Biocide free 'antifouling' for ships

Emissions from the underwater coating 'Eco-speed'

English translation of WD report 2008.057, of ‘Biocidevrije antifouling voor schepen, emissies vanuit de onderwater coating ‘Ecospeed’, dd.15 November 2008 from A. Wijga, E. Erdtsieck RWS ZL, J. Romeijn RWS ZH, R. Berbee, J. Tiesnitsch, S. Rotteveel, and L. Eibrink RWS WD.

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Summary

Antifoulings are used on ship hulls to prevent the fouling of organisms and thus to restrict the use of energy. Biocide-containing antifouling is in general considered as environmental problematic. From January 1 2008 onwards, the use of poisonous antifouling based on organotin is prohibited on ships. Thanks to the tributyltin-ban there has been an evolution towards the development of biocide free non stick coatings, this includes soft coatings based upon silicones but also hard coatings. Due to the negative effects of antifoulings on the quality of the water, Rijkswaterstaat (RWS) stimulates product innovation in this field. Ecospeed is a hard non stick polyester-resin based coating. For larger ships it forms an alternative to biocide-containing coatings releasing copper and organotin. Compared to the traditional antifoulings Ecospeed is more favourable because it doesn't contain any biocides.

Use of Ecospeed
Ecospeed is sprayed on ships in docks. When the resin is sufficiently hardened, the ship is launched in the water. The resin continues to harden even in the water. The used solvent styrene binds chemically to the resin-matrix, and evaporates partially at the same time.
After a certain period of time (minimum a day) the complete hardened Ecospeed needs to be polished. During this step the surface irregularities are removed and this results in a very smooth coated surface. In spite of the smoothness some growth can still occur (especially in the tropic regions). Therefore, ships with Ecospeed might have to be cleaned occasionally, whereby the organisms growing at the hull surface are removed.

Definition of the problem
RWS is confronted with questions of 'brushing'-companies to be allowed to polish and clean these treated ships (with Ecospeed) underwater by divers. The pollutions that come off this way will be released in the surface water. This poses the question if this burdens the surface water.

Pilots in surface water
There have been executed some pilot tests whereby the cleaning/polishing was done in surface water. Due to diluting phenomena these pilots did not gave enough insights in the possible effects. Therefore it was decided to undertake a project whereby under controlled conditions analyses are executed in test tanks. This testing procedure was set up in joint cooperation between the supplier of Ecospeed and RWS (Dept. 'Zeeland', 'Zuid Holland' and 'Waterdienst'). The results of the technical part of this project are described in this report. The findings of this report will be used for the decision-making whether underwater polishing and cleaning for RWS is acceptable, and if yes, under which circumstances this can be done.

Set-up of the project

For this project three periods here have been taken into consideration wherein emissions can take place: during the hardening of Ecospeed, the polishing and the cleaning.

Emissions during the hardening period

The experience is that during this period mainly aromatic solvents (incl xylene) are released, and at the beginning also styrene. The mentioned solvents are mostly to be attributed to the thinner that has been mistakenly used by the spraying company. Toxicity-tests on the water in the test tanks did not demonstrate any relevant effects. There were also no oestrogen effects. The analyses and tests in test tanks can be presumed as worst case. By underwater treatment of ships with ecospeed, there is a strong diluting effect in the surface water. Due to these results, it is expected to be unlikely that the leaching of substances will have any effect in practice.

Emissions during the polishing process

Floating substances are released during the polishing process as well as some styrene and diluents from the hardening component (diisobutylftalate). Toxicity tests and oestrogen tests performed on the water samples before and after the polishing process gave no evidence of effects by these substances.

Emissions during the cleaning

A test plate that has hung in the port of Zeebrugge during the period of one year has been cleaned. The same chemical substances are released as during the polishing process. During cleaning, when the resin is fully hardened, the surface structure is pulled open, which leads to the possible release of encapsulated chemical substances. There is more release of suspended matter during cleaning than during polishing. The nature of the suspended solids during cleaning is different than during polishing. The released suspended matter during cleaning exists mostly of grinded fouling. Due to technical reasons, the toxicity and oestrogen tests are not done during the cleaning process. No effects are expected considering the results during polishing.

Significance for the surface water

Scope was to translate the results to the real situation in practice. As theoretical exercise it has been assumed that a small cargo ship with a surface of 1500 m^2 is treated in a port. During the polishing of a ship of this size about twenty kilograms of suspended solids is released and during cleaning about eighty kilograms. Considering the results of the toxicity and oestrogen tests in the test tanks, there are no effects expected on the quality of the water or underwater bottom in practice.

The suspended solids that are released during *polishing* exists of very small parts that hardly sediment. Influenced by the flow in ports, this hardly decomposing grindings will spread out over a large distance. This grinding material is inert. The grinding that is released during the cleaning is composed of a coarse and a fine fraction. The coarse fraction sediments quite easily and will eventually end at the bottom of the harbour docks. The finer residues will be distributed over a larger area. The grindings that are released during cleaning are mostly constituted of biological material (remainders of grown organisms).[1]

[1] This report contains the results of a project performed by RWS. The responsibility of RWS is limited to the original report, in Dutch. The current report is a translation of this report into English by ERM, and represents as close as possible the context of the original Dutch RWS report.

1. Introduction

From the 1st of January 2008 onwards the use of poisonous antifouling based on organotin is prohibited. The reason for this decision is that this kind of antifouling has adverse effects on the water-environment. These harmful effects are also the result of the use of other kinds of antifouling with biocides. Partly due to the TBT-prohibition paint producers have developed biocide free non stick coatings, incl. soft coatings based on silicones, but also hard coatings.

