NATIONAL/INTERNATIONAL LEGISLATION ON ANTIFOULING

Managing of antifouling paints following the new Biocidal Product Regulation (BPR): a new running for products affecting the marine environment

Biocidal products in antifouling paints, used for protecting boat hulls from the unwanted accumulation of micro-organisms, plants, and animals on artificial surfaces (marine biological fouling), constitute a potential risk for the marine environment because of the presence, among other potentially toxic components, of organic compounds in their formulation, acting as biocide.
Due to their intrinsic properties and uses, biocidal products may pose health risks and be harmful to the environment. It is therefore crucial to ensure that only safe biocidal products are placed on the market. To this aim in the latest years several European directives and regulations have come into force

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Antifouling paints, utilities and uses

Boats spend a large proportion of their working life partly submerged in water. As with all objects subject to long periods of time in water, boat hulls are subject to colonization by the many micro-organisms which inhabit the aquatic environment. This colonization is known as *"fouling"*. Boat hulls are susceptible to all types of fouling, which can cause increased drag on the hull when it is not attended to, leading to increased fuel consumption, and eventually significant damage to the boat structure. It is, therefore, necessary to apply some coatings to protect the hull against infestation. These coatings are generally known as antifouling paints and are applied to the hull at regular intervals.
Antifouling paints usually contain a biocide, or toxin, held within the structure of the paint [1]. The coating is designed to leach biocide slowly into the marine environment, preventing any organism from adhering to the paint by poisoning the settling organisms.
The nature of a biocide is such that it can potentially have harmful effects, not only on the fouling organism it

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Active substances	International Chemical Identification	N. CAS	CLP Classification
Chlorothalonil	tetrachloroisophthalonitrile	1897-45-6	Skin Sens. 1; Eye Dam. 1; Acute Tox. 2; STOT SE 3; Carc.2; Aquatic Acute 1; Aquatic Chronic 1(*)
Dichlofluanid	N-dichlorofluoromethylthio-N',N'-dimethyl-N-phenylsulfamide	1085-98-9	Skin Sens. 1; Eye Irrit. 2 Acute Tox. 4; Aquatic Acute 1 (*)
Diuron	3-(3,4-dichlorophenyl)-1,1-dimethylurea	330-54-1	Acute Tox. 4; Carc. 2 STOT RE 2; Aquatic Acute 1; Aquatic Chronic 1 (*)
Irgarol 1051	N'-tert-butyl-N-cyclopropyl-6-(methylthio)-1,3,5-triazine-2,4-diamine	28159-98-0	Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1
Maneb	manganese ethylenebis(dithiocarbamate) (polymeric)	12427-38-2	Skin Sens. 1Eye Irrit. 2 Acute Tox. 4 Repr. 2 Aquatic Acute 1 Aquatic Chronic 1 (*)
Sea-Nine211	4,5-dichloro-2-octyl-2H-isothiazol-3-one	64359-81-5	Acute Tox. 4 Skin Corr. 1B Skin Sens. 1 Acute Tox. 3 Eye Dam. 1 Aquatic Acute 1
TCMS piridina	methyl-2,3,5,6-tetrachloro-4-pyridylsulphone	13108-52-6	Acute Tox. 4 Skin Sens. 1 Eye Irrit. 2 (*)
Thiram	tetramethylthiuram disulphide	137-26-8	Acute Tox. 4 Skin Irrit. 2 Skin Sens. 1 Eye Irrit. 2 Acute Tox. 4 STOT RE 2 Aquatic Acute 1, Aquatic Chronic 1 (*)
pyrithione zinc	pyrithione zinc	13463-41-7	Acute Tox. 3 Eye Dam. 1 Acute Tox. 3 Aquatic Acute 1
fenoprop	2(2,4,5trichlorophenoxy)propionic acid	93-72-1	Acute Tox. 4 Skin Irrit. 2 Aquatic Acute 1 Aquatic Chronic 1 (*)
Zineb	Zinc,ethylenebis(dithiocarbamate) (polymeric)	12122-67-7	Skin Sens. 1 STOT SE 3 (*)
Ziram	zinc bis dimethyldithiocarbamate	137-30-4	Acute Tox. 4 Skin Sens. 1 Eye Dam. 1 Acute Tox. 2 STOT SE 3 STOT RE 2 Aquatic Acute 1 Aquatic Chronic 1 (*)

(*) Harmonised classification, Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation)

TABLE 1 Active substances most commonly used in antifouling paints

is designed to deter, but also on other marine life forms unconnected with fouling activity.

