or application stage. Resins for water-borne coatings may require addition of biocidal agents as in-can preservatives. Finished products do no longer contain substantial concentrations. The typical content of organic solvents in water-borne coatings is sufficient to control biocidal activity without additional in-can preservatives.

Whereas the mentioned substance characteristics (CMR, PBT/vPvB, classification for environment, biological degradability, biocidal properties, availability of PNECs, range of PNECs) do not have an impact on the technical performance and do not affect the operational conditions, these parameters may be relevant for the extension resp. completeness of the environmental assessment.
2.2 Application technologies

Atomization of liquid coatings at industrial sites may occur manually or automatically, by means of spray-guns or high-rotation bells, with or without support of pressurized air, with or without electrostatic charging, continuously or discontinuously.

Per coating job, transfer efficiency may range between 30 and 90% depending on geometrical and electrostatic substrate properties, atomization technology and desired effect formation. State of the art application technology limits overall overspray and purge loss to maximum 40% for automotive OEM resp. 70% for automotive parts and smaller industrial objects. A mass flow diagramme for a typical case is displayed hereafter.

3 Emission relevance of operational conditions

A wet scrubber is one of the technical options to limit spray particle emissions to the environment (air). When using a wet scrubber, coating compounds are finally transferred to a process waste water stream. This applies also for paint losses due to colour change operations and small amounts of purging and rinsing liquids (the major part of purging liquids is collected separately and not transferred into the wet scrubber). This process-integrated RMM is linked to an add-on risk management measure comprising a system for separation of paint sludge and water for recirculation, and an industrial physico-chemical waste water treatment with discharge of pretreated wastewater to a municipal sewage treatment plant.
By continuously coagulating and removing paint sludge, the water volume of the wet scrubber can be recirculated for long periods and only needs compensation for evaporation loss. Residual paint content in the recirculated water is typically maintained at a level below 1%. However, due to increase of salt content and biological activity inside the recirculated water, and due to some paint adhering to surfaces of tubes and tanks, the total scrubber content needs to be exchanged, typically once or twice per year.

4 Application of risk reduction measures

Non-volatile compounds are captured in order to comply with regulatory requirements. For large installations, which are using a wet scrubber and which are considered by this SPERC, this RMM is obligatory. In addition, there may be technical reasons like air recirculation in spray-booths which also support the need for overspray retainment.

Volatile compounds are released from coatings in spray-booths, flash-off zone and drying ovens. Final release to environmental air depends on the required abatement to comply with directive 2010/75/EC and its national or local implementation. Abatement is not considered as an obligatory RMM in this
SPERC, as in practice the range of site specific requirements varies between no abatement (for water-borne coatings with enforced flash-off) and full abatement of exhaust air from spray-booths and ovens (for solvent-borne basecoats in new installations respectively in some EU member states). Nevertheless, a small part of the volatile compounds is retained in paint sludge and water as a side effect of the wet scrubber.

Paint sludge is continuously removed from the water recirculation system in order to avoid uncontrolled deposition inside tanks and tubes. The coagulation of paint sludge requires use of adapted coagulation agents. The removed paint sludge gets dewatered by filter bags or centrifugal units in order to generate a material with high calorific value, which may then be incinerated (either at incineration plants for hazardous waste or at combustion plants which are designed for co-combustion of such materials).

5 SPERC information Sources

The OECD Emission Scenario Document (ESD) for coatings contains a couple of assumptions on release factors. In context with this SPERC, the main issue with the coating ESD is that it clearly focuses on emissions to air. Figures for substance release to water (and soil) are just a side effect of the document and have not been determined as a base for environmental assessments under REACH. With exemption of marine coatings, release rate was assumed to be zero for most other sectors of use. Wet scrubbers are mentioned for one sector without further specification and explanation of the underlying process.