Ecospeed is an example of a new developed biocide-free underwater coating for larger (sea) ships. The product is a hard smooth underwater coating that results in the fact that organisms have difficulty to stick to the ship's hull coated with Ecospeed. The product is commercialised by the Belgian company Subsea Industries.
Rijkwaterstaat Zeeland is participating in an EU life project wherein practice experiences with Ecospeed are under discussion. Rijkswaterstaat (RWS) stimulates in this way the innovation concerning antifouling paints.

After been sandblasted the ships are sprayed with Ecospeed in drydocks. After minimum one day the ship is ready to be launched in the water. Then the Ecospeed-surface is polished under water by divers, whereby the last irregularities are removed.

Fouling of ships takes mostly place when ships lie still. Despite the fact that Ecospeed is a non-stick coating, some growth will occur. This fouling is stronger in tropic regions. It is unfavourable for the energy-consumption of the ships. This is the reason why the coating sometimes is cleaned underwater. Small growth (algae, slime, small animals, grass) are then removed and the original surface is repaired. When the ships sail in the tropic regions the cleaning frequency is at minimum once a year. In the Western-European zones the frequency is lower.

RWS Zuid Holland and Zeeland are regularly confronted with requests to allow underwaterpolishing of Ecospeed or cleaning in their surface waters. With this process of cleaning or polishing grindings are released in the surface water. *The question is if polishing or cleaning have adverse consequences on the surface water.*

Therefore pilot scale ships are polished/cleaned in the surface water in the port of Antwerp and Grave. During these pilots samples of the surface water were taken before and after the treatment of the ships. The samples were analysed by the Waterdienst laboratorium. Due to diluting effects there were no significant differences in concentration of the measured substances and no sound conclusions could be made. How-

ever, in Grave it was observed that the surface water got more clouded during the underwater treatment.
As a result it was decided in consultation between the cleaning company Hydrex[2], RWS Zeeland and Waterdienst to repeat the tests under controlled circumstances in small test tanks.
The purpose was to understand:

1. leaching of harmful substances in seawater during the hardening process (simulation of the situation after the application in the dock);
2. which substances are released in seawater during the polishing?;
3. which substances are released during cleaning?;
4. do the released substances have a toxic consequence?

Based upon the results of these tests RWS can evaluate if polishing and cleaning in surface water is acceptable or not. This information is required in order to grant a permit for underwater cleaning. The experience that is obtained in such a way can gain an understanding in which way new products should be evaluated.

Hydrex provided the lab-materials, the polishing and cleaning. The leaching tests were executed in the test-facilities of RWS Zeeland. RWS Waterdienst performed the specific analyses of the water. Besides this, RWS ordered toxicity tests on the leaching water (step 1) and the water after polishing (step 2).

The operating procedures and the results of the tests are described in this report. Based upon this, RWS will evaluate to what extent underwater polishing and/or cleaning of Ecospeed coated ships is acceptable or not.

2. Composition and use of Ecospeed

Composition of Ecospeed

Ecospeed is a polymer based on polyester mixed with styrene. Prior to the application a hardener is added. This results in the interweaving of the polymer chains, which leads to a network of connected polymers. The styrene binds also to the polyester chains. The product has such a chemical composition that it cannot be affected by the seawater. Details of the composition of Ecospeed are shown in table 1.

Table 1
Some data Ecospeed

Composition		unity
Polyester resin	60-70	%
Glass particles	30	%
Hardener	<1	%
Solvent styrene	2-20	%
Al	6100	mg/kg product
Ni	<1	,,
Ca	5200	,,
Co	120	,,
Cr	1,9	,,
Cu	<1	,,
Fe	1700	,,
Cd	<1	,,
K	5800	,,
Mg	150	,,
Na	12900	,,
P	260	,,
Sb	3,1	,,
Sr	4,4	,,
Sn	<1	,,
Pb	<1	,,
Te	18	,,
Ti	1500	,,
V	2,5	,,
W	18	,,
Zn	5900	,,
Ecospeed usage	1,6	l./m^2 ships hull

Application of Ecospeed

Ecospeed is applied in two layers on the ship in a dry dock. (Total layer thickness of approx. 1000 micron). The coating is sufficiently hardened after twenty-four hours and the ship is then launched in the water. Prior to application of Ecospeed the surface is sandblasted. This blasting has a cleaning function and results in a surface structure with small holes.

Figure 1.
Ecospeed after polishing

The coating is fully hardened after some days in the surface water and the material is then polished under water by divers. This is also called the “*under-water-conditioning”*. During this process the last irregularities in the top layer of Ecospeed are removed with a brushing equipment. The result of the sandblasting, coating and polishing is a smooth surface structure that is comparable with that of a golf ball. Due to the smooth surface of the underwater surface of the ship, this will result in a lower resistance in the water. As a result the ship will need less power to sail at the same speed and thus will have a lower energy-consumption. Moreover fouling will less likely attach to the surface after the polishing.

The polishing of Ecospeed has to be performed under water to absorb the warmth produced by the rotating brushes on the ships surface. Above water, burning spots would develop on the treated area. Another advantage is that the cleaning/polishing machine underwater can put more pressure on the surface of the ship. The rotating brushes in the water generate a sucking power towards the ship surface. For that reason is this working process more efficient under water. By performing it under water, one avoids also extra docking costs.

3. Execution aspects

Under surveillance of RWS Zeeland and Waterdienst the testing plates were coated on both sides with Ecospeed. Details about the application of Ecospeed are available in appendix A.

The test plates were 24 hours after application transported to RWS Zeeland and there placed in testing tanks filled with artificial seawater (tap water with sea salt). The top of the tanks were closed to avoid evaporation of substances from the water.

Leaching tests
During the leaching test two square coated steel plates (40 by 40 cm) were placed in one tank (140 l.). The water was lightly stirred with magnetic stirring rods. Water samples were taken and analysed after respectively 48 and 168 hours leaching. Artificial seawater without plates served as a reference (blank).
The conditions during the leaching process are described in detail in appendix B.

