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Paints and varnishes — Modelling of biocide release rate from antifouling paints by mass-balance calculation

Peintures et vernis — Modélisation du taux de lixiviation des biocides contenus dans les peintures antisalissures par calcul du bilan massique

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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ISO 10890 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 9, *General test methods for paints and varnishes*.

Introduction

The actual release rate of biocides from antifouling paints on ships' hulls into the environment will depend on many factors, such as ship operating schedules, length of service, berthing conditions, paint condition, as well as the temperature, salinity, pH, pollutants and biological community in a particular area. However, based on knowledge of the composition of the paint and its specified lifetime and application thickness, an estimate of the mean biocide release rate from an antifouling paint over its specified lifetime can be obtained by the mass-balance calculation method described in this International Standard. The calculation also allows an estimate to be obtained of the cumulative mass of biocide released over the first 14 days, and also the total mass of biocide released over the specified lifetime.

This method is intended to provide estimates of the amount of biocide released into the environment that are more suitable for use in environmental risk assessments than the results of laboratory-based test methods, such as ISO 15181 (all parts)[1], ASTM D6442[2] and ASTM D6903[3]. Biocide release rate data is a key input to the environmental risk assessment process for antifouling products, and so it is vital that the estimated biocide release rate that is used be both accurate and representative of the release rate to the environment in the relevant scenario and risk assessment case. In comparison with *in situ* biocide release rate values obtained by either direct or indirect measurements of the organotin and copper release rate from ships' hulls and from measurements made on panels exposed in harbours, all available data indicate that the results obtained using this calculation method overestimate the release rates of biocides under environmentally relevant in-service conditions. Published results demonstrate that the results of this calculation method are generally higher than direct *in situ* measurements of copper release rate from the hulls of harboured ships by a factor of about 4 or more for several commercial antifouling coatings[4]. A similar relationship is expected to be found for other biocides. Where the results of this calculation method are used in the process of generating environmental risk assessments, producing environmental loading estimates or for regulatory purposes, it is most strongly recommended that the relationship between calculated release rates and actual environmental inputs be taken into account to allow the most accurate and representative estimate of the biocide release rate from antifouling coatings under real-life conditions to be obtained. This can be accomplished through the application of appropriate correction factors[4].

Paints and varnishes — Modelling of biocide release rate from antifouling paints by mass-balance calculation

1 Scope

This International Standard specifies a method for estimating the mean release rate of biocide from an antifouling paint over its entire lifetime (in-service period) using a mass-balance calculation. If required, the cumulative total release of biocide over the first 14 days of the specified paint lifetime can also be calculated.

This International Standard is applicable to any antifouling paint that releases a biocide. Where an antifouling paint releases, or is assumed to release, more than one biocide, the calculation can be repeated to allow estimates of the release rate of each biocide to be obtained.

The calculated estimate of the total amount of biocide released by the coating over its lifetime can be considered as a worst case for the maximum amount released to the environment, and so the calculated mean release rate value should also be considered as the maximum possible mean release rate over the lifetime of the paint.

The calculated estimates are suitable for use in general environmental risk assessments, and the application of appropriate correction factors will allow the most accurate and representative environmental risk assessment to be made in the relevant scenario and risk assessment case[4].

There are no minimum or maximum limiting values of release rate which restrict the use of this method.

This International Standard is primarily directed towards the release of biocide from antifouling paints that have been applied to ship and boat hulls. It can, however, also be used for estimating biocide release from antifouling paints that have been applied to other objects.

2 Principle

The method is a generic empirical model of biocide release which is based on the underlying fact that the total amount of biocide released by an antifouling paint cannot exceed the amount of biocide which was originally present when the paint was manufactured and applied. In summary, the estimated mean biocide release rate over the lifetime of the paint is obtained by dividing the estimated mass of biocide that is released per unit area of painted surface by the lifetime of the paint. The estimated total mass of biocide that is released per unit area is derived from the percentage by mass of biocidal ingredient in the paint formulation, the mass fraction of the biocide in the biocidal ingredient, the percentage volume solids of the paint as manufactured, the density of the paint as manufactured, the dry-film thickness of paint applied and the estimated percentage of biocide that is released from the paint over its specified lifetime. It is normally assumed that 90 % of the biocide is released over the lifetime of the paint.