Organotin compounds (TBT or tributyltin) replaced the use of cuprous oxide (Cu_2O), giving better performance antifouling paints and increased service life. However, it became evident in the 1980s that their continued use was causing severe damage to shellfish communities and, in particular, dog whelk populations [2]. In fact, TBT

causes reproductive anomalies and population effects in certain species of marine snails at concentrations in the parts-per-trillion range, and has been implicated in endocrine effects on other organisms [3,4]. TBT is associated with immune suppression and other adverse effects in marine species, it is slow to degrade, and is very persistent in sediments, where many affected species live and feed [5].

This resulted in the implementation, in 1987, of a Europe-wide ban on the use of TBT in antifouling paints on boats. TBT-free antifouling paints have been developed since 1990. The ban on TBT resulted in a shift back to paints containing copper as the main biocide. Copper is included in antifouling paints most commonly as cuprous oxide, but also as cuprous thiocyanate and metallic copper powder. It is widely felt that although the performance of copper biocides cannot approach that of TBT, they remain the most effective alternative [6]. Currently there is a great deal of research into alternative forms of biocides, particularly those of organic origin. These, however, tend to be less universally effective than TBT and, in particular, may deter only specific types of fouling organisms. As a result of these 'species-specific' characteristics, antifouling paints on the market today contain a mixture of biocides in order to be effective against most of marine micro-organisms.

The most widely used biocides in paints today are shown in Table 1, with their classification according to Regulation (EC) No. 1272/2008/EU (CLP) [7].

Overview of legislation on antifouling paints

After an initial phase of national legislative measures to regulate the use of biocidal products in antifouling paints, in 2001 an action phase at European level began with the "Convention on the Control of Harmful Antifouling System on Ships" (AFS Convention) that prohibited the use of harmful organotins in antifouling paints used on ships, and established a mechanism to prevent against the potential future use of other harmful substances in antifouling systems.

Later Regulation (EC) 782/2003 [8] on the prohibition of organotin compounds on ships, imposed Member States the same deadlines and conditions of the AFS Convention; in this way also the Member States that had not ratified the Convention were forced to comply with the European legislation.

At the same time, the environmental legislation enacted in the same years had an impact on the use of organotin compounds in antifouling paints, particularly TBT. Directive 2000/60/EC (EU Framework Water Directive) [9] provided for the establishment of a priority list of substances as a basis for shared actions aimed at reducing or eliminating discharges and releases of hazardous pollutants in the aquatic environment (Decision 2455/2001/EC [10]) and the establishment of environmental quality standards (EQS) for the substances in surface waters (Directive 2008/105/EC [11]).

TBT was included among the priority hazardous substances of Decision 2455/2001/EC and its environmental quality standards were included in Annex I of Directive 2008/105/EC. The European environmental legislation in the first instance applied to surface water was then extended to the marine environment with Marine Strategy Framework Directive (Directive 2008/56/EC [12]), which aims to achieve good environmental status of the European seas by 2020.

Until 1 September, 2013, Biocidal Product Directive (BPD) 98/8/EC [13], concerning the placing of biocidal products on the market, was applied to antifouling paints. Among its objectives, this Directive had the establishment of a list of active substances which may be used in biocidal products, authorizing the placing on the market of biocidal products in the Member States and the mutual recognition of authorizations within the European Community. Starting from 1 September, 2013, the BPD has been repealed by the new Reg. (UE) n. 528/2012.

The Biocidal Products Regulation (BPR, Regulation (EU) 528/2012) [14] concerns the placing on the market and use of biocidal products, which are used to protect humans, animals, materials or articles against harmful organisms like pests or bacteria, by the action of the active substances contained in the biocidal product.