Polishing
A larger test plate (80 by 50 cm) coated on both sides was placed flat on the bottom in a larger tank with salt water (250 l) and subsequently leached out for 168/ hours. Then the plate was polished on one side. Water samples were taken before and after the polishing. The water has not been stirred during the leaching period.

Cleaning
A test plate that was placed in the Marine Port of Zeebrugge for a year has been used to evaluate the cleaning. During cleaning, there was noticed that this plate was only coated at one side. The not-coated side was somehow rusty as a result of the corrosive action of the sea water. There was some fouling of sea organisms shown on the coated side. The cleaning is executed in distilled water in order to be able to detect possible release of heavy metals during the cleaning.

Figure 2.
Before and after cleaning of a plate from Zeebrugge (1 year contact in seawater)

before cleaning

after cleaning

The analyse of heavy metals was abandoned because one side was rusty, The rust can lead to too high metal concentrations, which could result in inaccurate results.

One can find the executed sampling scheme in table 2.

Table 2.
analysis and sampling scheme

Analysis	leaching		polishing		cleaning	
	48 hours	168 hours	before	after	before	after
Chemical analyses	+	+	+	+	+	+
Toxicity-testing	+	+	+	+		

Table 3 shows the executed chemical analyses and table 4 shows the performed toxicity tests.

Tabel 3.
Overview of chemical analyses

Analyses	Explanation	Executing
VOC analysis	GC/MS analysis volatiles	Lab. RWS WD
GC/MS	Screening 'other' organic substances[a]	Lab. RWS WD
TOC	Total organic carbon	External lab
Susp. matter	Suspended matter	External lab
Chloride		External lab
Ftalates	Softeners	External lab
Oil		External lab
B(p)A	Bisphenol a	External lab
N kj	Nitrogen Kjehldahl	External lab

[a] non certified qualitative analysis

The idea of analysing heavy metals and BOD in the samples has been abandoned because the determination would be too inaccurate in (artificial) sea water. There is no additional value in the determination of COD due to the structure of the polymer (insufficient breakdown of the polymer by chrome acid in the COD-determination). The TOC has been determined instead of the previous.

Table 4
Executed toxicity tests

Toxicity test	Explanation	Execution
Microtox®	Bacterial test	Grontmij/Aquasense
Acartia tonsa	crustaceans	,,
Phaeodactylum tricornutum	general	,,

Oestrogen effects
Use of the ER-Calux provides an impression of the oestrogen activity of the substances in the sampled water. The analyses for oestrogen activities were executed by the company BioDetection Systems in Amsterdam. The ER-CALUX® assay detects the extent of activation of an oestrogen receptor. This activity is compared to the response of a well-known oestrogen compound, 17ß-estradiol, which is used as a reference. The eventual oestrogen activity is expressed as 17ßestradiolequivalents (EEQs).

4. Results

4.1 Composition of Ecospeed

During the coating of the test plates but before the addition of hardener and diluents, RWS has taken a sample of Ecospeed (yellow coloured). Preceding a sample has been obtained from the producer (grey coloured). Before the water samples were analysed, these samples were analysed on volatiles (VOC-analysis with GC/MS) and were also evaluated via a GC/MS screening (qualitative determination) in the lab of the Waterdienst.

The results of the analyses are shown in Table 5[2].

Table 5
Results Ecospeed analyses with VOC- en GC/MS screening

Substance	Ecospeed (mg/g product)	
	Yellow	grey
styrene[a]	172	208
2-Propenoic acid, 2-methyl-, 3-hydroxypropyl ester[b]	4	5
Benzene, 2,4-diisocyanato-1-methyl-[b]	27	28
Benzene, 1,3-diisocyanato-2-methyl-[b]	5	6
2-Propenoic acid, 2-methyl-, 2-hydroxypropyl ester[b]	4	6

[a] VOC-analysis [b]GC/MS screening

Styrene was the only volatile analysed. About 20 mass % styrene was present in the used Ecospeed. Some less volatile components were detected in the GC/MS screening. These are presumably decomposition products of the not yet hardened Ecospeed that are formed due to the thermic decomposition under high temperature in the GC/MS apparatus. When applying Ecospeed In surface water these components would not develop.

[2] There has been added extra styrene at the original product. The styrene content in the applied paint was actually higher.

4.2 Results leachingtests

4.2.1. Chemical components

The analyses results of both leaching tests, one in the small tank with two plates (140 l.) and the other one with the large plate in a 250l tank are presented in table 6 and 7.

In table 6 the general parameters and some specific oriented target-component analyses (phthalate softeners, bisphenol A) can be found. This table shows that during the leaching tests there are no spectacular changes in the concentrations of the analysed components. It is noticeable that the solvent *diisobutylphthalate* from the harder component is not found in the leaching samples.

Table 6.
Results general analyses

	Unity	blank seawater	2 plates in seawater	2 plates in seawater	1 plate in seawater
Leaching period	hours	168	48	168	168
Lab code		107107	107112	107106	107111
Component					
TOC	mg/l	3,4	4,8	5,6	4,1
Chloride	g/l	14,0	14,0	14,0	16,0
Kj N	mg/l	<0,5	<0,5	<0,5	<0,5
Susp. matter	mg/l	<4	9,0	<4	4,0
oil gc	mg/l	<0,05	<0,05	<0,05	<0,05
Diisobutylphthalate[a]	mg/l	<0,01	<0,01	<0,01	<0,01
Bisphenol A	µg/l	<0,001	<0,001	<0,001	<0,001
Volume seawater (l)		140	140,0	133,0	250,0
Ecospeed surf. (m^2)			0,6	0,6	0,4

[a] the concentrations of DEHP and other phthalates is 0 mg/l

Table 7.
Results analyses volatile components

Table 7 show the results of the analysed volatile components.

