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Thematic Strategy on Sustainable Use of Plant Protection Products – Prospects and Requirements for Transferring Proposals for Plant Protection Products to Biocides

Annex IV:
Case study on PT 21: Antifouling products

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Contents

List of Abbreviations

ACP	Advisory Committee on Pesticides
AFP	Antifouling Product
ANZECC	Australian and New Zealand Environment Conservation Council
BAT	Best Available Techniques
BCF	British Coatings Federation Ltd
BPD	Biocidal Products Directive
BUWAL	Bundesamt für Umwelt, Wald und Landschaft (Swiss Agency for the Environment, Forests and Landscape)
CEPE	European Committee for Paints and Inks
COWI	Consultancy within Engineering, Environmental Science and Economics
CPD	Controlled depletion polymer
DCOIT	4,5-dichloro-2-octyl-2H-isothiazol-3-one
DDT	Dichlordiphenyltrichlorethan
DIN	Deutsche Institut für Normung; German Institute for Standardization
Diuron	3-(3,4-Dichlorphenyl)-1,1-dimethylharnstoff
DIY	Do It Yourself
DK	Kingdom of Denmark
DMS	*N,N*-Dimethylsulfamide
EC_{50}	half maximal effective concentration
ECI	European Copper Institute
ESD	Emission Scenario Document
ESIS	European chemical Substances Information System
EU	European Union
FIN	Republic of Finland
FR-coating	Foul release coating
GNF	Global Nature Fund
GUV	Deutsche Gesetzliche Unfallversicherung
HPW	High pressure water washing
HSE	Health and Safety Executive
HVLP	High Volume Low Pressure- Technique
IMO	International Maritime Organisation
IPPIC	International Paint and Ink Council
Irgarol®	2-Methylthio-4-*tert*-butylamino- 6-cyclopropylamino-*s*-triazin
ISO	International Organization for Standardization
LimnoMar	Labor für Limnische, Marine Forschung und Vergleichende Pathologie; Laboratory for Freshwater, Marine Research and Comparative Pathology
M&R	Maintenance & Repair
MAMPEC	Marine Antifoulant Model to Predict Environmental Concentrations
MS	Member State
MSCA	Member States Competent Authorities

MSDS	Material Safety Data Sheet
N	Dangerous for the environment
NDMA	*N*-Nitrosodimethylamine
NL	Kingdom of the Netherlands
OECD	Organisation for economic Co-operation and Development
OSPAR	Oslo-and Paris-Conventions
PBT	Persistant, Bioaccumulative, Toxic
PDMS	Poly dimethyl siloxane
PPP	Plant Protection Products
PT 21	Product Type 21
QWASI	Quantitative Water, Air and Soil Interaction
R	Risk Statement
RA	Risk assessments
REACH	Regulation (EC) No 1907/2006 on the Registration, Evaluation, Authorization and Restriction of Chemicals
REMA	Regulatory Environmental Modelling of antifouling
RMM	Risk Mitigation/Management Measure
SDS	Safety Data Sheet
SE	Kingdom of Sweden
SED	Solvent Emission Directive (1999/13/EC)
SME	Small and medium enterprises
SPC	Self-Polishing Coating
STP	Sewage Treatment Plant
T	toxic
T^+	very toxic
TBT	Tributyltin Compounds
Teflon®	Polytetrafluorethene
TH	Technische Hochschule
TOT	Triorganotin
TRGS	Technische Regeln für Gefahrstoffe Technical Rules for Hazardous Substances
UBA	Umweltbundesamt; Federal Environment Agency, Germany
UK	United Kingdom of Great Britain and Northern Ireland
UV	Ultraviolet
UVV	Unfallverhütungsvorschriften
VDL/DSV	Verband der deutschen Lackindustrie
VOC	Volatile Organic Compounds
vPvB	very persistant very bioaccumulative
WFD	Water Framework Directive
WWF	World Wide Fund For Nature
WWT	Waste Water Treatment
WWTP	Waste Water Treatment Plant
Xn	Harmful
Zineb	zinc ethane-1,2-diylbis(dithiocarbamate)

1 Introduction

1.1 Target organisms

Micro- and macro organisms settle on surfaces placed in salt and fresh water within a short time. The type and intensity of fouling depends on different environmental factors e.g. temperature, salinity, nutrient supply and light. Fouling is more rapid in salt water because of the diversity of organisms. Up to 150 kg of organisms can settle on one m² surface area within six months (Peters et al. 2002, UBA, 2007). Fouling in general is unwanted e.g. as increased flow resistance on ships leads to an increase of fuel consumption – the frictional resistance can raise fuel consumption by up to 40% and this will result in increased bunker costs, expenses due to lost earnings or time delay; also, manoeuvrability is decreased and the possibility of premature corrosion is increased. Another negative effect is the potential for transmigration of species (UBA, 2007). Therefore, antifouling products are used to prevent surfaces from unwanted growth and settlement of fouling organisms. Target organisms are all microbes and higher forms of plant or animal species, micro- and macro organism (bacteria, algae and crustaceans) in sea water and fresh water that may possibly settle on ship hulls and other surfaces.

1.2 Use and user groups

The highest amount of antifouling product (AFP) is used for ship hulls (commercial and pleasure). The worldwide demand for this use is estimated at 95% of the total demand. Other uses are aquaculture equipment (e.g. fish nets), pipelines, and harbour and offshore constructions.

The use of AFP in offshore construction, e.g. drilling platforms, is considered as the most important after the use on ship hulls, approximately 2.5 % of the total global demand (van de Plassche et al., 2004; OECD 2005). Nevertheless, the use of AFP in German coastal waters may be less, because the life span of underwater constructions is much longer than the period over which release of an antifouling paint could guarantee a fouling free surface[1].

1 Personal communication B. Waterman, limnomar, 7.12.2009 and HSE corrosion protection – offshore technology report 2001/011

The application of AFP and paints for ship hulls takes place in ship building yards and maintenance and repair yards. For the latter, yards for commercial and for pleasure boats can be distinguished. Professional application on vessels of > 25 m and < 25 m length is carried out by both trained and untrained workers. The treatment of vessels < 25 m is mainly done by untrained professional users and amateurs. Yacht building and repair ranges in scale from craftsmen to large manufacturers and approximately 98% of these businesses are small and medium enterprises (SME). While in new construction the coating is generally agreed between shipyard and customer, in maintenance and repair yards the customer has more influence on coating choice and may purchase the coatings directly (UBA, 2007).

For other uses, AFP are mainly used by specifically trained amateurs.

1.3 Active substances

The Biocidal Products Directive defines PT 21 as “Products used to control the growth and settlement of fouling organisms (microbes and higher forms of plant or animal species) on vessels, aquaculture equipment or other structures used in water.”

Currently the 5th EU review programme contains 10 substances, organic and inorganic (metal-based), some of these are also used as PPP e.g. Tolylfluanid and copper thiocyanate. The most important substances in terms of production tonnage were DCOIT (4,5-dichloro-2-octyl-2H-isothiazol-3-one), Diuron[2], and Zineb (Kjolholt 2008 cited in COWI, 2009). Diuron is not longer included in the review programme for use in PT 21. Another important boosting antifouling agent is Irgarol 1051, which is used to supplement copper based paints (Gardinali et al. 2004). Irgarol 1051 was detected in surface waters from South Florida (Miami region). Table 1 gives an overview of active substance included in the 5th review programme and the classification found in the ESIS data base or self-classification by manufacturers.

[2] For Diuron a notification is only planned for PT 7 and 10.

Table 1: Substances included in the 5th review programme

Substance group	Substances	Classification
Organic	**Tolyfluanid** (dichloro-N-[(dimethylamino)sulphonyl]fluoro-N-(p-tolyl)methanesulphenamide, EC Nr: 211-986-9)	very toxic T+, R26, dangerous for the environment N, R 50
	Dichlofluanid (EC Nr: 214-118-7)	harmful Xn, dangerous for the environment N, R50
	Cybutryne/ Irgarol (N'-tert-butyl-N-cyclopropyl-6-(methylthio)-1,3,5-triazine-2,4-diamine), (EC Nr: 248-872-3,)	not classified in ESIS database (self classification: R 43, N ; R 50/53)
	DCOIT (4,5-dichloro-2-octyl-2H-isothiazol-3-one) (EC Nr: 264-843-8)	not classified in ESIS (self classification: Xn; R21/22, C; R34, Xi; R37, R43 N; R50)
Inorganic (metal based)	**Copper** (EC Nr: 231-159-6)	not classified in ESIS
	Dicopper oxide (EC Nr: 215-270-7)	harmful Xn, dangerous for the environment N, R50-53
	Copper thiocyanate (EC Nr: 214-183-1	not classified in ESIS (self classification: Xn; R20/21/22 R32 N; R50/53)
	Copperpyrithione Bis(1-hydroxy-1H-pyridine-2-thionato-O,S)copper (EC Nr: 238-984-0,)	not classified (self classification: T+; R26 Xn; R22 Xi; R41, R38 N; R50)
	Zineb (EC Nr: 235-180)	irritant Xi
	Zinc Pyrithione (EC Nr: 236-671-3)	not classified in ESIS (self classification: T, R23/24/25)

Organotin compounds for antifouling have been restricted by Commission Directives 1999/51/EC and 2002/62/EC. The International Convention on the Control of Harmful Antifouling Systems on Ships, developed by the International Maritime Convention Organisation (IMO), entered into force on 17 September 2007 and will end the use of organotin compounds globally. Nevertheless, sealed organotin antifouling paints and other antifouling substances no longer used in the EU can still be found on ship hulls and can be released during maintenance and repair and metal recycling.

