Dynamic Simulations of a Self-Polishing Antifouling Paint Exposed to Seawater

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A mathematical model for a self-polishing antifouling paint exposed to seawater was extended to handle dynamic simulations. The aim has been to investigate, quantitatively, the transient responses of the paint to changes in seawater temperature, pH, concentration of NaCl, and ship speed. The simulation study revealed that polishing and biocide release rates for a paint present on a ship bottom rarely reach stable conditions, because of the slow response of the paint to changes in temperature and ship speed. It was also found that the paint behavior stabilizes more rapidly from a temperature or speed increase than from temperature or speed reductions. These results are essential for the testing of paints on ships and useful information in the development of novel self-polishing antifouling paints.

The modeling approach underlying the simulations can be applied to any type of self-polishing antifouling paint provided that sufficient kinetic, solubility, and diffusivity data are available for the pertinent rate steps influencing the paint behavior.

INTRODUCTION

Ship surfaces exposed to seawater are inclined to settlement by animal and plant organisms. The biological process, which is termed fouling, can result in the formation of a thick and hard crust that poses several problems in relation to maintenance, fuel consumption, and operational availability of ocean-going ships.[1,2]

Various ways of avoiding the fouling have been tried,[3] but presently fouling is fought by the use of so-called antifouling paints, which slowly release biocides into the seawater.[4,5] The most effective, commercially available, antifouling paint system is based on the tributyltin self-polishing copolymer (TBT-SPC) and is used on approximately 70% of the world fleet of ocean-going ships.[6] However, environmental investigations have shown that the organotin is harmful to mollusks, such as oysters and marine snails.[7] According to Ryle,[8] this has motivated the Marine Environment Protection Committee (MEPC) under the International Maritime Organisation (IMO) to work towards a global legally binding instrument to ensure prohibition on the application of organotin compounds, which act as biocides in antifouling systems on ships by January 1, 2003, and a complete prohibition of these biocides in antifouling paints on ships by January 1, 2008. As a consequence, there have been many attempts to develop alternative antifouling systems using either a nontoxic or a less toxic coating.[5,6,8,9] Most of the present tin-free, biocidal paint systems rely on the use of soluble cuprous oxide (Cu_2O) pigment in combination with various organic boosting co-biocides for fouling control.[8] The effects of active copper ions (mainly Cu^{2+}) in the marine environment are probably minimal, compared to those of TBT-species, because most of the ions form less biologically active compounds such as $Cu(OH)_2(s)$ and $CuCO_3(s)$. The impact on the marine environment of the various co-biocides is presently under scrutiny.

In the search for novel antifouling paints, the approach has mainly been that of rotary-, raft- and ship tests.[5,10] Only a small number of theoretical studies have been reported over the years and these were all done on the insoluble matrix type paints, which is no longer a front-running antifouling technology.[11-16]

In our previous work,[9] it was shown how to develop a fundamental mathematical model of a self-polishing antifouling paint, which can be used to estimate polishing rates and the extent of pigment leaching at various condi-

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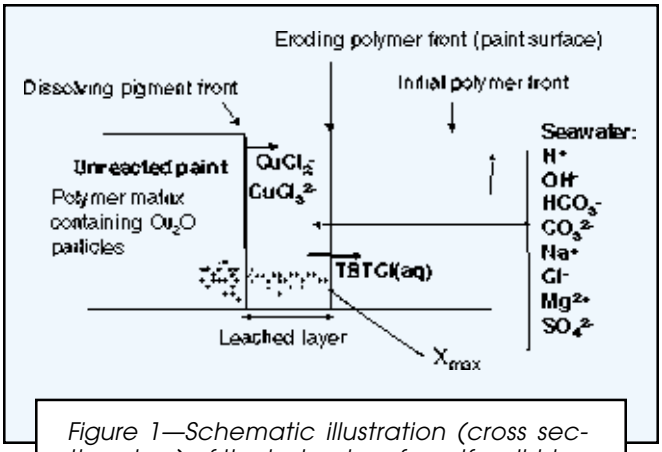