Leaching period	Hours	blank sea-water 168	2 plates in seawater 48	2 plates in seawater 168	1 plate in seawater 168
Lab code		107107	107112	107106	107111
Component	unity				
Methyl-t-butyl-ether[a]	µg/l	0,03	0,03	0,04	0,07
Diisopropylether[a]	µg/l	0,00	0,00	0,00	0,00
Chloroform[a]	µg/l	0,02	0,03	0,04	0,00
1,1,1-Trichloorethane[a]	µg/l	0,85	0,57	1,45	0,46
Benzene	µg/l	0,01	0,03	0,08	0,04
Cyclohexane[a]	µg/l	0,03	0,07	0,22	0,05
Methyl-methacrylate[a]	µg/l	0,05	0,09	0,34	0,06
Toluene	µg/l	0,00	1,45	0,07	0,84
Ethyl benzene	µg/l	0,02	39,86	46,02	14,19
p/m-Xylene	µg/l	0,01	0,35	0,00	0,28
Styrene	µg/l	0,01	128,19	0,02	0,01
o-Xylene	µg/l	0,01	40,13	51,30	20,69
Cumene	µg/l	0,00	0,36	0,28	0,08
n-Propylbenzene	µg/l	0,00	0,11	0,09	0,04
m-Ethyltoluene	µg/l	0,00	0,00	0,00	0,00
p-Ethyltoluene	µg/l	0,00	0,18	0,07	0,07
Mesithylene	µg/l	0,00	0,11	0,05	0,06
o-Ethyltoluene	µg/l	0,00	0,00	0,00	0,00
1,2,4-Trimethylbenzene	µg/l	0,00	0,00	0,00	0,00
1,2,3-Trimethylbenzene	µg/l	0,00	0,15	0,16	0,15
Naphthalene	µg/l	0,01	0,06	0,05	0,05
Volume seawater (l)			140	133	250
Ecospeed surf. (m^2)			0,6	0,6	0,4

[a] non aromatic solvent

In general it is shown that in the leaching samples there are volatile components present compared to the artificial seawater. The concentrations of certain components between the different samples are not comparable due to the fact that the amount of seawater is not always exactly the same, the leaching times are different or the metal surface/volume ratio is different(this applies for the far right column).

It is remarkable that there are aromatic solvents present in the leach samples. When taking the water samples after 168 hours, the water smelled indicating the presence of these solvents. O-xylene proves a clear example. This solvent is present in the leach samples in the highest concentrations. These are not present in the analysis of Ecospeed before spraying. These are not used in this product according to the supplier of the resin. Most probably, these come from the components of the thinner that is used in Antwerp to clean the spraying apparatus before and in between the application. This is confirmed by the spraying company (info M. Thomas, De Medts nv, d.d. 19 Aug. 2008). Normally, according to the specifications of the supplier of Ecospeed acetone needs to be used to clean.

At first, the component styrene was expected in the leaching samples. This component is only found in the first leaching sample after 48 hours. The explanation can be that the dissolved styrene is completely evaporated during the sampling, as there was a constant stirring with the result that volatilizing could easier take place.

Flux calculations are mostly used to test leaching data. A flux is the amount of components that is released per time unit and square meter. The flux will exponentially drop in function of the time.

Table 8 shows the fluxes calculated with respect to the leaching tests. The concentrations of the components in the blank are corrected in the calculations. The differences in available leaching surface and the decline in volume of seawater due to sampling after 48 hours is also taken into account. As the water was not renewed with fresh seawater in between, the flux calculations have to be considered as a first approach.

Table 8
Calculated fluxes volatile components during leaching

	Leaching flux mg/m^2.day		
	2 plates in seawater during 2 days	2 plates in seawater during 7 days	1 plate in seawater during 7 days
Component name			
Methyl-t-butyl-ether	0,000	0,000	0,004
Diisopropylether	0,000	0,000	0,000
Chloroform	0,000	0,000	-0,002
1,1,1-Trichloorethane	-0,031	0,018	-0,034
Benzene	0,003	0,002	0,002
Cyclohexane	0,004	0,005	0,001
Methyl-methacrylate	0,005	0,009	0,001
Toluene	0,158	0,002	0,075
Ethylbenzene	4,358	1,366	1,265
p/m-Xylene	0,037	0,000	0,024
Styrene	14,020	0,000	0,000
o-Xylene	4,388	1,523	1,846
Cumene	0,040	0,008	0,007
n-Propylbenzene	0,012	0,003	0,004
m-Ethyltoluene	0,000	0,000	0,000
p-Ethyltoluene	0,019	0,002	0,006
Mesitylene	0,011	0,001	0,005
o-Ethyltoluene	0,000	0,000	0,000
1,2,4-Trimethylbenzene	0,000	0,000	0,000
1,2,3-Trimethylbenzene	0,016	0,005	0,013
Naphtalene	0,005	0,001	0,004
sum	23,0	2,9	3,2

From the previous table it can be seen that the sum of the average fluxes are quite well comparable after 7 days. On top of that, it shows that the flux was significantly higher the first two days. This leads to the conclusion that the flux exponentially declines in function of the time span.

4.2.2. Toxicity/oestrogen effects leaching samples

In the table given below, the results of the toxicity tests are summarized.[3] Hardly any effects are observed. Only in the test with the crustacean *Acartia tonsa* a very, very small effect (EC50 94,1%) is noticed. Because of the fact that there is already some effect in the blank seawater, one can assume that the shown effect is nil. This means that the leached components don't lead to any shown effects. These samples are harmless compared to similar tests of some industrial discharges.