AFP based on copper contain it at up to 50% w/w as the main biocide (UBA, 2007). Copper-containing AFP is designed to leach out copper ions at a concentration at the surface of the vessel that repels organisms from attaching to the ship hull. Copper prevents barnacles, mussels, shells, weed and similar organisms (macro-fouling) from settling. Micro-fouling formed on the surface may promote macro fouling. Therefore, co-biocides are added such as Irgarol and Zineb (International Council of Marine Industry Associations, 2006). Other forms of biocidal products to be considered are substances used as booster biocides and co-biocides that intensify the effect.

For aquaculture equipment, copper is the most used product among OECD member countries. While in the UK and FIN cuprous oxide is used, in Spain chromium oxide is used (OECD 2005).

For the use of antifouling substances, a differentiation between vessels of > 25 m and < 25 m has been made as MS have different permits for use on yachts < 25 m, according to restrictions for triorganotin-containing paints (Readman et al. 2002 cited in COWI, 2009).

A study of AFP used in freshwater along the UK coastline was carried out in 2001 to target future monitoring (HSE, 2001). The study referred to initial reviews of the environmental effects of Triorganotin compounds (TOTs) following the restrictions already placed upon the use of TOTs on boats > 25 m long. As a result, it was considered that additional restrictions were likely to be placed upon the future use of TOTs. The Advisory Committee on Pesticides (ACP) was concerned that, if further restrictions were placed on TOTs, the main alternatives, which were copper compounds and organic biocides or combination of them, would be used much more widely. The study also referred to another review of copper compounds undertaken by HSE, which indicated that the restriction of use of TOTs would not result in an increase in the environmental concentration of copper that would pose a higher risk than TOTs (HSE, 2001). The copper review also highlighted a new concern; the use of biocides added to copper products to boost their effectiveness against copper-tolerant algae, known as booster biocides, is likely to increase following TOT restrictions. As a result, a review of booster biocides was carried out in 2000, which led to the use of two booster biocides (Diuron and Irgarol 1051) being revoked (HSE 2001). The aims of the survey were to:

- highlight locations with the highest boating densities, to help target questionnaires and future monitoring
- establish boating patterns in freshwaters (seasonal variability in pleasure vs. commercial craft, moorings vs. day trippers) to confirm highest boating densities
- establish the extent of usage of AFPs in freshwaters in order to find out whether an additional risk assessment and/or monitoring would be necessary
- collect the information needed to develop a new risk assessment strategy for 'lake' systems, including average boat size, and quantity/frequency of use of AFPs
- to identify the main AFPs used in freshwaters and hence the chemicals that may need to be monitored for.

In general antifouling coatings can be divided into eroding and non-eroding coatings (Table 2, Mukherjee, A., 2009, Waterman et al., 2004).

Table 2: Characteristics of different antifouling coatings

Coating	Characteristics
Non-eroding coating	
1) Insoluble matrix coating	Also called: contact leaching or continuous contact paint The polymer matrix (e.g. vinyl, epoxy acrylic, chlorinated rubber polymers) is insoluble, it does not erode after immersion in water, the biocide diffuses out of the polymer matrix into water, over a period of time the release rate falls below the level required to prevent fouling These coatings have a lifetime of 12 to 18 (up to 24) months and are difficult to recoat
Eroding coating	
2) Soluble matrix paint	Also called: conventional antifouling system, controlled depletion polymer (CDP) In this paint the active substance is physically dispersed in the matrix which is usually natural resin based. The active substance is incorporated into a binder mixture of gum rosin and plasticizer which can dissolve into water. Once the paint is in contact with water the rosin dissolves and the biocide can migrate to the surface. The soluble matrix paint does not loose antifouling efficiency as a function of time; the coating has a life time of about 12-18 months.
3) Self-polishing copolymer	This kind of antifouling paint is usually based on acrylic polymers. The biocide is incorporated into a soluble paint matrix. On immersion into seawater, the soluble pigment particles dissolve and leave behind the insoluble biocide-copolymer and backbone polymer matrix. This matrix is hydrophobic and therefore water can only fill the pores left free by the pigment. When the vessel is in movement the chemical binding between biocide-copolymer and backbone polymer is released and the surface is polished by depleting of the topmost layer. This permits a slow and controlled leaching rate. Under stationary conditions there is renewal of the paint layer. Typically, the polishing rate is between 5 µm and 20 µm per month. The polishing rate and the release of biocide can be altered to suit different applications like vessel speed, water routes. The efficiency can be increased by adding booster

Coating	Characteristics
	biocides. The life span is about 3 to 5 years and it is not necessary to remove old paint before the application of new paint.
4) Foul release coating	Does not prevent fouling but reduces the attachment strength of (micro)organisms. FR-coatings have restricted applications since they are only effective at high relatively speed (Dafforn et al. 2011).

Research and development on biocide free alternatives is still ongoing (Bergenthal, 1999; Waterman et al. 1999, 2003; WWF, 2002). There are biocide free antifouling coatings already available which act by their specially designed surfaces (low-friction and ultra-smooth) that inhibit the attachment of fouling organisms. Non-eroding and eroding coatings can also be distinguished here (Table 3).

Table 3: Characteristics non-biocidal antifouling coatings

Coating	Characteristic
Non-eroding coating	
1) Non-stick coating	These coatings are silicone- (poly-dimethyl siloxane PDMS) or Teflon®-based. They have extremely low surface energy, low micro-roughness, high elastic modules and low glass transition temperature. They are used on high speed and high activity vessels like passenger vessels, container vessels. Disadvantage of these coatings are their high costs, difficult application procedures, low resistance to abrasion and an average speed of 20 knots is needed. The life span is up to 5 years. Silicon-free non sticking coatings have only a low efficiency.
Eroding coatings	
2) self-polishing and ablative systems	These coatings perform similarly to biocide containing self-polishing coatings but use non-toxic compounds

Other kinds of biocide free anti-fouling systems include coatings containing nano-particles that reduce friction. According to a recent study by the German UBA (UBA 2010, Watermann et al. 2010), no information about the nature of the nano-particles is made available in the Technical Data Sheets or Safety and Health Data Sheets of the products. The study concludes that, due to the lack of proven efficiency, nanotechnology based antifouling systems and the additional use of biocides without declaration on leisure boats and on the professional market cannot be regarded as alternatives to antifouling systems which do not use nanotechnology.

1.4 Formulation types and mode of application

Antifouling substances used for ship hulls are often added to liquid paints. But AFP are also offered stand-alone and have to be mixed with paints and thinners before application.

Concerning different forms of application, the following sectors and user groups have to be distinguished:

- New building commercial ships: only professional users
- New building pleasure craft: only professional users
- Maintenance and repair – commercial ships: professional users
- Maintenance and repair – pleasure craft: professional and non-professional users

Sprayers: Paints used with airless spray guns normally consist of high amounts of solvents, whereas paints used by rolling and brushing are more viscous. Air spray application is not allowed according to the former TRGS 516 on antifouling paints and airless spray guns are normally used by professional users only.

Brushing and rolling: Non – professional users mainly use brush and roll techniques; professionals may also use a combination of these, together with spraying applications.

Other uses – Dipping: Fish nets are mainly dipped into the AFP.

2 Possible emission routes and available ESD

2.1 Antifouling products used on ship hulls

2.1.1 Emission during service life

The AFP on vessels continuously release to the water during service life. Therefore, this is expected to be the main environmental emission route. It is estimated that 1/3 – 2/3 of the applied paint is released to the water during use (Madsen at al. 1998 cited in Cowi 2009). According to a calculation method developed by CEPE, around 70% of the AFP is released during service life while 30% is retained in the paint film at the end of its specified lifetime (OECD 2005). This method is based on a mass-balance calculation with a default of 30% retention and therefore may not be a realistic worst-case approach[3]. Current laboratory methods are likely to over-estimate the leaching rate but can be used in a precautionary approach for environmental risk assessment. With regard to risk assessment, considering that most coatings work by erosion/polishing of the existing paint layer, the potential release of biocide over lifetime would be closer to 100%. Therefore, representatives of Members State Competent Authorities welcomed a proposal presented at a workshop for technical experts evaluating active substances that the anticipated loss of 90% should be used as a default unless alternative data are available. The CEPE mass-balance method will be used in the Review Program as the method to determine the steady state leaching rate (MSCA, 2007).

During the service life stage, AFP leach continuously, directly into surface water (marine or fresh water). Substances can adsorb to particle matter and subsequently settle in the sediment. Released to water, degradation (hydrolysis, photolysis), volatilisation to air and hydrodynamic transport have to be considered in the assessment of substances.

According to estimates by OSPAR, quite a substantial proportion (around 14 to 19 %) of all copper and all zinc entering the Greater North Sea are losses from antifouling coatings and ship anodes. It is expected that this ratio will increase with the substitution of TBT as an antifouling agent by copper-based paints (OSPAR, 2006).

Other emissions enter the environment (air, water, soil) through maintenance and repair and subsequent application (see next chapter).

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[3] In 2006 a workshop on the harmonisation of leaching rate determination for AFP was held, concluding that the standardised laboratory methods overestimate the leaching rate compared to the situation under field steady state conditions. The application of the CEPE mass-balance method in the Review Program has been accepted while the anticipated loss of the active substance to the environment in the CEPE mass-balance method was set at 90%. Because the mass-balance method may still overestimate leaching rates, compared to data from the U.S. Navy, a correction factor of 2.9 may be applied to the PEC/PNEC risk quotient in a second tier assessment based on a weight of evidence approach.