Figure 1—Schematic illustration (cross section view) of the behavior of a self-polishing antifouling paint comprised of an active polymer, a retarder, and Cu_2O particles. The partially hydrolyzed active polymer is released from the paint surface when the polymer surface conversion reaches a value equal to X_{max}. After Kiil et al.[9]

tions of seawater and ship speed. As a case study, paints based on the well-known TBT-technology were chosen. One of the reasons for this choice was that a detailed understanding of the unique mechanism of TBT-self-polishing copolymer systems may provide a basis for the development of alternative environmentally safe systems as suggested by Gerigk et al.[6] Furthermore, kinetic and solubility data, sufficiently detailed to develop a model, was only available in the literature for this particular polymer system. Finally, the principles used to model TBT-based paints are of a general nature and therefore applicable to other antifouling paints based on similar controlled release mechanisms. In a subsequent investigation,[17] a parameter study employing the mathematical model was performed.

In this work, a dynamic simulation study is performed using an extended version of the mathematical model. The influence of dynamic changes in seawater conditions and ship speed on the paint behavior is investigated. It is the aim of the work to support the development of novel self-polishing antifouling paints by providing detailed information on the dynamics of self-polishing systems. This knowledge may be useful for planning of rotary- or ship tests and in the process of designing paints with certain properties.

Table 1—Seawater Conditions and Composition of the Base Case Antifouling Paint. 1.0 knots=0.514 m/s=1.850 km/hr[a]

Parameter	
Seawater temperature (°C)	30
Seawater pH (-)	8.2
Seawater concentration of $MgSO_4$, $7H_2O$ (g/L)	14
Seawater concentration of $NaHCO_3$ (g/L)	0.2
Seawater concentration of NaCl (mol/L)	0.55
Ship speed (knots)	20
Paint content of Cu_2O (% by solids volume)	40
Paint content of active binder (TBTM/MMA copolymer) (% by solids volume)	54
Paint content of retarder (BMA/MMA copolymer) (% by solids volume)	6
Impurity content of Cu_2O (wt%)	4

(a) The seawater composition was obtained from Grasshof[19]

MATHEMATICAL MODEL

The mathematical model was developed and verified against experimental paint rotary data in our earlier work.[9] The experiments involved investigation of the effects of rotary speed, temperature, and paint composition on the polishing and leaching rates. Due to the large number of equations contained in the model, the contents of the latter will be described here in qualitative terms only. For a detailed and quantitative description the reader is referred to our previous work.[9]

The self-polishing antifouling paints, for which the model was developed, have a one-phase binder system consisting of an active copolymer of tributyltin methacrylate (TBTM) and methyl methacrylate (MMA) and a retarder (i.e., an inert hydrophobic copolymer which is present to reduce the solubility and increase the strength