This means in real terms that when a ship will be launched after 24 hours, it is out of the question that one can find toxic effects because of leaching components. It should be mentioned that the hardening of the coating happened very fast due to the high outside temperatures[4]

Table 9.
Resultats toxicity- en oestrogenitytests

	unit	blank seawater	2 plates in seawater	1 plate in seawater
Leaching time	hours	168	168	168
Lab code		107107	107106	107111
Toxicity tests				
Microtox (bactery-test)				
EC20	% vol.	>50	>50	>50
EC50	% vol.	>50	>50	>50
Acartia tonsa				
EC50	% vol.	>100	94,1	>100
NOEC	% vol.	32	10	100
Phaeodactylum tricornutum				
EC50	% vol.	>100	>100	>100
NOEC	% vol.	100	100	100
Oestrogen effects				
ER Calux	pg EEQ/l	<LOQ (72)	82	Not set

Univocal values for the activity measured with the ER-Calux assay (oestrogenic/gender influence) are not yet available. Based on experimental results are for the ER-Calux response values available that indicate effects or not on fishes in surface water. Measured values below 500 pg EEQ/l water indicate a low response because in experimental studies no effects were recognised. As the responsiveness

[3] Explanation on the interpretation of toxicity data can be found on the following website: http://www.helpdeskwater.nl/adviesgroepemissies/bibliotheek_fwvo/?ActItmIdt=883 FWVO 2003-03 TEB Deel T-1: Meten TEB parameters
for ER calux: www.helpdeskwater.nl/waterbodems_(akwa)/zoute_baggerspecie/uitleg/bio-assays/er-calux/

[4] Another hardener is advised by the producer when the outside temperatures are low..

increases also the possibility of actual effects increases. The leaching samples cause little oestrogenic activity. The detected effect level is much lower than the level known to result in effects on fish.

4.3 Polishing and cleaning of Ecospeed

4.3.1. Released substances

In table 10 and 11 the results of the analysis on chemical substances is listed. Also the calculated emissions (mg/m2) are presented in this table. In table 10 the data about the general parameters are represented and in table 11 those of the analysed volatile substances (VOC-analysis). Figure 3a en 3b give an impression of the turbidity created during the polishing and cleaning of the plates with Ecospeed.

Table 10.
Released substances (general parameters during polishing and cleaning)

Substance	unit	Before polishing	After polishing	Before cleaning	After cleaning
Lab code		107111	107110	107109	107108
TOC	mg/l	4,1	6,0	1,0	3,1
Chloride	g/l	16,0	16,0	< 0,01	< 0,01
Kj N	mg/l	<0,5	1,5	0,9	2,8
Susp. Sol.	mg/l	4,0	30,0	15,0	110,0
oil gc	mg/l	<0,05	0,1	<0,05	0,1
Diisobutylphtalate	mg/l	<0,01	0,26	<0,01	0,7
DEHP/DOP	mg/l	<0,01	<0,01	<0,01	0,04
Bisphenol A	µg/l	<0,001	0,01	0,2	0,3
volume (l)		250,0	231,0	250	231
Ecospeed surf. (m^2)		0,4	0,4	0,4	0,4

			emission		emission
TOC	mg/m^2		902,5		1165,3
Chloride	mg/m^2		n.a.		n.a.
Kj N	mg/m^2		866,3		1617,0
Susp. Sol.	mg/m^2		14825,0		54150,0
oil gc	mg/m^2		69,3		34,7
Diisobutylphtalate	mg/m^2		150,2		410,0
DEHP/DOP	mg/m^2		n.a.		23,1
Bisphenol A	mg/m^2		0,005		0,059

Figure 3 a en b
View of polishing and cleaning

3a polishing

3b cleaning water

Tabel 11
Released volatile substances during polishing and cleaning

Substance / Lab coder		Before polishing 107111	After polishing 107110	Polishing emission (mg/m2)	Before cleaning 107109	After cleaning 107108	Cleaning emission (mg/m2)
Methyl-t-butyl-ether	µg/l	0,07	0,09	0,004	0,15	0,14	-0,013
Diisopropylether	µg/l	0,00	0,10	0,058	0,00	0,00	0,000
Chloroform	µg/l	0,00	0,03	0,015	0,00	0,00	0,002
1,1,1-Trichloorethaan	µg/l	0,46	0,41	-0,056	0,41	0,38	-0,040
Benzene	µg/l	0,04	0,05	0,004	0,04	0,06	0,010
Cyclohexane	µg/l	0,05	0,04	-0,006	0,04	0,04	-0,003
Methyl-methacrylaat	µg/l	0,06	0,07	0,003	0,03	0,03	0,000
Toluene	µg/l	0,84	0,97	0,036	2,37	2,16	-0,230
Ethyl benzene	µg/l	14,19	15,21	-0,085	0,07	0,41	0,195
p/m-Xylene	µg/l	0,28	8,84	4,934	0,08	1,62	0,884
Styrene	µg/l	0,01	0,51	0,290	0,13	48,58	27,974
o-Xylene	µg/l	20,69	22,45	0,038	0,05	0,63	0,334
Cumene	µg/l	0,08	0,14	0,027	0,01	0,02	0,004
n-Propylbenzene	µg/l	0,04	0,10	0,030	0,01	0,01	0,003
m-Ethyl toluene	µg/l	0,00	0,14	0,078	0,01	0,02	0,008
p-Ethyl toluene	µg/l	0,07	0,19	0,062	0,01	0,00	-0,005
Mesitylene	µg/l	0,06	0,17	0,058	0,00	0,01	0,004
o-Ethyl toluene	µg/l	0,00	0,09	0,053	0,02	0,05	0,018
1,2,4-Trimethylbenzene	µg/l	0,00	0,09	0,052	0,02	0,05	0,018
1,2,3-Trimethylbenzene	µg/l	0,15	0,28	0,068	0,01	0,01	0,005
Naphthalene	µg/l	0,05	0,08	0,01113	0,02	0,03	0,006
Sum	mg/m^2			5,7			29,2
volume (l)		250	231		250	231	
Ecospeed surf.. (m2)		0,4	0,4		0,4	0,4	

From the results in table 10 and 11 it can be noticed that during polishing and cleaning substances are released. In fact the 'skin surface' of Ecospeed is "torn open" so that substances are released. Also from the cleaning tests of plates that were put in seawater for a year in Zeebrugge, 'enclosed' substances could be recognised. We see this effect for the general as well as for the volatile substances.