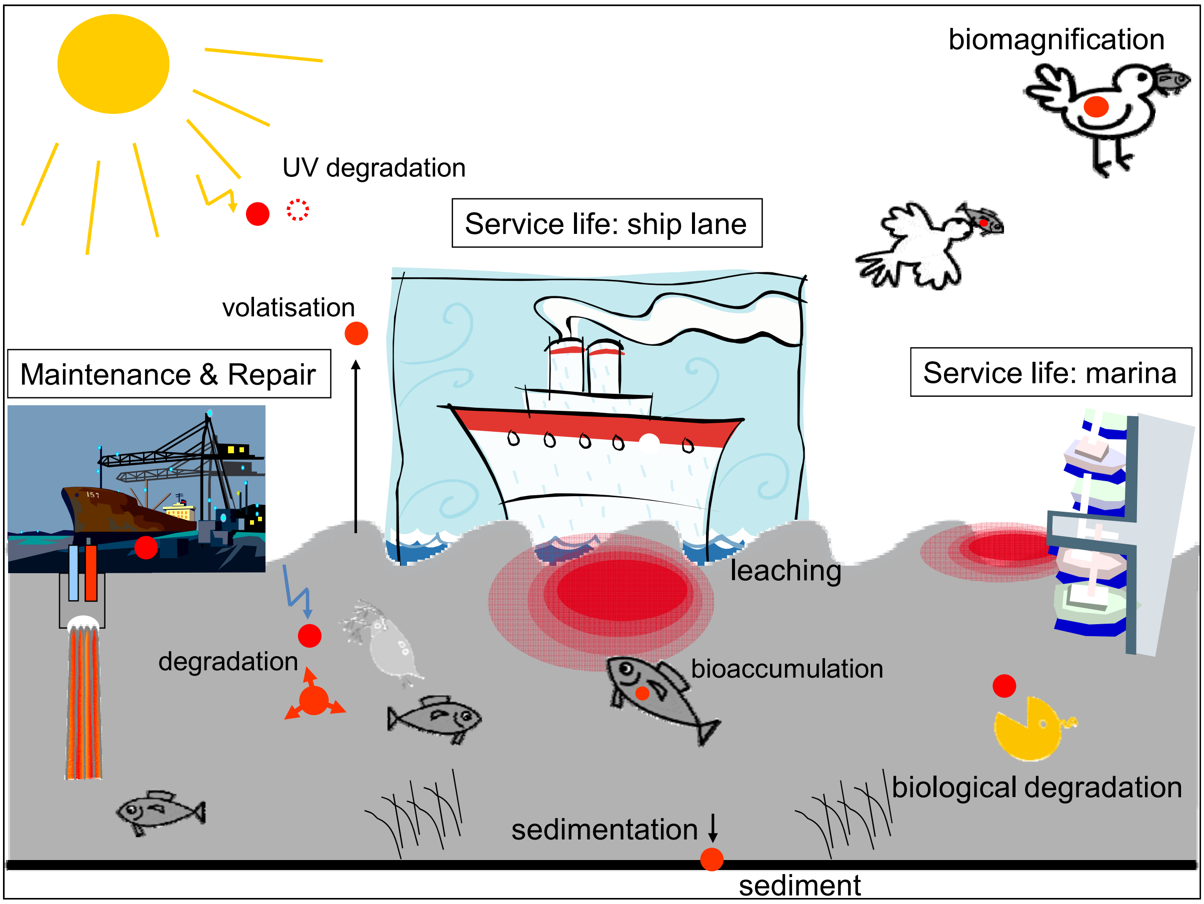

Figure 1: emission, fate and behaviour of AFP[4]

2.1.2 Emission during application of AFP

With regard to emissions from application, there is a difference between

1. new build ships and maintenance & repair (M&R); and also between

2. commercial boats and pleasure boats.

In the new building of ships, the abrasion of old exhausted paint is not necessary and work is mainly done indoors or in closed systems.

Possible emissions to the environment from shipyards and boatyards have to be considered. While several shipyards work with closed systems to prevent antifouling paints from entering the environment, other yards work in highly exposed environments (OECD 2005).

[4] modified and added to according to: presentation of Namekawa, Arch Chemicals, 19 June 2007, Developing an ISO Risk Assessment Standard for Antifouling Coatings

New build commercial/pleasure ship, professional users

During the application phase, emissions can take place during the different working steps. In each working step different emission routes can occur, depending on the location:

- **mixing, stirring and loading** (automatically or manually), and spillage: <u>Water, soil</u>
- **drying** on open air (mainly solvents, fewer antifouling substances): <u>Air</u>, water, soil
- **application** with airless spray gun because of overspray (max 30% of input material, UBA, 2007): <u>Air, water and soil</u>

The location where application takes place is important for the possible emission routes. A differentiation between the following places has to be made (van de Plassche et al. 2004; OECD 2005):

1. **Dock**
   a. on block painting cell: <u>no significant emission, possibly via STP</u>
   b. on block, open air: <u>direct emission into</u> <u>surface water</u> (river, harbour)
   c. Exposed floating dock, marine lift (open air, hard standing area, un-covered, graving dock (open air, hard standing area, covered: Emission:<u> directly into surface water (river, harbour)</u>
2. **Slipway**, open air, hard standing area near or above water surface: <u>directly into surface water</u>, <u>indirectly</u> by leaching into <u>water and soil (ground water)</u>.
3. **boat yard – outdoor**, hard standing area, compact earth, not near surface water, temporary covering: <u>Soil, water via STP</u>
4. **boat yard – indoor** hard standing area: <u>no significant emission directly, potential emission to water via STP</u>

2.1.3 Emission during Maintenance & Repair (M&R) of ship hulls

2.1.3.1 Application

The application of AFP during M&R includes three steps:

- **cleaning of the surface**: mainly done with high pressure water washing (HPW) at up to 6 bar that removes the leached layer from exhausted paint but has a minor influence on old paint. For pleasure boats, the leached layer typically represents 20% of the paint film originally applied, containing a fraction of 5% of the original concentration of active ingredient.

- **removal of old paint and preparation of surface**: abrasive blasting (re-blasting, spot blasting) or hydro blasting or abrasive water treatment; non-professional users mainly use manual abrasive techniques. Abrasion in combination with high pressure water washing will remove 30% of the paint film containing the leached layer plus an additional layer containing a fraction of 30% of the original concentration of active ingredient.

- **application of new coating:** selection of an appropriate product, application of subsurface coating if necessary, if old TBT-coating exists, sealing is required; application with airless spray guns, brushing and rolling.

Depending on the condition of the surface, the damaged areas are cleaned and recoated or the paint is completely removed from the hull for repainting. A complete removal is also necessary if a different kind of coating is applied (e.g. a silicone coat on a SPC).

2.1.3.2 Removal

There are three principal methods for the removal of antifouling systems (IMO, 2008):

1. scraping: sanding, grinding, or scraping by hand to scrape off the paint
2. blasting: grit blasting /dry blasting, wet blasting
3. water blasting washing (low, medium, high pressure)

The possible emission routes from maintenance and repair (removal of old paint and application of new paint) also depend on the place where the work is done e.g. a factory work room or roofed area with hard standing or dockyard in contact with or near to surface water (dry docking in graving or floating docks). Table 4 gives an overview on the characteristics of removal of AFP.

Table 4: Characteristics of removal of antifouling coatings

Removal by actor	Work place characteristics	Technique	Emission route
Commercial ship, professional user	Exposed floating dock or marine lift (open air, hard standing area) or graving dock (open air, hard standing area)	Surface preparation with high pressure water washing (HPW) or abrasive blasting (re-blasting, spot blasting) or hydro blasting or abrasive water treatment	surface water (river, harbour), waste water (and disposal as waste after waste water treatment, filtering)
Pleasure ship, professional user	Repair shop in boat yard (hard standing area or compacted earth) or boat yard (hard standing area)	Surface preparation with HPW, abrasion	soil, waste water
Pleasure ship, non-professional user	Semi-closed to closed room or open air (compacted earth, washing area) or open air (hard standing area)	HPW	soil, waste water

The collected waste water should be adequately treated (e.g. by ultrafiltration, adsorption, electrochemical or biological treatment, solvent extraction, photodegradation (Pangam, 2009). No information is available on whether this recommendation is followed in practice.

Figure 2 gives an overview of the main exposure routes to environmental compartments.

General overview on the application of antifoulings on ship hulls and possible emission routes

Application incl. mixing/stirring + drying, storage

- **New building**
  commercial ships + pleasure crafts (only professional user)
- Application: Airless spraying guns

- **Maintenance and repair**:
- commercial ships (professional user)
- pleasure crafts (professional and non-professional user)
- Removal, washing:
  - High pressure water washing and brush (HPW)
  - Abrasion (entire ship hull, spot blasting) by dry sandblasting or wet sanding (sand washing)
- Application:
  - Airless spraying gun
  - Brush and roller
  - Combination of both techniques

= Dockyards (indoor (painting cells) and outdoor (hard standing)

➢emission:

- ➢directly in dockside and sourrounding to water and soil by drift of aerosol and
- ➢indirectly by dried paint on dock walls to air and water by leaching
- ➢emission into surface water small

= slipway (outdoor, open ait)

➢emission: directly by drift of aerosol possible in dockside and sourrounding (water and soil) and indirectly by dried paint on dock walls (leaching)

➢Potential emission to surface water

Removal

Service life

- **Shipping lanes**
- **Open Sea**
- **Commercial harbour**
- **Estuarine and coastal marina**
- **Marinas in lakes**

= surface water

➢ direct emission: leaching rate 90% of applied antifouling

Waste

- **Disposal of**
  - Solid waste from application
  - Paint residues in cans
  - Sludge from STP
  - Fibre glass reinforcded plastic hulls on landfills
- **Waste water discharge - Waste Water Treatment (WWT)**

= via landfill

= via waste water collection system

➢Potential emission to soil,

➢Emission to water low (to moderate)

Figure 2: General overview on the application of AFP and emission routes from ship hulls of PT 21

2.2 Other uses: fish nets

The application of AFP to fish nets is normally done by immersing the nets directly into the container filled with antifouling paint. After immersing the nets are hanged up for drying. This is only allowed in authorised shipyards with waste water collection systems and normally done by professional users. The cleaning occurs by high pressure hosing and flushing. It is assumed that nearly 100% of the AFP is released into water during service life. There are no specific requirements for the waste treatment of fish nets. Disposal to landfill is expected.