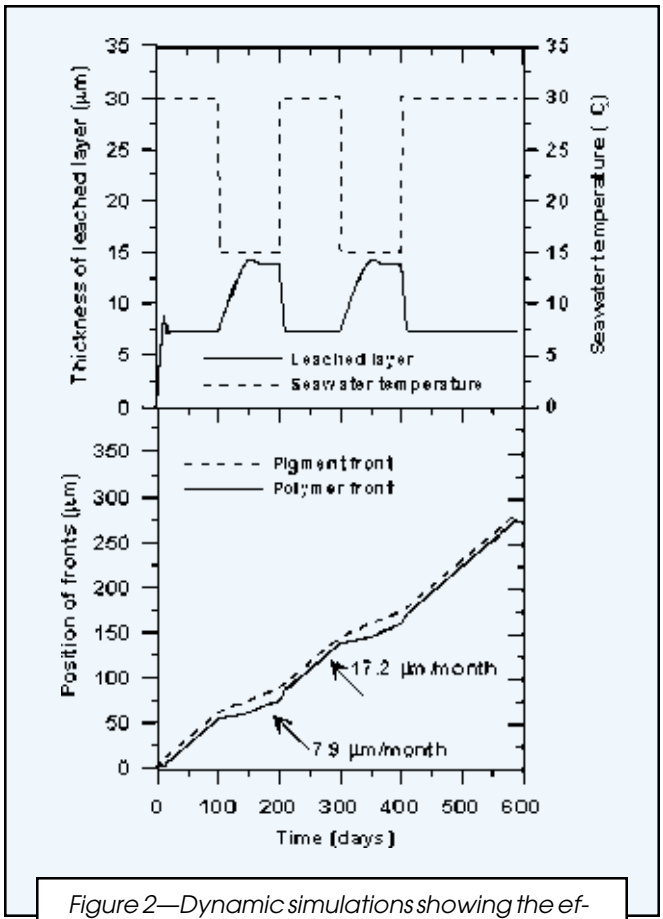

Figure 2—Dynamic simulations showing the effects of step changes in seawater temperature on the rate of movement of the pigment and polymer fronts, as well as the thickness of the leached layer. Two points of stable polishing rates are indicated with arrows. Other parameters are given in Table 1.

of the binder phase) of butyl methacrylate (BMA) and MMA. The particulate phase is made up of the commonly employed pigment Cu_2O, which has a biocidal effect upon dissolution. The influence on the paint behavior of the presence of additives, extenders (or fillers), and insoluble pigments in the paint are not included in the model. However, the polishing rates of the paint systems considered are comparable to those exhibited by typical commercial tin-based paint systems[9] and so the model contains the most essential chemistry and mass transport phenomena needed to describe the basic paint behavior.

The physical processes that arise when a TBT, retarder, and Cu_2O-based antifouling paint is exposed to seawater is visualized schematically in *Figure* 1. Ions, present in seawater, diffuse into the porous water-filled polymer matrix ahead of the eroding polymer front (i.e., the paint surface), and dissolve the pigment particles at the dissolving pigment front, resulting in the formation of a leached (i.e., Cu_2O depleted) layer. Hence, the porous polymer matrix (i.e., the leached layer) is visualized as a templete of Cu_2O particles which have dissolved. The porosity of the unreacted paint film (i.e., prior to seawater exposure) is assumed to be 0.

The reactions that take place at the dissolving pigment front are:

$$\tfrac{1}{2}\, Cu_2O(s) + H^+ + 2Cl^- \rightleftarrows CuCl_2^- + \tfrac{1}{2}\, H_2O(l) \quad (1)$$

$$CuCl_2^- + Cl^- \rightleftarrows CuCl_3^{2-} \quad (2)$$

Reaction (2) is also in equilibrium throughout the leached layer. The copper complexes formed ($CuCl_2^-$ or $CuCl_3^{2-}$) subsequently diffuse out through the leached layer and across the paint surface-seawater boundary layer (the latter is not shown in *Figure* 1 for visual reasons). In the bulk seawater, the complexes are oxidized to Cu^{2+}.

In the leached layer, seawater slowly reacts with the active TBT-polymer (hydrolysis), thereby releasing biocidal groups in the form of TBTCl(aq)

$$\underset{\text{TBTpolymer (insoluble)}}{Polymer - COO - TBT(s)} + Na^+ + Cl^- \rightleftarrows \underset{\text{Acid polymer (soluble)}}{Polymer - COO^- Na^+ (s)} + TBTCl(aq) \quad (3)$$

A TBT-polymer conversion profile is developed in the leached layer, as evidenced by experimental data.[9] The surface conversion, at which the partially hydrolyzed TBT-polymer is released to seawater, is termed X_{max} and the physical erosion process (self-polishing effect) can be written as

$$Polymer - COO^- Na^+(s) \xrightarrow{X_{max}} Polymer - COO^- Na^+(aq) \quad (4)$$

Consequently, two distinct moving fronts, the dissolving pigment front and the eroding polymer front, are established (*Figure* 1). After some time at uniform seawater conditions, the thickness of the leached layer becomes constant. This condition is referred to as the stable leached layer thickness.