The various water samples before and after polishing or cleaning were also analysed with a GC/MS screenings-method. This revealed the softener that was put into the hardener substance (diisobutylphtalate), but also other similar cracking products as found in Ecospeed (see annex C).

The samples taken after polishing are shaken and then observed whether the solids settle rapidly. This was not the case. The suspended solids consist of very small particles that more or less keep floating. It seems that the particles after a longer period (1 week) somewhat start to conglomerate. Some flocculation occurred. Removal of the small particles coming from the polishing by sedimentation seems from a practical viewpoint not to be a valid option.

So the sedimentation seems to be a valid option and linked with this phenomena the removal of the small particles that originated from the polishing.

A water sample derived from the cleaning was also stirred. In this sample the larger parts, mainly rests of organisms, settled in a few minutes time. After 10 minutes it seemed that the smaller parts remained floating. After standing one night the liquid was clear.

4.4 Toxicity/oestrogenic effects before and after polishing

In table 12 the results of the toxicity tests before and after polishing are summarized. The results show that substances released during polishing do not result in effects on the three test organisms.

No toxicity tests on fish were performed. In general fish are less sensitive than the organisms cited in the table below. Based on the chemical composition of Ecospeed effects on fish are not expected[5].

[5] Ecospeed is a high molecular non iogenic polymer. Experience within RWS shows that only cationic polymers result in toxicity effects.

Tabel 12.
Results of toxicity- and oestrogenic tests

	unit	Water toxicity before polishing	Water toxicity after polishing
Leaching time	uur	168	168
Lab code		107111	107110
Toxicity test			
Microtox (bacterialtest)			
EC20	% vol.	>50	>50
EC50	% vol.	>50	>50
Acartia tonsa			
EC50	% vol.	>100	>100%
NOEC	% vol.	100	100
Phaeodactylum tricornutum			
EC50	% vol.	>100	>100
NOEC	% vol.	100	100
Oestrogenic effects			
ER Calux	pg EEQ/l	192	104

The results of the oestrogenic tests are also presented in table 12. De oestrogenic activity is slightly decreased after polishing. The demonstrated activity is low and below the level that effects are observed in studies on fish.

5. Applying of the laboratory results in practice.

The results of the tests reveal that by using Ecospeed emissions to the surface water will occur. To get a feeling of the meaning of these emissions calculations have been performed to what extent emissions take place when harbour ships are treated with Ecospeed, as well as during polishing and cleaning. The Citterharbour, in the control area of RWS ZEELAND, has been used as 'model harbour'. This harbour is situated in the Sloe area (industrial area in Vlissingen).
Assumption has been made that a ship with an external surface of 1500 m^2 is treated. This is a small cargo vessel with a length of 80 meters.

The Citterharbour measures in width 400 m, in length 820 m and has a depth of max. 14,5 m. This results in a theoretical maximum volume of 4.756.000 m^3.

It has to be taken into account that when interpreting the calculations below, that the results represent only a rough estimate of the reality.

Emission by leaching
The emission data of table 8 have been used for this; i.e. the first two days a strong leaching followed by 5 days with a lower leaching. This results for this ship in a leaching of 98 grams of dissolvent in the surface water during the first week. This corresponds with an overall averaged concentration in the harbour of 0,02 µg/l. The concentration of dissolvent is not limited to the harbour only as the dissolvent will be distributed over a larger area as the ships sail to other areas as soon as they left the dock. Looking at the result of this calculation it has to be taken into consideration that other coatings on other ships also will emit volatile dissolvents. The results of the toxicity tests with test organisms show that leaching in practice most probable will not lead to effects.

Emission by polishing
Emission data of table 10 and 11 are used. Via polishing 22 kg suspended solids (Ecospeed grinding), 0,2 kg diisobutyl phtalate en 0,008 kg dissolvent is released in the harbour. Based on the results of the toxicity tests most probably no toxic effects will be noticeable. As a result of the polishing an overall increase of 0,005 mg/l of the suspended solids will occur in the harbour. By exchange with the surface water this will be diluted further. The suspended solid concentration in the Westerschelde is usually some tens of mg/l.

Emission by cleaning
Emission data of table 10 and 11 are used. By cleaning of five ships in a timeframe of a year 81 kg of suspended solids (mainly removed bar-

nacles), 0,6 kg diisobutylphtalate en 0,04 kg solvents are released in the harbour. Possible toxic substances resulting from the cleaning have not been investigated. As no effects have been found for the leaching and polishing also no effects are expected during cleaning. With the cleaning process mainly fouling organisms are removed.

The volumes of suspended solids that are released during polishing and cleaning seem to be important. To frame these loads they are compared with the suspended solid release of an industrial waste water plant that discharges into the Citterharbour and treats the wastewater of the companies of the Sloe area. The yearly released volume of suspended solids is approximately 68000 kg.

It cannot be excluded that during polishing or cleaning a visual contamination because of suspended solids can be noticed. When cleaning is done underwater the suspended solids are released in the direct vicinity of the ships hull. This is what most probably was noticed during the practical test in Grave when the Ecospeed surface of an oil recovery ship was polished.

6. Conclusions

Based on the results of the model experiments with testing plates coated with Ecospeed in artificial seawater, the following can be concluded:

1. During the experiments it became clear that emissions related to the application of Ecospeed occur at three distinctive moments:
   a) During the hardening phase of Ecospeed aromatic solvents (xylene, styrene) are released in the surface water by leaching.
   b) During polishing of Ecospeed the last irregularities are removed by nylon brushes. During this process polymer grinding is released as well as solvents and softeners from the applied hardener.
   c) During cleaning of ships coated with Ecospeed the (slight) fouling of algae, small animals and grass is removed with brushes. The experiments have revealed that apart from the (crushed) organisms the same chemical substances are released as during polishing.