A dataset of experimentally determined release rates for a range of biocides and antifouling paint types, measured using ISO 15181 (all parts)[1], ASTM D5108[5], ASTM D6442[2] and ASTM D6903[3], shows that the biocide release rate typically changes over the immersion period. Generally, the biocide release rate is highest in the period immediately following immersion of the paint film. An estimated value of the cumulative biocide release over the first 14 days can be obtained by applying an appropriate multiplier to the estimated mean biocide release rate over the lifetime of the paint. Based on this typical behaviour, the default value of this multiplier is 30.

NOTE The calculation of the mean biocide release rate over the lifetime of the paint is independent of whether the release rate remains constant, falls, rises or varies in any regular or irregular way over the specified lifetime, including short-term changes in the release rate that arise in service for a vessel from alternating periods in motion and at rest. The calculated estimated release rate values are therefore most suited for use in environmental risk assessments where the modelled environmental scenario accounts for the presence of multiple vessels at different points in their service life.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
biocide
biocidally active chemical element, compound or species derived from a biocidal ingredient and released from an antifouling paint

NOTE Also known as “active substance”.

3.2
biocidal ingredient
substance in its supplied or manufactured state, including additives, impurities, by-products generated during production and degradation products generated after production, used in an antifouling paint to exert a controlling effect on harmful organisms by chemical or biological means

3.3
dry-film thickness
representative value of the mean thickness, after drying or curing, of an antifouling paint that is specified for application to a vessel or other object to provide antifouling protection for the lifetime of the paint

3.4
lifetime of the paint
representative value of the specified in-service period between planned painting and re-painting operations for a vessel or other object that is coated with the antifouling paint in question

4 Calculation and expression of results

4.1 Calculation of the estimated total mass of biocide released per unit area of antifouling paint film over the lifetime of the paint

Calculate the estimated total mass of biocide released per unit area of paint film over the lifetime of the paint, m_{rel}, in micrograms per square centimetre (μg·cm^{-2}), using Equation (1):

$$m_{rel} = \frac{L_a \times a \times w_a \times \rho \times DFT}{NV_V} \quad (1)$$

where

L_a is the percentage of biocide that is released from the paint film during the lifetime of the paint;

a is the mass fraction of biocide in the biocidal ingredient;

w_a is the content of biocidal ingredient in the paint formulation as manufactured, in % by mass;

ρ is the density of the paint as manufactured, in kg·dm^{-3} (g·cm^{-3});

DFT is the dry-film thickness specified for the lifetime of the paint, in μm;

NV_V is the non-volatile-matter content (volume solids content) of the paint, in % by volume.

This calculation is equivalent to multiplying the mass of biocide present per unit area of paint film by the percentage of biocide that is released over the lifetime of the paint (L_a).

Based on experience of antifouling paints, a value of $L_a = 90$ % should be used to represent a realistic worst-case maximum amount of biocide released over the lifetime of the paint. This value may be decreased or increased in cases where a lower or higher percentage of biocide is released over the lifetime of the paint.

The values for a, w_a, ρ, DFT and NV_V will depend on the particular composition of the paint and on its specified use characteristics. These values would normally be obtained from the paint supplier for any particular paint.

EXAMPLE

The calculation can be illustrated for the release of copper from the US Navy Formula 121 antifouling paint composition:

The paint composition is given in Table 1.

Table 1 — US Navy Formula 121 antifouling paint composition[6]

Component	% by mass
WW rosin	10,51
Tris(isopropylphenyl) phosphate	2,44
VAGH vinyl resin	2,69
Cuprous oxide	70,42
Anti-setting agents	0,25
Methyl isobutyl ketone	8,07
Xylene	5,62
Total	100,00

The paint formulation parameters are given in Table 2.

Table 2 — Paint formulation parameters for US Navy Formula 121 antifouling paint composition

Parameter	Value
Density, ρ, in kg·dm^{-3} (g·cm^{-3})	2,365
Volume solids content, NV_V, in % by volume	60,8
Specified lifetime of the paint, t, in months	24
Specified dry-film thickness, DFT, of the paint for the lifetime of the paint, in µm	150

The characteristics of the biocidal ingredient and biocide are given in Table 3.