Overview on the application of antifoulings in other uses (fish nets) and possible emission routes

Application	Storage and Handling	Removal / Cleaning
•Immersing of nets directly into paint •drying		1. high pressure washing 2. Flushing 3. Large scale washing machines
= authorised dockyards ➢ potential emission into sourrounding (dropping, spill) → soil ➢Potential emission via STP		= authorised dockyards ➢ potential emission into sourrounding (dropping, spill) → soil ➢Potential emission into water via STP = other places ➢ potential emission into sourrounding (dropping, spill) → soil

Figure 3: General overview on the application of AFP and emission routes from fish nets

3 Elements of sustainable use

3.1 Risk Mitigation Measures

Status

In the framework of the BPD, no risk assessments (RA) of AFP have been carried out so far.

For copper a voluntary risk assessment was carried out by the European Copper Institute (ECI[5]). It covers copper and dicopper oxide but no specific risk mitigation measures are described.

Only few existing standards refer to specific uses of AFP. The international standard ISO/NP 13073-1[6] on risk assessment is still under development.

The former TRGS 516 “Application and removal of antifouling” has been withdrawn and partly implemented in the new TRGS 401 “hazard by dermal contact – evaluation, assessment, measures” but TRGS 516 can be used for further hazard assessment concerning AFP in case antifouling-specific measures are needed. Therefore, air spray application is not allowed. For airless spraying, workers must keep a distance of 15 m from ship surface (see also chapter 3.5). The HSE document recommends that, if work is done on a movable platform, it should be done from bottom to top.

Technical rule TRGS 516 contains general provisions on risk mitigation measures to minimise overspray and emissions to the environment:

Application:

- In general, application must not lead to negative effects on the environment, releases into soil or water should be avoided: therefore, preference for brushing or rolling and coverage of the work place, and use of screens on windy sites is recommended

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5 http://www.eurocopper.org/kupfer/copper-ra.html

6 ISO/NP 13073-1: Ships and marine technology – Risk Assessment on anti-fouling systems on ships – Part 1: Marine environmental risk assessment method of active substances used for anti-fouling systems on ships

- max. wind speed is defined:
    - o max. wind speed of 13.8 m/s (6 Beaufort) in inner dock yard
    - o max. Wind speed of 5.4 m/s (3 Beaufort) above dock yard in open fields, and in case the paint dries slowly – stop work; work must be done at lower wind speeds
- selection of less emissive forms of application e.g. proper spray nozzle, spray angle 90°, distance appr. 0.2 – 0.3 m
- application is only allowed where paint particles can be collected, wash off of particles into water has to be prevented e.g. by relevant techniques
- leftovers (paint, solvents) have to be re-used or handled according to waste legislation

Maintenance and repair

As the removal of exhausted and old paint is necessary before new paint is applied, abrasive techniques are usual. TRGS 516 recommends using suction head blasting (closed system), high pressure water blasting and wet air pressure blasting. If needed, a screen should be placed in the main wind direction to avoid emission into air and water and to allow collection of particles. Dry air pressure techniques are only allowed where other techniques are not technically feasible. In this case, the work place should be covered and/or properly housed. Further abrasive techniques are only allowed where leftovers can be collected and wash off avoided by collection systems. Waste water has to be collected and cleaned or disposed of properly.

As work is often done outdoors and near surface water, housing to reduce air movement and the installation of local exhaustion ventilation is part of BAT to reduce emissions into the environment by driftage into air (Rentz, 2002). The use of high pressure abrasion is only applicable where there is a waste water treatment plant. Nevertheless, dockyards have to be cleaned before the dock is flooded again.

(See also chapter 3.11 on integrated antifouling control measures.)

Another possible pathway is the cleaning of ship hulls: here, mechanical measures used in a dock yard or below the waterline in specific locations in a harbour or marina can be optimised to reduce the emission of antifouling biocides. While costs for underwater cleaning are lower, emissions into water are much higher and it is therefore not often carried out (Kätscher, 1999). In addition, the risk of releasing foreign species into the water increases and underwater cleaning is therefore forbidden or should be avoided in some countries (Anzecc, 1997). Efficient cleaning is particularly important for biocide free coatings of ship hulls (Hornemann, 2003).

Options

As for many substances, data for the assessment of the environmental risks are not sufficient but data gaps will be filled during the authorisation process. However, a further comparative assessment of AFP during service life is not foreseen.[7] A user may therefore not be able to decide which product is the lower risk product, as many other technical details e.g. the matrix surface and use of the ship in salt water or fresh water, high or low speed, also have to be considered.

Here a need for further action is seen in assessing active substances, research and development and subsequently promoting low risk and biocide free products. A feasibility study for a new eco-label for biocide-free AFP has still not been implemented (Watermann et al. 2004). Currently, different methods are being assessed that allow a more controlled release of AFP, such as self eroding of hard antifouling products, encapsulation of active substances / reservoir membranes. Research & development in this field could be supported under a Thematic Strategy.

3.2 Training

Status

In Germany, training for professional workers is done during professional training (e.g. ship building industry, painter skills). The use of AFP may be only one part of training in the handling of dangerous substances and mixtures e.g. paints and varnishes.

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[7] The draft Biocides Regulation currently being discussed includes measures for comparative risk assessments at the product level.

In general, only professional users (painters and ship building craftsman) are trained, but in many cases untrained staff are engaged in ship yards (Bleck et. al, 2005; 2008). Maintenance and repair in particular is carried out by specialised corrosion companies but, because of the hard work and the low pay in this sector, untrained workers are often engaged part time.[8]

Pleasure boats are often treated and painted by the untrained ship owner (consumer) unless the owner pays professional boat repair shops. Training for non-professional user (owners of small vessels) is not usual.

Staff working on commercial ships only rarely come into contact with antifouling products.

The former TRGS 516 requires that at least one skilled person has to be employed who supervises the work. As antifouling paints are often hazardous mixtures, relevant operation instructions have to be provided and the workers have to be instructed at least once a year. The instructions have to be repeated in each new work place.

Options

A mandatory training programme for professional users who are involved in the application of AFP could be established. Because of the international trade in ships and diverse workplaces, EU wide harmonisation should be explored.

For paints sold to the general public, suitable use instructions for untrained applicants could be made mandatory.

3.3 Requirements for sales of pesticides

Status:

In general, products for professional use applied to new build ships and used in larger ship repair dockyards are sold directly by the manufacturer of the AFP. Other products in smaller packages are also sold by manufacturers, retail (DIY) or by distributors directly but also via the internet and mail-order catalogues.

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8 However, it should be noted that the majority of ship repairs are carried out in Asia and the Middle East (see ESD for PT 21, van de Plassche et al. 2004, p. 41).

In general, sale of products classified as very toxic, toxic or harmful is not allowed to the general public, but only to professional users (REACH, Annex XVII).

Specific requirements apply to AFP on commercial ships – often the decision is made by ship owners according to the specific needs arising from the system used by the ship builders.

AFP which have to be mixed (e.g. copper powder and paint, for example the product “international V 17m”) which are used in small ship yards (Bleck et al., 2005) are also available to the general public via the internet. From the information given on the internet, it is often hard to find information on the classification of the mixture and the ingredients.

Options

Currently, antifouling paints are often not clearly labelled as a biocidal product, as some of the substances are not yet classified (which is not allowed according to the Biozid-Meldeverordnung). Often advertising includes antifouling characteristics but non-trained users in particular have difficulty in identifying and assessing the ingredients.

Restrictions on the sale of dangerous products to amateurs via the internet or mail-order catalogues could be established. Specific information for amateurs on how to choose the optimal product for their purpose is lacking and should be developed. Only ready to use products should be available for non-trained users.

In general, requirements for sales of all biocides as foreseen in the Directive on Sustainable Use of Pesticides should be implemented.

3.4 Awareness programmes

Status

Non-Professional users (normally the owner of the boat) often select an AFP based on information from other owners or manufacturers about efficiency in the specific area, and carry out the application themselves. For users of pleasure boats, the aesthetic factor plays a major role in decision making. Often industry provides information on its products[9].

Small marinas often have separate places for cleaning and repair where waste water and old paint is collected, treated and then disposed of according to the relevant (local) regulations. Currently, amateurs are unaware of those requirements, e.g. that there is special disposal of paint scrapings, as a survey in the UK shows (HSE, 2001). There are also initiatives like “Green Blue” in UK, supported by the British Marine Federation and the Royal Yachting Association, which aims to raise general awareness on potential environmental impacts and how to avoid them and provides more readily available information about environmental impacts e.g. leaflets like “Antifouling and the marine environment” that explicitly addresses users of pleasure boats.

The label “Blue Flag (Hafen Blaue Flagge)” requires that the manager of the harbour/marina must prove that he offers up to three environmental training activities for users and members carried out within the Blue Flag season.

Support and information in deciding on the correct product can be provided, e.g. the test-kit developed by LimnoMar which indicates which product is suitable for the antifouling in the particular area.

In Germany, a booklet is available that gives easy to understand information about fouling and the use of anti fouling paints (Bewuchs-Atlas e.V. Hamburg, 2010). In the main part AFP are listed according to the following 5 categories:

- Biocide-free antifouling coatings
- Biocide-free - technical / mechanical systems
- Nano particle coatings
- Biocide-containing coatings
- Biocide-containing technical systems

9 International Yacht Paint, 2009: Anstrichfibel für Yachten; http://iyp.yachtpaint.com/germany/

The description of each product contains e.g. information about water type, possibility of self-application, durability.