To complete the description of the seawater-paint chemistry, the two equilibria of seawater, which are both established throughout the water-filled leached layer, must be included

$$HCO_3^- \rightleftarrows H^+ + CO_3^{2-} \quad (5)$$

$$H^+ + OH^- \rightleftarrows H_2O(l) \quad (6)$$

In summary, the model includes the following rate-influencing steps: dissolution of pigment particles, hydrolysis and erosion of the active TBT-polymer binder, effective diffusion in the leached layer, and external mass transport of relevant species. The overall purpose of the model is to estimate the position of the moving polymer and pigment fronts at all values of time and any relevant parameter combination. It should be pointed out that all the rate-processes are strongly coupled. For example, the rate of movement of the dissolving pigment front is dependent on the position of the polymer front because the rate of diffusion of reaction products from the dissolution ($CuCl_2^-$ and $CuCl_3^{2-}$) is determined, in part, by the diffusion path (the width of the leached layer). Similarly, the rate of movement of the polymer front is determined by the TBT-conversion profile in the leached layer,[9] which again is a function of the time of seawater exposure of the binder phase. The magnitude of the latter is controlled by the relative rate of movement of the pigment and polymer fronts.

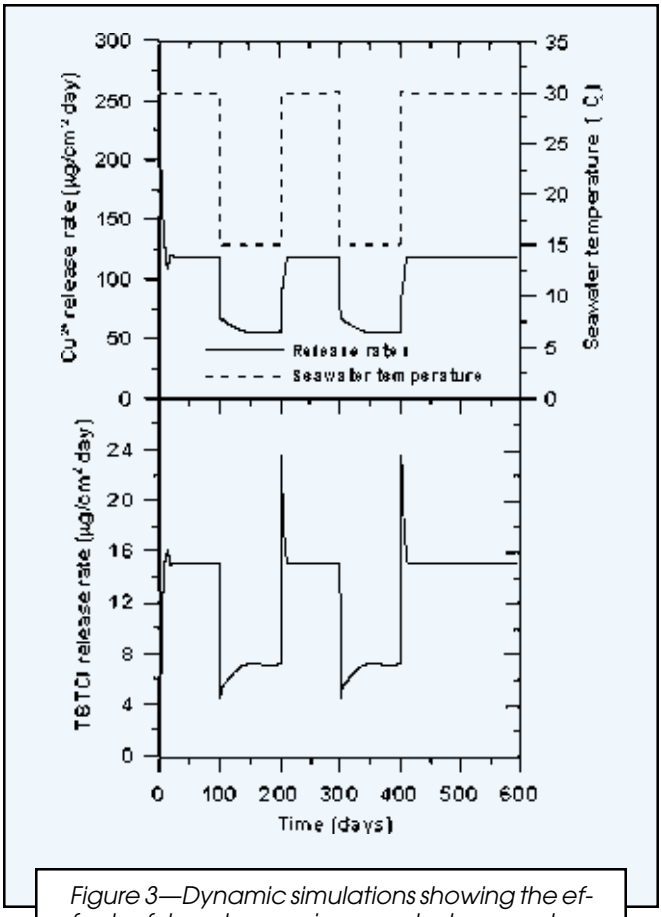

Figure 3—Dynamic simulations showing the effects of step changes in seawater temperature on the release rates of TBTCl (aq) and Cu^{2+}. Other parameters are given in Table 1.

The most important assumptions underlying the model development are:[9]

- The rate of dissolution of Cu_2O particles is sufficiently fast, compared to diffusion of ions in the leached layer, that it takes place at the dissolving pigment front only (i.e., the leached layer is particle-free).
- The pigment volume concentration (PVC) of Cu_2O particles in the solid paint film is high enough to ensure that all particles are in sufficiently close contact with

other particles to create an interconnecting pore network (according to the osmotic pressure mechanism of Marson[11]) in the leached layer when the particles dissolve. On the other hand, the PVC of Cu_2O should not exceed the critical pigment volume concentration (CPVC).[9]

- The hydrolysis of the TBT-polymer takes place throughout the leached layer, except at the dissolving pigment front, and the only TBT-product of the reaction is TBTCl.
- There is no penetration of any species beyond the dissolving pigment front (i.e., into the unreacted paint film).
- The walls of the porous polymer matrix, comprising the leached layer, are stable over time and no water swelling occurs.