To overcome this data gap, the German society for research on surface treatment (Deutsche Forschungsgesellschaft für Oberflächenbehandlung – DFO in Neuss), especially its committee on safety and environmental protection, took the initiative to collect and interpret information about substance releases from application processes to the environment. DFO has members from coating manufacturers, installation manufacturers, coatings users and research institutes. The task force which was created end of 2010 comprised Daimler, Ford, Volkswagen, Helcotec, BASF Coatings, Chemetall, Dupont Performance Coatings, Hydro, Kluthe, Wörwag, Dürr, and VdL. Further support was leveraged via the European automotive manufacturers association (ACEA) and included BMW, Hyundai/Kia and JaguarLandrover.

The aim of the task force was to get a realistic idea about substance transfer rates under reasonably conservative assumptions. A conservative transfer rate is derived from input of critical substances at the lower end and output at the higher end of expectations.

The critical point of this data collection is that besides COD values, values for non-volatile content and monitoring values for standard parameters (Pb, Cr, Cu, Ni, Zn, AOX), no real measured values for individual substances were available and achievable. Nevertheless all participants agreed on the results in form of derived release rates.

In order to become officially agreed and accessible by registrants and downstream users, the obtained results were aligned inside the Task force Environmental Protection of the European association of vehicle manufacturers (ACEA) and brought into the agreed SPERC format. This alignment resulted in a confirmation of the DFO work and allowed ACEA to take over full responsibility for the content.
5.1 Justification of use rates

Large installations may use up to 1,000 kg/d of a specific volatile compound in coatings. (20,000 kg/d spray coating applied in EU’s largest automotive OEM plant, typically with a maximum of 5 % overall content of an individual substance, including aquatically hazardous substances, e.g. hydrocarbon blends).

Large installations may use up to 1,000 kg/d of a specific non-volatile compound in coatings. (20,000 kg/d spray coating applied in EU’s largest automotive OEM plant, typically with a maximum of 5 % overall content of an individual substance, including substances to which an aquatic hazard is assigned; this is a theoretical case as e.g. zinc compounds are not used in OEM coatings for vehicles or plastic parts, and catalysts, UV absorbers and special pigments are used at considerably lower level).

These are maximum use rates of substances per industrial site whereas the release factors are derived from minimum use rates of coatings per individual installation (one spray booth with wet scrubber).

5.2 Justification of days emitting

The whole process is split into a continuous part with release to air and waste and an intermittent part with release to water (and to waste at very low level). The days emitting for the release to water depend on the capacity of the receiving sewage treatment plant (STP) for biological degradation of volatile compounds which are dissolved in effluent water (for details see ch. 5.3.2). There is no pre-defined relation between uses days and release days.

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**Diagram:**

- **Continuous process**
  - Volatiles
    - Transfer eff. 30-90 %
  - Non-volatiles
    - Atomization

- **Intermittent process**
  - RMM eff. 99 %
  - NV content 60 %
  - Scrubber
  - Reservoir
  - Sludge tr.

- **RF air**
  - 0.01

- **RF waste**
  - 0.1-0.7

- **RF water**
  - 0.00001

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**Diagram:**

- **Continuous process**
  - Volatiles
    - Atomization
  - Optional RMM
  - Non-volatiles

- **Intermittent process**
  - RMM eff. 0 %
  - Scrubber
  - Reservoir
  - Sludge tr.

- **RF air**
  - 0.9-0.93

- **RF waste**
  - 0.05-0.07

- **RF water**
  - 0.002-0.05
5.3 Justification of release factors

5.3.1 Continuous release
Volatile compounds are released to air in spray-booths, flash-off zone and drying ovens. Final emission to air depends on the required abatement to comply with directive 2010/75/EC. Ovens are often connected to abatement which reduces emission to air by 5 to 30 % for solvent-borne coatings and by 10 to 50 % for water-borne coatings; abatement for spray-booths is only typical for solvent-borne basecoats in few EU countries, including Germany and Sweden. Due to this unpredictable situation, abatement is not considered as an obligatory RMM in the context of this SPERC. The release factor to air is between 0.9 and 0.93.

A small fraction of volatile compounds is retained in the paint overspray, transferred into the aqueous phase and finally extracted via the paint sludge route as a side effect of non-volatiles retention.