The website www.bewuchs-atlas.de addresses professional and private user of AFP and offers various information on fouling and antifouling systems. The website http://www.biozid.info/ also offers information on biocides and alternatives, but the part on AFP is still under development.

Options

Promotion of alternatives (no use of antifouling products and only mechanical treatment without chemicals, biocide-free products, and promotion of new surface materials) should be further strengthened and assessed.

Voluntary labelling (e. g. Blue Angel, EU Flower) of low risk and biocide-free products could be developed and promoted.

Promotion of “eco-labelled” marinas e.g. Deutscher Segler Verband (DGU: “Blue Flag – Hafen Blaue Flagge”) could enhance awareness amongst the general public.

3.5 Certification and inspection of equipment in use

Status

As antifouling paints are often added to solvent-containing paints, requirements exist with regard to explosion protection. Here several standards exist (see table in appendix).

Only airless spray guns are allowed which generally have a pressure of 160 to 200 bar, nozzle diameter in a range of 0.65-0.79 mm. It is assumed that airless-spray with these high pressures generate a significant overspray (Koch et al. 2004) up to max. 30% of the material (UBA, 2007).

As air spray guns are not allowed, the former TRGS 516 recommends that workers should remain a distance of 15 m from ship surface and the use of spraying nozzles at an optimal application angle to avoid overspray. The HSE (2001) also recommends the selection of appropriate spraying nozzles and the adjustment of spraying pressure to minimise overspray and dust. HVLP-spray guns are recommended.

Options

Harmonised EU standards on technical-organisational measures (e.g. automatic spraying techniques, mixing) could be further developed. The scope of the Directive on machinery 2006/42/EC could be extended to include equipment for the application of pesticides.

3.6 Form of the biocide and mode of application

Status

Spraying of antifouling paints on ship hulls is normally done by professional users in dock yards.

One study showed the only impact on the environment while spraying was that the sprayer with the lowest exposure to airborne copper worked in strong winds, the wind blowing the paint overspray away from his breathing zone. The effect of the wind on exposure, however, varied depending on the direction of the wind in relation to the direction of spray and the position of the spray operator (HSE, 730/15). The overspray is directly released to the environment. In practice, problems arise if the ship is bigger than the dock, buildings and cranes constrain the construction of screens or housing.

Certain amounts of old and exhausted paint may also be emitted during repair and application.

Options

Setting of strict requirements for use: e.g. spraying to be allowed only by trained professionals.

Specifications for maintenance and repair (removal and waste treatment of old coatings and waste water) can be further regulated.

Especially with regard to waste water and waste collection, specific requirements (e.g. closed systems) could be developed – here interfaces with waste regulation are obvious.

The efficiency of risk management measures could be defined by relevant standards – harmonised tests are needed.

3.7 Specific measures to protect the aquatic environment

Status

Currently among the substances included in the ongoing review programme, only few active substances (dicopper oxide, dichlofluanid, tolyfluanid, Irgarol, copper thiocyanate, and Copperpyrithione) are classified as dangerous for the environment (see table 1). No environmental classification exists for copper, Zineb and Zinc pyrithione. This information gap will be closed during the authorisation process.

As the leaching rate determines the emission of antifouling agents from the surface of a ship's hull to the environment, which in turn depends e.g. on the formulation of the biocidal product and the surface to be protected, the determination of leaching rates under realistic environmental conditions is one prerequisite for the identification of less risky AFP.

Provisions for the treatment of ship hulls in freshwater bodies exist in some MS e.g. in DK, NL, UK, SE (COWI, 2009). There are also regional restrictions in German Bundesländer e.g. for Lake Constance, the Wakenitz and the Ratzeburger See in Schleswig-Holstein. Also, the Swiss BUWAL (Bundesamt für Umwelt, Wald und Landschaft), as riparian of Lake Constance, published a list of permitted antifouling products (BUWAL, 2003).

The leaflet "Use of antifouling paints on vessels" from the Bavarian Environment Agency (Leaflet 4.5/16, 1 July 2005) contains a list of recommended coatings (silicone, teflon® hard coatings and hydro viscose coating) and less recommended products based on copper but without booster biocides. With regard to silicone, it has to be considered that this kind of coating shows some drawbacks: it is comparatively costly and the coating is quite sensitive, it is not practical for all ships. Further, unbound silicone oils can leach out and can have impacts on marine environments because they are persistent, adsorb to suspended particulate matter and may settle into sediment, and if films build up on sediments, pore water exchange may be inhibited (Nendza, 2007).

Options

The release of antifouling agents to water prevents ship hulls from fouling. In this sense, direct emission to water is the intended function of an AFP during service life. Hence almost the whole amount of antifouling substance added to ship hulls will end up in water and will subsequently be degraded and/or adsorbed to sediment[10]. In this sense the reduction of the total amount of antifouling agent used will be the first approach towards a sustainable use of AFP. However, fouling, especially on commercial ships, will lead to higher fuel consumption (IPPIC, 2009) and this has to be taken into account in a thematic strategy on sustainable use. So, a balance has to be found here, especially as commercial shipping is a global business and needs international coordination[11].

Another point that has to be kept in mind is that antifouling coatings limit invasions of foreign organisms. Hull fouling transported by global vessel traffic is an important pathway for the spread of non-indigenous marine species into local regions. The risk through detachment and dispersal of viable material and subsequent spreading could be managed by removal of the vessel to land for de-fouling in dry-docks. In-water cleaning is often used for small vessels and large vessels outside their dry-docking schedule (Hopkins & Forrest, 2008). But in-water cleaning is restricted in some countries e.g. New Zealand, Australia (ANZECC, 1997) - see also chapter 3.11 on Integrated Pest Management.

Nevertheless, the inclusion of AFP and their metabolites in monitoring programmes at EU level and the development of international Risk Assessment Standards would be an option for a better environmental exposure assessment.

With regard to inherent substance properties which are subject to the authorisation process, the fate and behaviour of the substance and the formation of metabolites after release in particular have to be assessed. A recent study on the “acute toxicity of pyrithione photodegradation products to some marine organisms” (Onduka et al.

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[10] The COWI study also mentioned that the release of up to 90% of the AFP applied to ship hull will not necessarily occur, as a Danish study showed that the release of organotin from Danish vessels to the inner Danish Waters accounts for 12-35% (Lassen et al. cited in COWI, 2009).

[11] In general R&M of commercial ship can be done all over the world, sot where a ship is treated and how it is done will be a decision based on the costs and the relevant provisions of the country

2007) suggests the necessity of risk assessments not only for the pyrithiones but also their photodegradation products.

A restriction on PBT, vPvB substances for AFP should be assessed at EU level.

More concrete local measure can be found with regard to application and M&R. Extension of specific provisions for the treatment of ships in freshwater bodies should be considered, e.g. no treatment of ship hulls below the water surface. Also, strict regulations for the treatment of waste, waste water collection and sewage treatment plants – STP - from maintenance and repair could be established.

Further the use of AFP for aquaculture could be restricted and specific requirements for off-shore constructions should be developed, but there is also need for more data gathering and this could be done AT EU expert level.

Models should be further developed and used for the identification of (regional, local) areas to be protected. There are models developed by HSE like REMA[12] (Regulatory Environmental Modelling of antifouling - for marinas and estuaries) and QWASI[13] (Quantitative Water, Air and Soil Interaction - for a quantitative assessment of the interaction of water, air and sediment), and MAMPEC[14] (Marine Antifoulant Model to Predict Environmental Concentrations).

3.8 Emission during service life

Status

There are two situations that lead to an emission during service life: continuous leaching into water bodies during operation as a main pathway and emissions during M&R as a minor pathway.

The efficiency of an AFP depends on the inherent properties and is one important criterion for the selection of an AFP (Daehne, 2008). As a result, an important amount of antifouling agent is released directly into surface water during service life - emission can be seen as a function of the biocide. As about 70-90% of the AFP is

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12 http://www.hse.gov.uk/biocides/bpd/environmentalexposure.htm

13 http://ecb.jrc.ec.europa.eu/biocides/

14 http://www.antifoulingpaint.com/downloads/mampec.asp

released during the service life, it is seen as the main source directly into the aquatic environment and this is hard to control through sustainable use. Nevertheless, maximum leaching rates of antifouling substances are already defined in some standards.

Depending on the different types of antifouling coatings, maximum periods of service are expected (CEPE cited in HSE, 2002).

Type of coating	Soluble matrix	Insoluble matrix	TBT self polishing co-polymer	TBT-free self polishing
Maximum period of service	18 months	24 months	5 years	5 years

Considering the release of up to 30% residual AFP during M&R and the washing of ship hulls,[15] a release directly in to water is also possible. This is a lower total release compared to the release during continuous leaching, but it is of regional relevance e.g. in harbours or in marinas. Emissions during M&R can be controlled by reduction measures (see chapter 3.11 on Integrated Pest Management).

Options

As the main pathway is continuous leaching, a requirement for improvement of ideal leaching rates of AFP can be seen as an option under a Thematic Strategy. In this framework e.g. maximum leaching rates can be defined in national action plans for specific water bodies.

An option for reduction of the use of antifouling coatings seems to be to clean the hulls of pleasure boats by mechanical measures e.g. by brushing or scrubbing or high-pressure cleaning (Hornemann, 2003) used in a closed system with water collection. A requirement to provide the necessary infrastructure in marinas can be a measure within a thematic strategy.

Additionally, the use of FR-coatings as biocide free alternative coatings would be an option. But there are still limited possible applications (high speed vessels) and further research is necessary.