2. Toxicity tests with bacteria, crustaceans and algae have indicated that the substances released during leaching and polishing do not show any effects. Tests have been performed on testing tanks and should be seen as a worst-case approach. In practice a much lower concentration of chemical substances will be released in the harbours than described in the experiments of this report. This makes that in practice also no effects are expected.

3. No oestrogenic effects have been noticed as a result of the released substances during leaching or polishing of the testing plates treated with Ecospeed.

4. The suspended solids that are released during polishing (mainly polymeric grinding) and cleaning (mainly brushed off fouling and polymeric grinding) will be released in the surface waters of the harbour. The quantities of suspended solids are limited to ca. 20 kg during polishing and 80 kg during cleaning a small cargo ship with a surface of 1500 m^2. As a reference point a biological industrial waste water plant releases yearly about 68.000 kg of suspended solids.

5. Polymeric grinding that is released during polishing and under water cleaning has a very fine nature and settles very slowly. In practice these inert suspended solids will be distributed from the harbour over larger areas as a result of the present currents. The organisms brushed off or grinded organisms during

cleaning seem to sediment much faster and will end partially at the bottom of the docks in the harbour.

6. The test method used in this evaluation (testing tanks) is also suited for evaluating other coatings when required. When other questions arise from suppliers of antifouling products, it is advised that they discuss the results of similar tests with RWS. RWS considers the evaluation at hand as an once-only pilot study.

Annex A: Coating testing plates

Application date paint: 13 May 2008-05
Location: Grinding hangar of Fa. Demedts, Ketenislaan 2, Kallo (Harbour of Antwerp).

Present: A. Wijga en R. Berbee van RWS, M. Hofman van Hydrex, K. Verhelst van ERM (during the first coating) and personnel of Demedts.

In advance the testing plates were sandblasted by hand in a blasting cabin at both sides.

Coating of the plates
Two steel plates of 40*40*0,5 cm and one steel plate of 80*50*0,5 cm are coated twice with Ecospeed on both sides. One paint layers was yellow (RAL 1018, zinc yellow) and the second was grey (Ral 7000, squirrel grey). The drying period between the two sprayings was one hour. The reason that the second layer was in another colour was intentional, as this made it easier to guarantee that the second layer was applied sufficiently. The colour difference allowed the sprayer to easily judge he covered the whole surface adequately.

The yellow paint was constituted of Ecospeed filled up with a small quantity of styrene. 1 litre styrene was added to 20 litre of Ecospeed. Then to 6 litres of this mixtures was 30-35 ml Butanox LPT (harder/catalyst) added. Next the plates were sprayed. After the first application the painting equipment was cleaned with thinner.

The temperature in the testing hall was after 24 hours hardening of the coating 27degrees Celsius. During the application the temperature was comparable.

Layer thickness Ecospeed:
Plate 40*40 nr. 1: thickness of the layer varied slightly along the plate (1205- >1600 micron). The thickness of the layer was below 2000 micron because no drops had formed.

Plate 40*40 nr. 2: thickness of the layer varied slightly along the plate (1359 - >1600 micron). The thickness of the layer was below 2000 micron because no drops had formed.

Plate 80*50: the thickness of the layer has not been measured. It can be assumed that the thickness was comparable to that of the smaller plates. The manner of spraying was similar to that of the smaller plates.

Testing plate cleaning

A testing plate (80*50* 0,6 cm) is coated at one side and has been submerged in the marine port of Zeebrugge. This plate was coated with Ecospeed red (RAL 3003, ruby red)

Annex B: Leaching, sampling, polishing and cleaning

Conditions

Leaching is performed in the testing facilities of RWS Zeeland. The leaching started on May 14 at quarter past three.

The two smaller Ecospeed coated steel plates (40*40*0,6 cm) are placed in a glass tank filled with salt water? This aquarium measured 50*50*80 cm, glass thickness was 1,8 cm. The water in this tank was kept in a slow motion with two magnetic stirring rods. The water was composed of 140 litres tap water to what 5 Kg aquarium salt has been added (supplied by Instant Ocean).
An identical aquarium with salt water but without the steel plates was used as reference blank. Both tanks were placed on a laboratory table with underneath them the magnetic stirrers. The temperature in the laboratory was 18 degrees Celsius.

The large Ecospeed plate (80*50*0,6 cm) was also placed in an aquarium filled with salt water. This tank measured 60*100*80 cm and had a glass thickness of 2,2 cm The water was also composed of tap water and aquarium salt (250 liter tap water en 8,880 kg Aquarium salt). The salinity of the water measured 34,30 gram/kg water. The water in this tank was not kept in motion. The steel plate was resting on the bottom of the tank and as such only one sided leaching took action.

All three tanks were sealed with a glass plate. To prevent evaporation from the water, the small holes were sealed with packing tape.

The pH was at the start of the test 7.73 in the three tanks.

Furthermore a cleaning test has been performed from a fouled Ecospeed plate that has been put in demineralised water on May 20th. This plates id subsequently cleaned. Sampling has been done before and after cleaning.

Sampling

On 16 May, 72 hours after the first coating (=48 hours leaching), the first samples have been collected. The second sampling took place on 20 May, 198 hours after the first coating (168 hours leaching)

On 16May only the small tank with the two plates has been sampled.

Overview of the seawater volume in the tanks (l).

tank	16 May	20 May sample 1	20 May sample 2
microcosm a	140 l.	140 -> 121 l.	

blank			
microcosm b leaching	140 l. -> 133 l. (-5%)	133 l. -> 114	
microcosm c polishing	250 l	250 l. -> 231 l. (-8%)	231 -> 212 l.
microcosm d cleaning		250 l. -> 231 l. (-8%)	231 -> 212 l.