This regulation is aimed at improving the functioning of the biocidal products market in the EU, while ensuring a high level of protection for humans and the environment. The new Regulation will also remedy a number of weaknesses that were identified during the

11 years of implementation of Directive 98/8/EC.
In fact, the new text simplifies and streamlines the requirements for approving active substances and authorizing products. The new provisions will also reduce animal testing by making data sharing compulsory and encouraging a more flexible and intelligent approach to testing. A dedicated IT platform (the Register for Biocidal Products) will be used for submitting applications as well as recording decisions and disseminating information to the public [15].
The text is also a major breakthrough for the internal market with the creation of a Union authorisation of biocidal products, which will allow industry to directly place their products on the entire Union market.
The text of the BPR was adopted on 22nd May, 2012, and it entered into operation on 1st September, 2013, with a transitional period for certain provisions, repealing the Biocidal Products Directive (Directive 98/8/EC).

Definitions

The BPR (art. 3.1.a) defines active substances and biocidal products as follows:
"Active substance" is *"a substance or a micro-organism that has an action on or against harmful organisms."*
"Biocidal product" is:
- *any substance or mixture, in the form in which it is supplied to the user, consisting of, containing or generating one or more active substances, with the intention of destroying, deterring, rendering harmless, preventing the action of, or otherwise exerting a controlling effect on, any harmful organism by any means other than mere physical or mechanical action;*
- *any substance or mixture, generated from substances or mixtures which do not themselves fall under the first indent, to be used with the intention of destroying, deterring, rendering harmless, preventing the action of, or otherwise exerting a controlling effect on, any harmful organism by any means other than mere physical or mechanical action.*

The new Regulation on biocidal products contains provisions, which apply not only to biocidal products but also to all articles which have been treated or incorporate a biocidal product. According to article 3.1.l, a treated article is defined as *"any substance, mixture or article which has been treated with, or intentionally incorporates, one or more biocidal products".*
According to the regulation, articles can only be treated with biocidal products containing active substances approved in the EU. This is a change from the BPD (repealed by the BPR from 1st September, 2013), where articles imported from third countries could be treated with substances not approved in the EU – such as, wood treated with arsenic, and sofas and shoes containing DMF.

Differences between old and new legislation

The aim of the new Regulation is to improve the functioning of the internal market in biocidal products whilst ensuring a high level of environmental and human health protection.
Furthermore, the new Regulation aims to simplify the approval of active substances and authorisation of biocidal products and introduces timelines for Member State evaluations, opinion-forming and decision-making. It also promotes the reduction of animal testing by introducing mandatory data sharing obligations and encouraging the use of alternative testing methods.
As in the previous directive, the approval of active substances takes place at Union level and the subsequent authorisation of the biocidal products at Member State level.
This authorisation can be extended to other Member States by mutual recognition. However, the new regulation also provides applicants with the possibility of a new type of authorisation at Union level (Union authorisation – art. 3.1.n) for biocidal products which have similar conditions of use, with the exception of biocidal products that contain active substances that fall under Article 5 (exclusion criteria) and those of some product- types – e.g., rodenticides, avicides, piscicides, control of other vertebrates and antifouling products (art. 42.1).
Before they are put on the market, all biocidal products must be authorized and all the active substances present in the biocidal products must be previously approved.
Compared to the previous regulatory framework, the main differences concern greater safety of products on the market, the simplification of the authorization procedure and greater speed in the marketing.

In terms of safety, controls are strengthened to prevent biocides from being harmful to humans and the environment; most hazardous substances, such as carcinogens, mutagens or toxic to reproduction will be prohibited in principle; specific rules for security checks are provided on products marketed in nanoform, for which there is also a labeling requirement.
In terms of simplification, the existing authorisation procedures are simplified, except for biocidal products containing nanomaterials; the sale will be made more quickly by setting new deadlines for submission of authorization applications; mutual recognition between Member States becomes easier.