Kinetic expressions, derived from literature data and provided in Kiil et al.,[9] are used to quantify the rate of dissolution of Cu_2O and the rate of hydrolysis of the TBT-polymer. Estimation of physical and chemical constants (i.e., effective diffusion coefficients, rate constants, activation energies, equilibrium constants, solubility products, external mass transfer coefficients, and mean-ion activity coefficients), needed in the model, as well as the uncertainties of these, is discussed in our previous work.[9] However, the model contains an adjustable parameter, X_{max}, which deserves elaboration. The parameter has a physical meaning, as mentioned above, because it represents the conversion of TBT-groups at the surface of the paint film at which the active polymer is released into seawater. It may vary, to various degrees, according to any changes in seawater conditions, paint composition, or ship speed.[9] No method has yet been identified which allows the value of X_{max} to be estimated in advance. Presently, however, it is possible to estimate the value of X_{max}, for a paint that has been exposed to given conditions, using scanning electron microscopy (SEM) combined with energy-dispersive X-ray (EDX) analysis.[9] The actual values of X_{max} used in the present work is discussed in a subsequent section. It should be mentioned that no adjustable parameters, apart from X_{max}, are contained in the model.

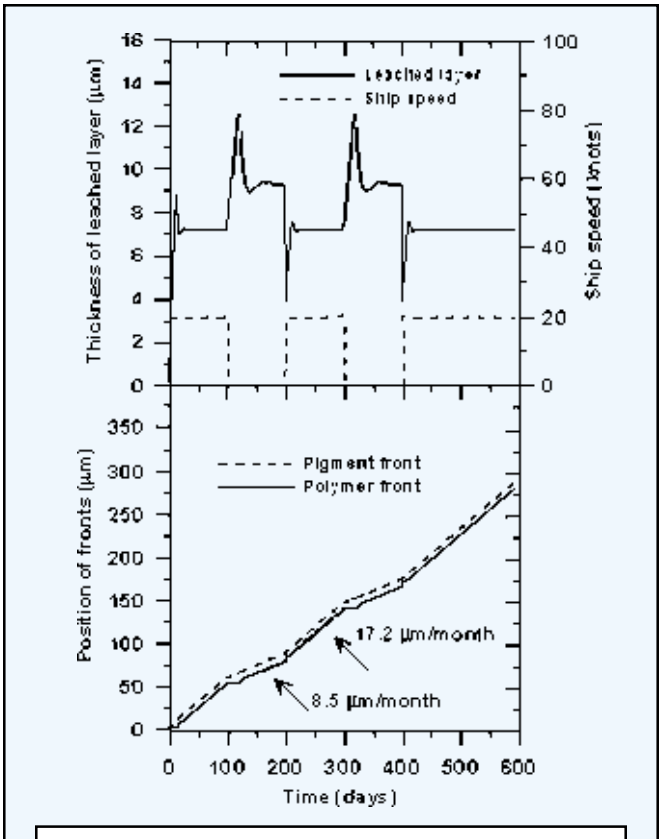

Figure 4—Dynamic simulations showing the effects of step changes in ship speed on the rate of movement of the pigment and polymer fronts, as well as the thickness of the leached layer. Two points of stable polishing rates are indicated with arrows. Other parameters are given in Table 1.

Prior to a description of the model extensions required to perform dynamic simulations, it may be useful to qualitatively discuss which rate-processes in the seawater-exposed antifouling paint that the pertinent process parameters to be considered in the simulations of this work, will affect. The relevant parameters are: seawater temperature, pH and concentration of NaCl, and ship speed.