Polishing and cleaning

The purpose of the underwater conditioning, also known as underwater polishing, is to achieve a surface roughness that is below 15 µm. This corresponds with level A on the Rubert Scale.

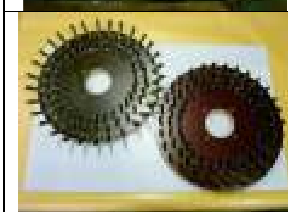
After applying two layers of Ecospeed (1000 µm DFT) the surface feels a little rough. After one polishing step with hydraulically driven brushes specifically designed for this job, the surface is smoothened.

The smoother surface of the underwater part of the ships hull, results in a lower friction of the ship with the water. This means the ship will need less power to maintain the desired speed. At the same time fouling will have more difficulties to stick to the hull now it has been conditioned.

The brushing materials used for the underwater conditioning exist of sanding nylon.

Picture brush type	Brush type	Material	Application
	Ecospeed	Sanding nylon	Conditioning Ecospeed

Based on the type of fouling that develops after a certain time span on the Ecospeed surface, a different cleaning brush is selected. In the table below an overview of these type of brushes is given. The brushes can be applied with the underwater hydraulic cleaning machines used for conditioning (underwater polishing).

Picture brush type	Brush type	Material	Application
	Rilsan	Nylon	Gras Slime Small bar-nacles
	Rilsan scraper	Nylon Metal scrapers	Barnacles
	Polyprop	Polypropene (polypropylene)	Gras Slime (special for sensitive surfaces)
	Steel wire	Steel wire	Hard and dense foul-ing
	Steel grass	Steel wire	Strongly and densely grass cov-erage
	Steel scraper	Steel wire Metal scrapers	Very abun-dant and dense foul-ing
	Standard scraper	Metal scrapers	Extremely dense and heavy foul-ing

Annex C: Results of GC/MS screening

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In the table below the results of the GC/MS screening are summarised. This methodology attempts with via an automated system to identify compounds in (waste)water. The mass spectrum of these detected compounds is compared with a library containing about 100 000 spectra of known substances. Also comparisons are made with compounds that are regularly detected in surface waters by RWS. It is a qualitative method. The identification is not 100% as is also the case for the measured concentrations. The applied GC/MS volatile method is much more accurate. The concentrations should be seen as comparatively (a lot present or very limited)

	Concentrations ug/l	blank seawater	Leaching 2 plates	Leaching 2 plates	Large tank with plate before polishing	Large tank with plate after polishing	Distilled water with plate - short contact Before cleaning	Distilled water with large plate After clean-ing
	Contact time (hours)	168	48	168				
cas number	Substance name	107107	107112	107106	107111	107110	107109	107108
100-42-5	Styrene		1853			92		323
100-51-6	Benzyl Alcohol							2
100-52-7	Benzaldehyde					35		31
106-42-3	p-Xylene		74	82	23	29		4
107-93-7	2-Butenoic acid, (E)-			6				
108-38-3	Benzene, 1,3-dimethyl-		70	87	23	39		2
108-94-1	Cyclohexanone					2		
109-16-0	2-Propenoic acid, 2-methyl-, 1,2-ethanediylbis(oxy-2,1-ethanediyl) ester					3		
122-78-1	Benzeneacetaldehyde					9		19
141-02-6	2-Butenedioic acid (E)-, bis(2-ethylhexyl) ester					7		9
1461-27-4	Cyclohexene, 1-methyl-5-(1-methylethenyl)-, (R)-		3		3			
15206-55-0	Benzeneacetic acid, à-oxo-, methyl ester					3		6
16106-59-5	1-Hexene, 4,5-dimethyl-							2
1674-30-2	Benzenemethanol, à-(chloromethyl)-		2	3	3	6		
20780-53-4	Benzene, (epoxyethyl)-, (R)-					40		37
2129-89-7	Phosphine oxide, methyldiphenyl-					2		2

	Concentrations ug/l Contact time (hours)	blank seawater 168	Leaching 2 plates 48	Leaching 2 plates 168	Large tank with plate before polishing	Large tank with plate after polishing	Distilled water with plate - short contact Before cleaning	Distilled water with large plate After clean-ing
23250-03-5	(2-Hydroxyethyl)-triphenylphosphonium chloride					6		18
25552-17-4	1-Hexanone, 5-methyl-1-phenyl-					3		
3622-84-2	Benzenesulfonamide, N-butyl-					22		6
3878-45-3	Triphenylphosphine sulfide							5
3-9-2-76-1	2-Propenoic acid, 2-methyl-, 3-hydroxypropyl ester		4	7	13	145		76
4376-20-9	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester					2		208
495-71-6	1,4-Butanedione, 1,4-diphenyl-							4
496-11-7	Indane		2					
507-45-9	Butane, 2,3-dichloro-2-methyl-	4		4	4	4	4	4
542-10-9	1,1-Ethanediol, diacetate						2	
583-05-1	1,4-Pentanedione, 1-phenyl-							2
584-84-9	Benzene, 2,4-diisocyanato-1-methyl-				3	898		544
68494-08-6	4,5-Bis(benzoylthio)-1,3-dithiole-2-thione							2
770-35-4	1-Phenoxypropan-2-ol					2		
77-90-7	Tributyl acetylcitrate		2		2	4		
79-41-4	2-Propenoic acid, 2-methyl-							2
84540-57-8	Propanol, methoxy-, acetate					10		
84-69-5	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester			11		423		1214
84-74-2	Dibutyl phthalate				2	2		21
91-08-7	Benzene, 1,3-diisocyanato-2-methyl-					220		131
923-26-2	2-Propenoic acid, 2-methyl-, 2-hydroxypropyl ester		9	16	23	192		132
95-47-6	o-Xylene			89	29	13		6
98-86-2	Acetophenone			2		8		26