The Revision Programme

According to the BPD, active substances in biocidal products, placed on the EU market prior to 14th May, 2000 (all notified active substances), had to be reviewed in a Community program to be carried out within 14 years. If, after the review, they were accepted for use in biocidal products in specific product types, they would be included in ANNEX I, IA or IB to the BPD.
The first phase of the review program was established by Commission Regulation (EC) 1896/2000 [16], which provided for the identification or notification by producers and formulators to the European Chemicals Bureau of all existing active substances before 28th March, 2002. The second phase of the review program was established by Commission Regulation (EC) 2032/2003 [17]. This Regulation has been amended by Commission Regulation (EC) 1048/2005 [18] and by Commission Regulation (EC) 1849/2006 [19].
On 4th December, 2007, the Commission adopted Regulation (EC) No 1451/2007 [20], which repeals Regulation (EC) No 2032/2003 and entered into force on 31st December, 2007. The Regulation (EC) 1451/2007 regards the second phase of the 10-year work program established by article 16.2 of BPD.

Approval stage of active substances

Most of the active substances used in antifouling paints are still included in the review program of the BPD. At the moment only one substance (dichlofluanid - Dir. 2007/20/CE) has been approved. Three substances were banned for this use: Chlorothalonil, Diuron and Ziram. Some other substances are under evaluation for this use.
The next antifouling active substances (biocidal Product Types 21 – PT21) [21] for which a decision is expected to be taken are Zineb, DCOIT and copper pyrithione.
For this reason the European Commission's DG Environment is studying a work programme finalized to decide which active substances could be used in antifouling paints. To this aim the following actions are proposed:

- To approve all active substances in antifouling products (PT21) on the basis on the same generic conditions. Additional specific conditions could be added on a case-by-case basis (for instance, if the substance is a skin sensitizer, the standard paragraph related to treated articles should be added).
- To establish the same expiry date of approval for all existing active substances (ASs) placed on the market for PT21, in order to evaluate the renewal of their approval at the same time.
- To flag specific concerns related to each individual active substance in the assessment report.
- Furthermore it is proposed to have a common date of expiry of the approval: this date could be set on 31/12/2025.

In order to respect this date and then to have a clear situation on which active substances can be used safely in antifouling paints, the following time schedule has been proposed (Figure 1).
In view of this work programme, authorisations for antifouling paints will be subject to the following conditions:

(1) To manage the risks for industrial/professional users when they apply the biocidal product (BP), safe operational procedures and appropriate organizational measures shall be established. Where exposure cannot be reduced to an acceptable level by other means, products shall be used with appropriate personal protective equipment.
(2) Considering that antifouling products are very specific products, and considering good practices of use of biocidal products, the Commission's services could consider acceptable to impose that