A change in seawater temperature influences hydrolysis, dissolution, and diffusion rates, with the reaction rates being more temperature-sensitive than diffusion rates.[9] Changes in seawater pH and concentration of NaCl both affect, to various degrees, the rates of dissolution and hydrolysis because the kinetic expressions, used in the model, are functions of these parameters.[9] Diffusion rates of species in the leached layer and across the external paint surface-seawater boundary layer are also influenced by pH and concentration of NaCl because of the strong coupling among the various diffusion rates.

In the model, the effect of ship speed on the paint behavior is accounted for by means of the model parameter X_{max}. The value of this parameter, at specified paint composition and seawater conditions, is a quantification of the conversion at which the TBT-polymer solubility and the shear stress exerted by the seawater on the paint surface result in a release of the partially hydrolyzed TBT-polymer. In other words, ship speed, apart from its influence on the external mass transfer coefficients, is lumped into the parameter X_{max} as discussed in more detail in the next paragraph.

Model Extensions

Certain modifications of the mathematical model were necessary in order to perform dynamic simulations. In the cases of changes with respect to seawater temperature, pH, and concentration of NaCl, the model extensions did not involve any additional model assumptions or equation alterations except that it was assumed that the value of the polymer release conversion, X_{max}, is independent of pH, temperature, and concentration of NaCl.[9] This assumption was justified in Kiil et al.[9] with respect to temperature (25-35°C), but it has not been verified in the cases of pH and concentration of NaCl. Some dependency might be anticipated because pH and the concentration of NaCl may influence the seawater solubility of the partially hydrolyzed TBT-polymer and thereby X_{max}. However, for the parameter range studied (see later), the effects are expected to be small in comparison to the influence of these parameters on chemical reaction rates.

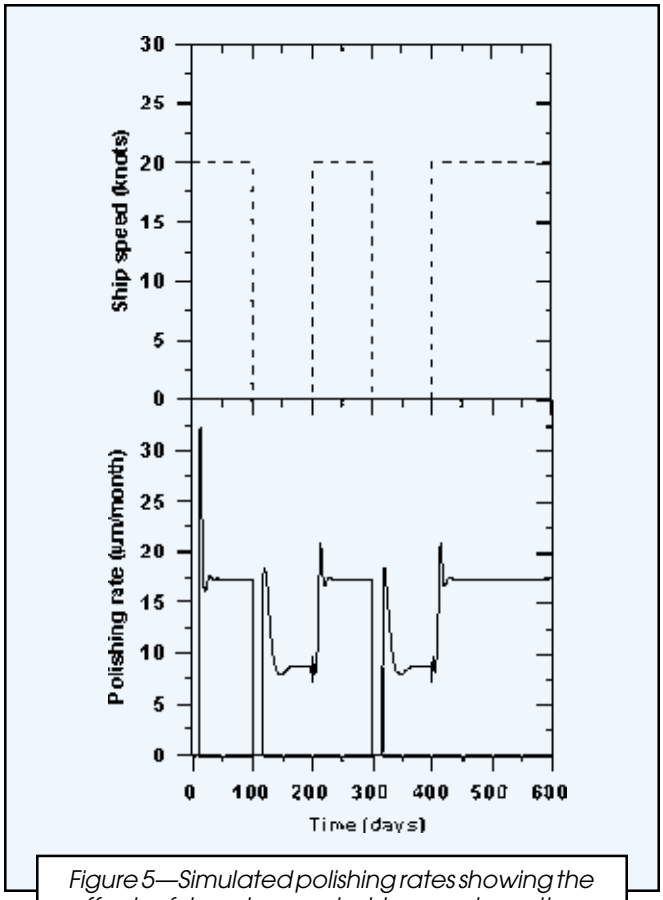

Figure 5—Simulated polishing rates showing the effects of step changes in ship speed over time. The changes in the polishing rate shown in the figure correspond to the simulations of Figure 4. Other parameters are given in Table 1.