[15] www.globalnature.org, http://www.uft.uni-bremen.de/chemie/ranke/docs/Vorstudie_AF_Zus_UFT_marum.pdf

3.9 Reduction of pesticide use in sensitive areas

Status

A survey on the acute toxicity of zinc pyrithione and copper pyrithione, used as booster biocides, and their six main photodegradation products to three marine organisms representing three trophic levels (algae, crustacean, and a fish) showed that risk assessment is needed not only for the pyrithiones but also for their photodegradation products (Onduka et al, 2007).

Provisions to prevent non-target organisms need to be defined. A study on the toxicity of antifouling paint to non-target organisms on three trophic levels

- bacteria *Vibrio fischeri*,
- red macroalgae *Ceramium tenuicorne* and
- crustacean *Nitocra Spinipes*

from Ytreberg 2009 showed that the release rate of Cu was highest for ship paints (from ships > 12 m), at 3.2−3.7 μg cm^{-2} $day^{-1,}$ compared to chemically-acting pleasure boat paints (< 12 m) (0.7−1.0 μg cm^{-2} day^{-1}). The physically-acting paints released significantly more Zn (4.8−8.1 μg cm^{-2} day^{-1}) than the chemically-acting pleasure boat paints (1.8−2.9 μg cm^{-2} day^{-1}) and the ship paints (0.7−2.2 μg cm^{-2} day^{-1}). The macroalga, Ceramium tenuicorne, was the most sensitive species tested for both Cu (EC_{50} = 6.4 μg L^{-1}) and Zn (EC_{50} = 25.4 μg L^{-1}). Further, it was shown that the active substances were responsible for the observed toxicity for the ship paints, but Zn and other substances leached from the pleasure boat paints, and in particular the physically-active paint, could also be responsible for the toxicity (see also Karlsson et al. 2010).

The leaflet “Use of antifouling paints on vessels” from the Bavarian Environment Agency (Leaflet 4.5/16, 1 July 2005) recommends owners of pleasure boats to survey if an antifouling paint is really needed. For example, if the boat is used often or only used in freshwater and mechanically cleaned several times, an AFP may be not necessary. In case an AFP is needed, biocide free coatings are recommended. If these are not applicable, copper based coatings should be selected. Of these, copper powder should be preferred to copper oxide. Additional booster biocides are not recommended to be used.

Options

Surface water, soil and groundwater can be regarded as sensitive areas *per se* – therefore specific RMM (e.g. no removal or washing in surface water where collection is not possible, cleaning and M&R only on hard standing or with permanent cover, closed systems and treatment for waste water) should be implemented to prevent emissions into these compartments.

The development and application of further ecotoxicity tests with representative marine organisms from different trophic levels, e.g. bacterium *Vibrio fischeri*, the red macroalga *Ceramium tenuicorne* and harpactacoid copepod *Nitocra spinipes*, which can be used for risk assessment (Ytreberg et al. 2009) should be encouraged.

3.10 Handling and storage of pesticides and their packaging and residues

Status

For the coating of ships, the coating material is generally supplied in 20 litres buckets although 100 litre re-useable containers are used for large applications. The implementation of the Solvent Emission Directive (SED 1999/13/EC)[16] leads to the situation that buckets used in larger docks are taken back by the formulator.

Antifouling paints have to be stored properly (TRGS 516) and only competent staff are allowed to handle them. Residues (and solvents) must not be mixed and disposal has to be carried out according to the relevant legislation, waste has to be handled in line with the local waste legislation (see also Chapter 3.1).

Options

Limitations on package sizes and only ready to use products for amateurs could be implemented.

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[16] COUNCIL DIRECTIVE 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations

Establishment of a collection and recycling system similar to that for PPP could be useful for professional use. In Germany the collection of residues could also be carried out at special collection sites.

3.11 Integrated antifouling control measures

Status

Good / best practice on AFP is not yet available but is covered in BAT for surface treatment and coating (UBA, 2007).

Several guidance documents concerning best management practice also exist

- IMO: Draft Guidance on best Management Practices for removal of Anti-Fouling Coatings from Ships, including TBT hull paints – submitted by the United Kingdom, 21 July 2008
- HSE: Health and Safety Executive: Safe use of tin-free, marine anti-fouling coatings. Information document HSE 730/15
- ANZECC: Code of Practice for Antifouling and in-water hull cleaning and main using
- British Coatings Federation Ltd (BCF): Safe use of antifouling coatings
- VDL/DSV: Unterwasseranstriche – So wenig Antifouling wie nötig = so viel Umweltschutz wie möglich
- CEPE: Personal health protection during application of antifouling paints and Guidance on the Safe Application of Yacht Coatings – Personal and Environmental Protection - Do's and Don'ts

The IMO submitted draft guidance on Best Management Practices for Removal of antifouling coatings from ships, including TBT hull paints (IMO, 2008) as the implementation of sound practices can reduce the release into the environment. It includes two main methods:

- Source-control methods: e.g. vessel covering, sweeping, covering waste piles, and bermed storage for waste and paints

- Collection, filtration and treatment methods e.g. hull wash water settling tanks, and filter.

Basic facility requirements for the removal of AFP are

- Good housekeeping practices: thorough record-keeping, securing of materials and equipment, instructions of workers together with clear frame work for safe operations and responsibilities, and clear code of practice.
- Facility design: at a minimum all facilities should have an impermeable floor or work surface for dry paint removal and cleaning after work, waste water collection and containment system, suitable air cleaning system
- Facility staff: designated staff with responsibilities for waste, waste water
- Collection of waste: separate storage, properly labelled
- Waste water collection: collection should be done separate from non-contaminated water, settlement of particles should be allowed by containers left standing
- Handling of waste water: separation of particles from water and proper disposal
- Discharge water: a certain particle load may be allowed e.g. 100 mg/L, pH should be between 6.5 and 9; discharge into sensitive marinas should be avoided

Example Code of Practice:

The ANZECC code of practice aims to identify best practices for the application, use, removal and disposal of antifouling paints and is targeted at owners and operators of boats of all sizes, whether for recreation or commercial uses, and providers of boat-cleaning facilities. It proposes measures which should be taken to minimize the release of AFP to the surrounding environment. It includes some similar measures to those already described in TRGS 516. Although some of the mentioned practices are forbidden in Germany, they could be still allowed in other MS. In the following only measures are mentioned which have not already be mentioned elsewhere in the text:

General provisions:

- Excessive abrasion or hosing on the boat should be avoided
- M&R of all vessels should be conducted at an appropriate facility, either above the tidal zone, or in a dry dock, no removal of antifouling products should be undertaken while the vessel is in the water, on beaches or below the high tide limit.

- Scrapings and debris should be collected for disposal and stored in sealed containers until removed by licensed waste disposal contractors (or as otherwise specified by regulatory agencies).

Provisions for facilities:

- Where large vessels (>25 m) exclusively or predominantly operate in confined waterways, bays, rivers or estuaries (e.g. ferries, barges fishing boats, work vessels, privately-owned pleasure craft), they may be a significant source of toxic substances in the locality. The relevant State agency may prohibit use of particular antifoulants on such vessels (e.g. those containing tributyltin). Therefore, operators and those responsible for vessel maintenance should check with the relevant State agency before applying antifoulants.
- Development of a uniform licensing procedure for such facilities:
    - New dry docks, slipways and hardstands - no water should run off work areas without treatment to remove toxic substances, turbidity and discolouration. New facilities should be designed and managed so as to allow for eventual disposal to sewer of treated waste water and first-flush runoff.
    - Existing dry docks, slipways and hardstands - measures should be adopted to minimize water runoff and certain potentially toxic, turbid or discoloured discharges. Bunds may be used on sealed concrete. Sumps may be used to contain waste water and spillages. Straw bales and woven fibre material may be used to retain suspended solids. Existing facilities should plan for upgrading to allow for eventual disposal to sewer of waste water and first flush runoff

Techniques for Pollution Abatement

- Preparation areas should be bunded to ensure accidental spillage cannot escape to water.
- Spillage should be treated with a suitable absorbent and disposed of as a controlled waste.
- All plant and equipment from work areas should be subject to regular preventative maintenance programs to ensure optimum performance.
- Preparation of all antifoulants should take place in areas protected from traffic, with overhead cover.
- Site operators should assume any removed coating is contaminated with biocides and dispose of in accordance with requirements of local environmental and/or waste disposal authorities.
- Measures must be undertaken to contain wash waters and to segregate wash water from non-contaminated flows.
- Established written operational procedures should exist.

Specific Requirements During Application - All Vessels

- Cleaning using water is preferred to chemicals, high pressure liquid cleaners that operate with detergents, solvents, caustic or acid should only be used if a system exists for collection of waste waters.

• Low pressure, high volume spray guns are preferred over high pressure guns.
• Efficient use of all antifouling paints, during their application, should ensure that total losses due to all causes do not exceed 30% of the coating to be applied to the substrate.
• Consideration should be given to:
  o maximising coating transfer efficiency during application;
  o blowing back hose lines to the pump on completion of work;
  o using returnable bulk containers;
  o careful planning of coating operations to minimise coating residues and losses;
  o application during optimal weather conditions, if possible.