Non-volatile compounds are captured in the wet scrubber. Residual emission is typically below 3 mg/m³. For a spray-booth with 50,000 m³/h exhaust air volume this limit value would result in maximum 150 g/h of emission. When e.g. 15 kg/h of paint would be atomized this leads to a release factor of 0.01. This is a worst case estimate as paint consumption is typically higher for the considered cases.

Paint sludge which is mechanically extracted from the sludge removal tank and filtered contains more than 60 % of paint non-volatiles, few percent of paint volatiles and around 30 % of water. Depending on pigmentation its calorific value is around 15 MJ/kg. So it cannot be deposited without pretreatment and is thus typically used as secondary combustion material. In some cases, paint sludge is dried prior to mixing with other solid combustion materials.

The associated release factor to waste depends primarily on the achieved transfer efficiency. The broad range of achievable transfer efficiency between 30 and 90 % results in a release factor between 0.1 and 0.7. It is not viable to define a certain minimum transfer efficiency as mandatory requirement.

Release factors to water are linked to intermittent release.

5.3.2 Intermittent release
Circulating water in a wet scrubber needs to be replaced typically once per year due to increase of salt content and activity of microorganisms and for cleaning of tube and tank walls. The total amount of released substances is depending on their solubility in water under process conditions and on the exchanged water volume per period (replaced water volume x practical solubility rate).

In a wet scrubber (Venturi or similar), a minor amount of volatile compounds remains in the circulating water. Volatile compounds are retained in circulating water only at low levels, as huge air volumes and water movement lead to a relatively low equilibrium stage, far below theoretical dissolution levels of solvents. Individual substances cannot be measured analytically under real life conditions with reasonable effort at very low levels (in the range of PNEC values). Typically concentrations are < 0.1 % for solvent-borne coatings, < 0.01 % for solvent-borne coatings with major content of solvents with very low water solubility, < 1 % for water-borne coatings, measured as COD < 2,500 mg/l, < 250 mg/l respectively < 25,000 mg/l (relation between solvent content and COD based on butanol, butyl acetate and butyl glycol as reference solvents). The released amount per spray-booth water exchange is then e.g. 50 m³ water x 0.1 % solvent concentration = 50 kg solvent (500 kg in case of solvents in water-borne coatings).
This borderline solvent concentration is reached after a relatively short time of paint application (less than 5 days application of solvent-borne coatings, less than 25 days application of water-borne coatings). For calculation of a release rate, 115 days of paint application were considered for one water exchange cycle (230 d/a, two exchanges per year), resulting at a release of 0.44 respectively 4.35 kg/day. In this respect, day stands for the use days, not for the release days. The release rate or release factor is derived as kg (minimum) solvent input per use day divided by (maximum) solvent release per use day.

As only few installations provide biological treatment on-site, transfer to a municipal STP is considered as standard. Available data for all typical solvents indicate biological degradation > 75 % according to OECD standard tests (e.g. OECD 301A-F), > 90 % for oxygenated solvents of water-borne coatings. In order to avoid overload of treatment plants (physico-chemical on-site, municipal biological STP), exchanged water from wet scrubbers is typically transferred into a buffer tank from which it can be released at appropriate amounts (e.g. 10 m³/d) for a longer period. Three release days per spray-booth water exchange can be considered as average. Total release days per site depend on total number of batches (largest installation has about 30 spray booths with wet scrubber, 10 booths is a realistic figure for many sites) and capacity of the available STP (water volume to be treated biologically and COD freight).

Non-volatile compounds may be partly dissolved in circulating water at low concentrations. Due to the inclusion of pigments and additives into the polymer matrix, measured values for such compounds (e.g. zinc in sanding dust of refinishing activities) are ten times lower than theoretical dissolution levels.

Waste water is typically monitored for Pb, Cr, Cu, Ni and Zn and does not show concentrations > 0.5 mg/l even before further treatment. Nevertheless on-site physico-chemical treatment (precipitation, sedimentation, filtration, dewatering) is considered usual for treatment and reduction of other parameters (e.g. solid matter, AOX). The RMM efficiency for the monitored compounds (typically 90 %) is assumed to be valid for all non-volatile compounds.