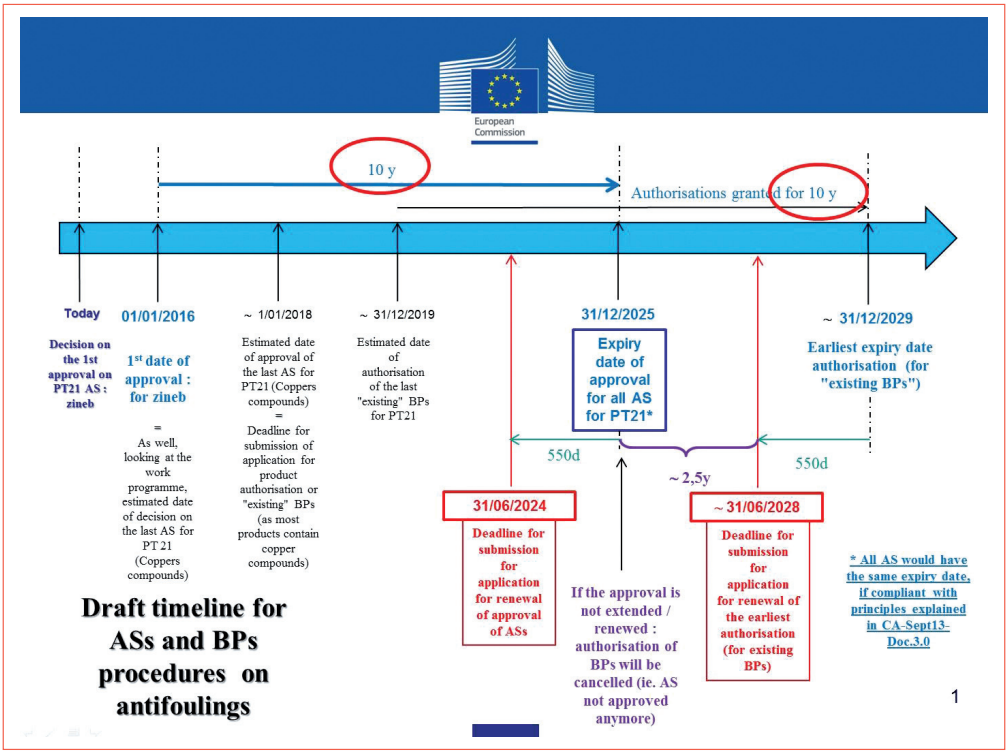

FIGURE 1 Time schedule for active substances and biocidal products on antifoulings

all products for use by non-professionals are sold with the appropriate protective gloves, and give indications on whether other PPE shall be used. Therefore, Products authorised for non-professionals user shall be sold with the appropriate protective gloves. Labels and, where provided, instructions for use shall indicate whether other personal protective equipments shall be used.

(3) To manage the risks for the environment (soil organisms, groundwater, and run-off to surface water, etc…) during the application, maintenance and repair activities when they apply the biocidal product labels and, where provided, safety data sheets of products authorised shall indicate that application, maintenance and repair activities shall be conducted within a contained area and on impermeable hard standing with binding to prevent against direct leaching and minimize emissions to the environment, and that any leaching or waste containing [the substance] shall be collected for reuse or disposal.

(4) To manage the potential uses where there might be the need to settle or review existing MRLs (fishnets coatings, small professional boats used in mussels/oyster production, paints used to cover artificial ponds for growing fish/seafood products, etc…), for products that may lead to residues in food or feed, the need to set new or to amend existing maximum residue levels (MRLs) in accordance with Reg. (EC) No 470/2009 [22] or Reg. (EC) No 396/2005 [23] shall be verified, and any appropriate risk mitigation measures shall be taken to ensure that the applicable MRLs are not exceeded.

As far as possible, decisions of authorisation of antifouling products should be harmonised. Nevertheless, Member States could derogate from the mutual recognition and decide to refuse to grant, or restrict the use of antifouling products at the regional/

local level, in accordance with Article 37 of the BPR, for instance to ban the use in sensitive areas, specific marinas, specific coastal zones etc.
It has to be noted that boats are "treated articles", as they have been treated with a biocidal product (i.e., antifouling paint). Boats that are *placed on the market* (i.e., the first made available on the EU market according to Article 3(1)(j)) have to comply with provisions of the BPR. So have fishnets treated with an antifouling, or other aquaculture equipments.

Conclusions

To date it is not possible to avoid the use of antifouling paints. The deadlines foreseen by the European Commission still imply a long use of these products, with consequences on the environment. The new EU regulation on biocides will have the result of banning some products, introducing some measures for increasing human health protection and some geographical restrictions, but antifouling paints containing biocidal products will continue to be sold for decades. This environmental and safety issue cannot be solved only by regulating the substances, but also by meaningful R&D outcomes.
At present, mitigating measures could be represented by silicone-based antifouling paints, which work by preventing or greatly reducing the adhesion of marine "fouling" to boat hulls. They are used from time to time on immersed parts of some military ships and on submarines where metal-free paints are needed. Recently these silicon based paints have been used on immersed parts of great freight ships.
Other developments could arise from the use of paints containing biomolecules with antifouling properties and from antifouling action developed by physical means, as reported in a recent communication of an Italian company, describing the antifouling action of CO_2 bubbles developed on immersed parts by enzyme-based paints [24].

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