Removal of paint • Removal processes on small craft (<25 m) should use the best available techniques that do not entail excessive cost. • Use of tarpaulin and sheeting would allow cheap collection of wastes for offsite disposal, No removal while the vessel is in the water, on beaches or in the intertidal zone – only at appropriately equipped and approved facilities. • Old antifouling coatings are not to be burnt off, Biological materials (marine biota) should be disposed of as solid waste in accordance with local requirements e.g. to landfill. • Where antifouling paints have been removed from old vessels (greater than 10 years old), it should be assumed that the paint residue contains tributyltin, unless test results prove otherwise … the paint residue should be disposed of at the approved local landfill facility. Antifoulants removed from vessels constructed before the 1970's may contain a variety of extremely hazardous chemicals, including substances like arsenic, mercury and DDT, and should be disposed of at a local approved landfill facility in which leachates are contained.
Releases to Air • Wet abrasion is preferable to dry abrasion - Use of wet methods controls particulate emission to air but generally creates high volumes of liquid waste. Ultra high pressure water blasting, with lower volumes of liquid waste, is likely to become widely available in the future. • Vacuum blasting, or containment blasting, with reusable abrasives and separation equipment is the current best option for removal of used antifouling coatings. If vacuum or containment blasting is employed emission targets should be as follows:- • if operating without wet particulate arrest, exhaust emissions of 35 mg/m^3 should be targeted; • if operating with wet particulate arrest, exhaust emissions of 20 mg/m^3 should be targeted.

The "Best Practice Advice Flyer" from The Green Blue[17] summarises the similar measures appropriate for non-professional users.

17 http://www.thegreenblue.org.uk/publications/Antifouling.pdf

Topside and antifouling paints and varnish including used brushes, solvents, rollers and trays are hazardous waste and should be disposed of accordingly.
The key is to prevent anti-foulant from unnecessarily entering the water. Skirt the hull when scrubbing down or painting the hull and use a tarpaulin to catch the flakes and drips. Don't leave a coloured patch under your boat!
If washing off on a slipway, use a device such as loop of rope to trap any paint particulates and then sweep up and dispose as hazardous waste.
Look into alternative hull paints, such as hard vinyl, silicone or Teflon®, which are suitable for in-water hull cleaning systems.
Dust from sanding paint and antifouling coatings is toxic. Using a dustless vacuum sander will also protect your health.
If you use scrubbing piles, only scrub off the fouling and not residue paint – be careful not to let old or new paint enter the water.
Select a marina, club or boatyard which has a closed loop scrub-down facility which collects residues and wash down.
Select the right type of antifouling paint for your craft and boat usage – take advice from your chandlery. Use water-based paints where possible or low VOC (Volatile Organic Compounds) paints.
Apply the right amount of antifouling paint required and do not spill it – when applying use a sheet to collect drips.

The international label "Blue Flag" (http://www.blueflag.org, www.blaue-flagge.de) requests that advice on the handling of water, waste and energy, the use of environmental friendly products and health and safety issues is offered by the site operator. Further, sufficient and appropriately labelled and separated containers for the storage of contaminated waste (paint, solvents, removed paint, AFP, batteries…) have to be offered. In 2004, 123 pleasure boat marinas were certified in Germany, in 2009 650 marinas worldwide were awarded the label.

Criteria were developed for the award of "Environmentally Sound Ship" but these mainly cover emissions resulting from operation of ships (Bornemann et al. 1999).

Several standards for the application, removal and determination of the leaching rate exist, they are not always specific for antifoulants but they have relevance for the use of AFP e.g. DIN EN ISO 15181-2[18]: (see also table in Annex 6).

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[18] Beschichtungsstoffe – Bestimmung der Auswaschrate von Bioziden aus Antifouling-Beschichtungen

However, with regard to the global ship traffic in several fields on the use of AFP the need for an international harmonisation is demanded by different organisations besides IMO. So some organisation want the ISO to be responsible for the development e.g. of standards on risk assessment standard for antifouling coatings and respective methods (Namekawa, 2007).

There is no information about examples of good practice for the use of antifoulants for fish nets or offshore constructions.

Options

Because many applications are carried out outdoors, every measure that encloses the working area would reduce emissions e.g. covering, sealing the ground, exhaust ventilation, waste water collection and treatment.

Promotion of efficient alternatives (e.g. biocide-free - silicon based, encapsulated substances with optimised leaching) is already part of good practice but it seems that more information is needed, especially for non-professional users.

Research and development activities and promotion of alternatives are still needed and may be a measure for sustainable use of biocides.

Integrated Pest Management should also include biosecurity risks from ship hull fouling releasing non-indigenous pest into recipient regions. These risks arise not only from releasing adult or planktonic life stages, but also through dispersal of fragments of some species e.g. sponges, bryozoans which can spread in recipient regions. Assuming suitable environmental conditions for the organisms, e.g. salinity, temperature, the risk is likely to increase with the residence time of a vessel in a recipient region. Compared to no management and possible release of fouling organisms, the in-water hull cleaning through mechanical removal of fouling may pose less risk but this depends on the method. Regular defouling in dry dock and retaining of foulants by filters and containment tanks with a subsequent reapplication of antifouling paint may be the most efficient method for preventing settlement of non-indigenous organisms (Hopkins & Forrest, 2008; IPPIC, 2009). Invasive species can be a threat to fishery and aquaculture (IPPIC, 2009). Summarising, a balanced weighting of the conflicting objectives is required in the context of a sustainability framework.

3.12 Indicators

Status

Reliable and up-to-date data on the manufacture and consumption of antifouling substances are hard to find. From the COWI report it is known that, from 1998-2001, the total production volume for 60% of the substances in PT 21 was 668 tonnes and the three most important substances made up 88% of the total. However, one of the most important substances, dicopper oxide, is not included.

It is also known that a large share of antifouling paints is imported (Koch et. al).

Some AFP, especially the use of Pyrithionate, are relatively new; more research is needed to identify relevant metabolites and their environmental fate (Onduka et. al, 2007; Ranke et al. 2002).

There is almost no information available on the use of AFP in other uses e.g. offshore and harbour construction, fish nets.

Options

Data on manufacture and consumption of AFP is needed for the evaluation of amounts used in the context of sustainable use of biocides. Therefore, the inclusion of biocides into regulation 1185/2009/EC concerning statistics on pesticides would be an appropriate option for gathering data.

Relevant metabolites should be identified and used as indicators in monitoring programmes, not only in the framework of the WFD but possibly also for the marine environment. Sediment as sink for antifouling substances should be included in monitoring programmes.

Data on other uses (fish nets, offshore constructions, harbour construction) is missing and should also be collected.

4 Example: Application of antifouling paint on pleasure boat

Use pattern	Application on pleasure boat
Target organism	Micro- and macro organism, in fresh water (lakes), brackish water, salt water (e.g. North sea, Baltic Sea)
User/applicator	Owner of the boat, non-professional
Location	Small marina, open air (compacted earth, some covering)
Active substance	Biocidal product: Solid antifoulant[19], package: 750ml or 2.5l Liquid paint: Tolylfluanid 1-2.5%, copper 25-50% (mixture is classified as dangerous: harmful Xn, dangerous for the environment N) Mixture contains also other substances which are classified as dangerous
Mode of application and dosage	Stirring before and while using <u>Application:</u> rolling, brushing <u>Mixing:</u> product is used undiluted – “ready-to-use” <u>Application:</u> airless spraying (air spraying not allowed) <u>Mixing:</u> depending on temperature up to 5% solvent is allowed No abrasion is needed before application if similar self-polishing coating is already on boat Drying time: Dust dry: 0.5 hour Rain safe: 1 hour Water safe: 4 hours <u>Dosage:</u> new coating: 2 coatings, repair: 1 coating theoretical application rate: 10 m²/L Average thickness of layer: 100 µm wet and 10 µm dry
Main emission route	Rolling brushing, airless spray → air, **soil**, potential to water via WWTP or STP Waste from residues, cleaning, used tools (e.g. stirring tool, brush), gloves
Environmental behaviour	Tolylfluanid degrades to *N, N*-Dimethylsulfamide (DMS), which is a precursor of the carcinogen *N*-Nitrosodimethylamine (NDMA) during drinking water ozonisation. In Germany DMS has been detected in surface water (50 ng/L to 100 ng/L) and ground water (100 ng/L to 1000 ng/L) (Schmidt et al., 2008).
Training	<u>Status:</u> Training for non-professional workers (owner of the boat) is not foreseen <u>Options:</u> Training could be an additional topic in lessons for awarding boat certificates, for further measure see awareness programme

[19] The product name has been made anonymous.

Requirements for sales of pesticides	Status: Product must be classified and labelled properly, no advertising phrases that play down the risks are allowed. The product can be ordered through internet sale, no further advice is required by any regulation, a Safety Data Sheet (SDS) and a Material Safety Data Sheet (MSDS) are normally also available by download from the internet but non-professional users are not able to understand SDS, so the product information is the basis for adequate application Options: Information used by professional users as TRGS, UVV, SDS is not available (and normally not understandable) for non-professional users. Product information (or MSDS) could be used for giving more (understandable) information for non-professional users e.g. which important issues, risk and respective risk management measures the user should be aware of e.g. more detailed information on handling, requirements for working place (covering, hard standing area, information on waste handling). A harmonized format for this kind of product could be developed.
Awareness programmes	Status: In some cases AFP are not necessary for pleasure boats. Some marinas have relevant facilities for application, maintenance & repair, waste handling and trained persons who are responsible for compliance with existing regulation Options: Information for non-professional users on the availability of alternatives and the effects and risks of antifouling products could be made publicly available, Obligation to have a trained person in marinas Promotion of “eco-labelled” marinas (“Blaue Flagge”)
Certification and inspection of equipment in use	Status: No certification scheme for equipment in use Options: In this case further need for certification of equipment,
Information to the public	The web-based information system of the German Federal Environment Agency provides useful information (www.biozide.info)
Form of the biocide and mode of application ➔ Emission during life cycle	Status: Paint is a insoluble matrix coating that releases the biocide tolylfluanid and copper by diffusion, the release is high in the beginning and decreases with time, copper reacts to copper carbonate which is insoluble Options: Promotion of biocides where leaching rates are controlled better
Specific measures to protect the aquatic environment	Status: Paint is not allowed to enter the surface water, waste, waste water must be collected and is not allowed to enter the water body. Options: A minimum distance from location of use and surface water could be introduced Restriction on use of any AFP for pleasure boats under a certain size e.g. < 25 m