For determining release factors, the ACEA SPERCs consider general model assumptions (volume of receiving process water system, solubility of volatile and non-volatile compounds) in combination with sector-specific modifying factors. Minimizing factors are: volatilization of solvents due to turbulent movement of water and huge air volumes, inclusion of partly soluble non-volatile compounds in a polymer matrix. Increasing factors are: formation of azeotropic mixtures, presence of detergents (the latter being out of scope of this SPERC).

The release factors of these SPERCs are based on a calculation model which has been derived from industrial data collected in the automotive industry (OEM, tier 1 and 2) and from expert judgment.

For volatile compounds, the model distinguishes three cases with regard to transfer rates: standard solvents in solvent-borne coatings, solvents with low water solubility (< 10 mg/l) in solvent-borne coatings, and solvents in water-borne coatings.

For non-volatile compounds, the model only refers to compounds with low water solubility (< 10 mg/l) which is applicable for all known relevant compounds.
6  Conservatism

(Intermittent) release to the aquatic environment is determined by volume of exchanged process water and concentration of dissolved substances. Same basic concept is applied by hydrocarbon manufacturers (Petrorisk model). The volume of exchanged process water is set at 100 m³ per spray-booth per year taking into account a system volume of 50 m³ and two complete exchanges per year. Data collection (see enclosed excel spreadsheet in ch. 5) shows volumes between 32 and 50 m³ and 0.33 to two exchanges per year. Other standard models would assume lower volume of receiving process water (down to 1 m³). Based on COD measurements for mixtures, substance concentrations are assumed to be more than 10 times higher than expectation values for pure substances. E.g. isotridecanol has a theoretical solubility in water of 2 mg/l, corresponding to a COD of 5 mg/l, hexane has a theoretical solubility in water of < 100 mg/l, corresponding to a COD of < 250 mg/l. The SPERC calculates with COD values of 250 mg/l resp. 2,500 mg/l in order to cover potential effects of azeotropic mixtures.

A release rate or release factor is derived as kg substance input per use day divided by substance release per use day. A release rate / release factor is conservative if substance input figures are taken from the lower end of the data collection and substance release figures are taken from the upper end of the data collection. The enclosed excel spreadsheet (see ch. 5) shows that all considered input figures are at the lower end of reported ranges: 30 units coated per hour, 16 hours run-time per day, 1.5 kg paint applied per unit, 12 % solvent content in water-borne basecoats, resulting in 86.4 kg/d calculated solvent input; average figures (40 u/h, 20 h/d, 2.5 kg/u, 15 % solvent) would result in 300 kg/d; upper end figures would amount to 1,730 kg/d. The release to water is calculated at 4.35 kg/d based on 50 m³ water volume and 2 exchanges per year. The resulting release factor of 0.05 (4.35 kg/d divided by 86.4 kg/d) is the highest achievable value for the described calculation. Average factors would be 5 to 10 times lower.

OECD exposure scenario documents expect far lower release rates to water.

7  Applicability of SPERC

Data collection for this SPERC is mainly focused on automotive OEM installations for light vehicles, vans, truck cabins and plastic parts. Sophisticated wet scrubbers as described in this SPERC are typically used in large installations where use of dry filters for overspray collection would disturb continuous production and might lead to contamination of installations by dust particles after filter exchange.

Installations in other industries with less paint consumption would reduce water volume in wet scrubbers proportionally.

7.1  Tiered assessment

Due to this set of characteristics we consider the coating SPERCs suitable for use in standardized, lower tier REACH assessments of the vast majority of their ingredient substances. Their envisaged use is for risk assessors to distinguish trivial substances and emission situations from problematic ones based on standardized emission estimates. Based on this distinction, additional efforts can be focused on assessments of situations beyond the defined scope.

7.2  Regional assessment

This SPERC is meant for local sources.
8 References


T. May, Axalta Coating Systems Research Report, Development of a Sector Specific Environmental Release Categories (spERCS) Concept (Wuppertal, 2013)