Table 3 — Characteristics of the biocidal ingredient and biocide for US Navy Formula 121 antifouling paint composition

Characteristic	Value
Biocidal ingredient [cuprous oxide (Cu_2O)]	
Biocidal ingredient purity (% by mass)	97
Content of biocidal ingredient in the paint formulation as manufactured, w_a, in % by mass	70,42
Biocide [copper (Cu)]	
Mass fraction of biocide in the biocidal ingredient, a	0,86

From Equation (1),

$$m_{rel} = \frac{90 \times 0,86 \times 70,42 \times 2,365 \times 150}{60,8} = 31\,802 \ \mu g \cdot cm^{-2} \text{ of copper}$$

NOTE In this case, the mass fraction of biocide in the biocidal ingredient is derived from the number of copper atoms per molecule of cuprous oxide (= 2), the atomic mass of the biocide (= 63,55), the molecular mass of the biocidal ingredient (= 143,09), and the purity of the biocidal ingredient (= 97 %), and so

$$a = 2 \times \frac{63,55}{143,09} \times \frac{97}{100} = 0,86$$

4.2 Calculation of the mean biocide release rate over the lifetime of the paint

Calculate the mean biocide release rate over the lifetime of the paint, $\overline{R}$, in micrograms per square centimetre per day ($\mu g \cdot cm^{-2} \cdot d^{-1}$), using Equation (2):

$$\overline{R} = \frac{m_{rel}}{\left(\frac{365 \times t}{12}\right)} = 0,032\,9 \times \frac{m_{rel}}{t} \qquad (2)$$

where

m_{rel} is the estimated total mass of biocide released per unit area of paint film over the lifetime of the paint, in $\mu g \cdot cm^{-2}$ (see 4.1);

t is the lifetime of the antifouling paint, in months;

12 is the number of months in a year;

365 is the number of days in a year;

0,032 9 is a factor to convert months to days.

EXAMPLE

For the paint described in the Example in 4.1, where $m_{rel} = 31\,802\ \mu g \cdot cm^{-2}$ of copper and $t = 24$ months, substitution into Equation (2) gives:

$$\overline{R} = 0,032\,9 \times \frac{31\,802}{24} = 43,6 \ \mu g \cdot cm^{-2} \cdot d^{-1} \text{ of copper}$$

4.3 Calculation of the 14-day cumulative biocide release

If required, calculate the 14-day cumulative release of biocide, $R_{0,14}$, in µg·cm^{-2}, using Equation (3):

$$R_{0,14} = \overline{R} \times f \tag{3}$$

where

$\overline{R}$ is the mean biocide release rate over the lifetime of the paint, in µg·cm^{-2}·d^{-1} (see 4.2);

f is an empirical factor that reflects the relationship between the cumulative release of biocide over the first 14 days following entry to service and the estimated average release rate over the lifetime of the paint ($f = 30$).

The default value of $f = 30$ is based on the typical behaviour observed for a range of biocides and antifouling paint types. Alternative values may be used if the paint does not exhibit this typical behaviour.

Equation (3) may be modified to calculate the cumulative release of biocide over other periods by selecting a suitable value of f to reflect the behaviour of the paint.

EXAMPLE

For the paint described in the Example in 4.1, where $\overline{R} = 43{,}6$ µg·cm^{-2}·d^{-1} of copper and $f = 30$, substitution into Equation (3) gives:

$$R_{0,14} = 43{,}6 \times 30 = 1\,308 \text{ µg} \cdot \text{cm}^{-2} \text{ of copper}$$

5 Test report

The test report shall contain the following information:

a) all information necessary for the identification of the paint on which the procedure was performed;

b) a reference to this International Standard (ISO 10890:2010);

c) the identity of the biocide(s) for which the release rate was calculated;

d) the identity of the biocidal ingredient(s) in the paint;

e) the values of the parameters specified in 4.1, Equation (1), i.e.:

— the percentage of biocide that is released from the paint film during the lifetime of the paint, L_a,

— the mass fraction of biocide in the biocidal ingredient, a,

— the content of biocidal ingredient in the paint formulation as manufactured, w_a, in % by mass,

— the density of the paint as manufactured, ρ, in kg·dm^{-3} (g·cm^{-3}),

— the dry-film thickness, DFT, specified for the lifetime of the paint, in µm,

— the volume solids content (volume of dry paint film versus volume of paint as manufactured), NV_V, in % by volume;

f) the specified lifetime of the antifouling paint, t, in months [see 4.2, Equation (2)];