Reduction of pesticide use in sensitive areas ➔ protection of non-target organisms ➔ surface water ➔ soil	Status: Options: RMM e.g. covering, working only on hard standing, could be compulsory as a minimum requirement Restriction on use of AFP in specified areas e.g. lakes
Handling and storage of pesticides and their packaging and residues	Status: Information on handling and storage is given on product information Options: Limitation on packaging size for amateurs Special information for waste disposal on packaging – waste collection of empty containers and unused residues Maybe spray cans for non-professional user could be an alternative packaging because stirring and refilling, cleaning can be avoided but drawbacks may be from the aspects of occupational health
Integrated Pest Management	Status: good / best practice First of all checking if antifouling coating is necessary at all; maybe cleaning at regular intervals is sufficient Checking if alternatives (e.g. silicon based) are applicable is part of good practice but non-professional users are seldom aware of it Options: Promotion of efficient alternatives (e.g. biocide-free - silicon based, encapsulated substances with optimised leaching, cleaning) Information on use
Indicators	Status: Leaching during service life is the main emission route, but a significant amount of substance can also be emitted to the environment during application, mixing& stirring Options: As there is no data on consumption, collection on this is needed, also monitoring programmes in marinas (coastal areas, lakes and rivers) should reflect the use of AFP in this area and include the substances themselves and the relevant metabolites It could also be checked if research on emissions to soil and groundwater bodies is useful and needed

Conclusion

The service life of AFP is the service life stage, with the main emissions into the environment. Leaching from the ship hull can be seen as an intended function of the AFP. The consequences could be partly subject to the authorization process. For example, criteria for the leaching rate of a product, the efficiency and the risk assessment of metabolites could be defined and evaluated in the authorization procedure. In the framework of a Thematic Strategy, the focus could be on the promotion of low-risks products or biocide free alternatives.

The maintenance & repair phase is the other relevant path of emissions into the environment, even though minor in magnitude. However, this phase can be influenced by measures laid down in a Thematic Strategy.

The use of antifouling products by non-professional amateurs offers the following exemplary measures of sustainable use (not complete):

- Collection of data about consumption of AFP by amateurs
- Training and awareness raising of this group of users on
    - Information as a basis on decision making whether an AFP is necessary at all and, if it cannot be avoided, which one would be the one with the lowest risk → development of a guidance that reflects the crucial information
    - Training for environmentally sound handling, storage, application and waste handling → as part of “boat pilot permission” or in the framework of the promotion of “eco labelled” marinas
- Restriction of sale to amateurs → no sale of products classified dangerous for the environment by internet sale or catalogues
- Restriction of application, M&R only in yards equipped with appropriate surrounding (hard ground, covering), waste water collection system with filtering, waste collection sites
- Restriction of AFP in sensitive areas e.g. lakes

5 Appendices

5.1 Overview on standards, BAT and other relevant documents

Best Available Practices	Not yet available for AFP,, partly covered in BAT for surface treatment and coating: Bericht über Beste Verfügbare Techniken (BVT) im Bereich der Lack- und Klebstoffverarbeitung in Deutschland -Teilband I: Lackverarbeitung- Deutsch-Französisches Institut für Umweltforschung (DFIU) und Universität Karlsruhe (TH), August 2002 European Commission: Best Available Techniques on Surface Treatment using Organic Solvents. August 2007
Standards	Several Codes of practice for application and removal of antifouling coatings from different sources (also non-EU) available but no elaborated standards
Standards	
ISO/DIS 13073-1	Risk assessment on anti-fouling systems on ships - Part 1: Marine environmental risk assessment method of biocidally active substances used for anti-fouling systems on ships
ISO/CD 13073-2	Risk assessment on anti-fouling systems on ships - Part 2: Marine environmental risk assessment method for anti-fouling systems on ships using biocidally active substances
ISO/WD 13073-3	Risk assessment on anti-fouling systems on ships - Part 3: Human health risk assessment for the application and removal of anti-fouling systems
DIN EN 1829-1, (Norm-Entwurf)	Hochdruckreiniger – Hochdruckwasserstrahlmaschinen – Sicherheitstechnische Anforderungen – Teil 1: Allgemeine Beschreibung; Deutsche Fassung prEN 1829-1:2007
DIN EN 1829-2 (2008-06)	Hochdruckwasserstrahlmaschinen – Sicherheitstechnische Anforderungen - Teil 2: Schläuche, Schlauchleitungen und Verbindungselemente; Deutsche Fassung EN 1829-2:2008
DIN 24375, Ausgabe: 1981-06	Oberflächentechnik; Flachstrahl-Düsen für luftlos zerstäubende Spritzpistolen; Maße, Prüfung, Kennzeichnung
DIN 55945 2007-03	Lacke und Anstrichstoffe – Fachausdrücke und Definitionen für Beschichtungsstoffe und Beschichtungen
DIN EN 13966-1, Ausgabe: 2007-11	Bestimmung des Auftragswirkungsgrades von Spritz- und Sprühgeräten für Beschichtungsstoffe – Teil 1: Flächenbeschichtung; Deutsche Fassung EN 13966-1:2003
DIN EN ISO 10890 (Entwurf , 2009-08)	Beschichtungsstoffe - Modell für die Biozid-Auswaschrate von Antifouling-Beschichtungen durch Berechnung der Mengenbilanz (ISO/DIS 10890.2:2009); Deutsche Fassung prEN ISO 10890.2:2009
DIN EN ISO 15181-1 (2007-10)	Beschichtungsstoffe - Bestimmung der Auswaschrate von Bioziden aus Antifouling-Beschichtungen - Teil 1: Allgemeines Verfahren zur Extraktion von Bioziden (ISO 15181-1:2007); Deutsche Fassung EN ISO 15181-1:2007
DIN EN ISO 15181-2 (2007-10)	Beschichtungsstoffe - Bestimmung der Auswaschrate von Bioziden aus Antifouling-Beschichtungen - Teil 2: Bestimmung der Kupferionen-Konzentration im Extrakt und Berechnung der Auswaschrate (ISO 15181-2:2007); Deutsche Fassung EN ISO 15181-2:2007
DIN EN ISO 15181-3 (2007-10)	Beschichtungsstoffe - Bestimmung der Auswaschrate von Bioziden aus Antifouling-Beschichtungen - Teil 3: Berechnung der Auswaschrate von Zink-Ethylenbis(dithiocarbamat) (Zineb) durch Bestimmung der Konzentration von Ethylenthioharnstoff im Extrakt (ISO 15181-3:2007); Deutsche Fassung EN ISO 15181-3:2007
DIN EN ISO 15181-4 (2009-02)	Beschichtungsstoffe - Bestimmung der Auswaschrate von Bioziden aus Antifouling-Beschichtungen - Teil 4: Bestimmung der Konzentration von Pyridintriphenylboran (PTPB) im Extrakt und Berechnung der Auswaschrate (ISO 15181-4:2008); Deutsche Fassung EN ISO 15181-4:2008

DIN EN ISO 15181-5 (2008-09)	Beschichtungsstoffe - Bestimmung der Auswaschrate von Bioziden aus Antifouling-Beschichtungen - Teil 5: Berechung der Auswaschrate von Tolylfluanid und Dichlofluanid durch Bestimmung der Konzentration von Dimethyltolylsulfamid (DMST) und Dimethylphenylsulfamid (DMSA) im Extrakt (ISO 15181-5:2008); Deutsche Fassung EN ISO 15181-5:2008

Authorities and employers mutual insurance association	
TRGS 401	Gefährdung durch Hautkontakt - Ermittlung, Beurteilung, Maßnahme Ausgabe: Juni 2008 (replaces TRGS 516) The TRGS 150 und 531 have been integrated into the new TRGS 401. In individual cases the previous TRGS can be used further on as auxiliary means for the assessment of working place safety while applying antifoulants.
TRGS 516	Antifoulingfarben (has been withdrawn). Can partly be used according to the VCI for antifoulant applications but is not available online any longer.
GUV-V D25	(VBG 23) Verarbeiten von Beschichtungsstoffen (außer Kraft gesetzt infolge des Inkrafttretens der Betriebssicherheitsverordnung BetrSichV)
GUV-V C28	(VBG 34) Schiffbau
GUV-V D26	(VBG 48) Strahlarbeiten
GUV-V D15	(VBG 87) Arbeiten mit Flüssigstrahler
GUV-V	(VBG 119) Gesundheitsgefährlicher mineralischer Staub (außer Kraft ersetzt durch (BGI 5047))
BGI 5047	Mineralischer Staub
GUV-V C21	Hafenarbeit
BGR 217	BG-Regel: Umgang mit mineralischem Staub, zurückgezogen
BGI 639	Merkblatt: Maler- und Lackierarbeiten
BGI 557	Merkblatt: Lackierer
BGI 740	BG-Information: Lackierräume und –einrichtungen – bauliche Einrichtungen, Brand- und Explosionsschutz, Betrieb
BGI 536	Merkblatt: Gefährliche chemische Stoffe, zurückgezogen
BGI 621	Merkblatt: Lösemittel
BGI 546	Sicherheitslehrbrief Umgang mit Gefahrstoffen (bisher ZH 1/93) Vereinigung der Metall-Berufsgenossenschaften 2001
BGI 595	Merkblatt reizende Stoffe / ätzende Stoffe
VDMA	Diverse 'Einheitsblätter' zu Anforderungen, Prüfmethoden, Sicherheit etc. von Geräten
STG	Diverse Richtlinien zu Korrosionsschutz sowie ein 'Datenblatt für Beschichtungsstoffe', Druckwasserstrahlen. Antifouling kommt in den Datenblättern nicht vor.

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