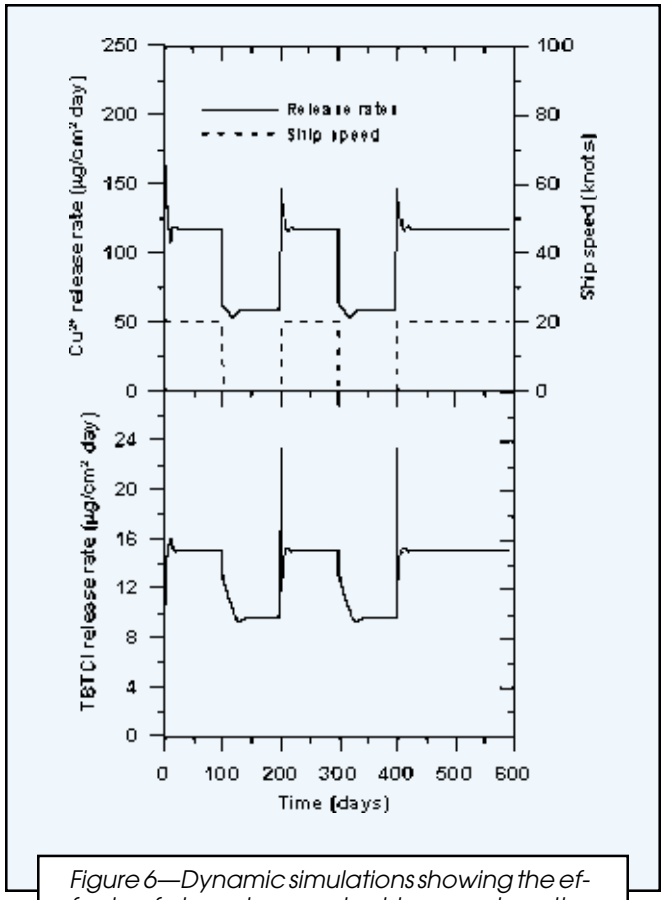

Figure 6—Dynamic simulations showing the effects of step changes in ship speed on the release rates of TBTCl (aq) and Cu^{2+}. Other parameters are given in Table 1.

Dynamic changes in ship speed required some model modification because the value of X_{max} is dependent on the speed of the ship.[9] The higher the speed of the ship the lower the value of X_{max}. Thus, if a ship reduces its speed then the value of X_{max} will increase and the polishing will stop until the hydrolysis reaction has produced a value of the TBT-polymer surface conversion equal to X_{max}. On the other hand, when a ship increases its speed, the value of X_{max} will decrease and the partially hydrolyzed TBT-polymer is released instantly down to the film position where the conversion is equal to the new lower value of X_{max}. This conversion level is reached somewhere in the leached layer because the hydrolysis reaction takes place throughout the leached zone. Estimation of X_{max} at a given value of ship speed can be done using the data supplied in Kiil et al.[9] In the present work, two values of ship speed, 0 and 20 knots, are employed (see later) corresponding to X_{max} values of 0.96 and 0.75, respectively.

Finally, in the simulations presented in subsequent sections, the external mass transport coefficient, for any relevant chemical species at zero speed, was calculated according to mass transfer from a solid slab into a stagnant liquid.[18] At ship speeds of 20 knots (the other value of speed for which simulations were conducted), the model was practically insensitive to the value used for the mass transport coefficient.[9]

RESULTS AND DISCUSSION

To study the effects of dynamic changes in seawater temperature, pH, concentration of NaCl, and ship speed on the paint behavior, simulations were performed using the mathematical model. Essential output variables, such as thickness of the leached layer, rate of movement of the polymer and pigment fronts, and release rates of biocides (i.e., Cu^{2+} and TBTCl), were all considered.

A set of standard parameter values (*Table* 1) for the paint composition and seawater conditions was chosen as a Base Case and the dynamic changes then involved perturbations from this Base Case with respect to the above-mentioned four parameters. The CPVC of the Base Case paint was estimated to about 57 vol% using density and oil absorption data for Cu_2O.[20] The initial paint behavior (i.e., at times less than about 25 days) was considered in detail in Kiil et al.[9] and will not be discussed in this work. For the sake of illustration, step changes in the pertinent parameters are considered useful and will therefore be employed in the initial part of the simulation study. Subsequently, in order to see the effect on the paint behavior of the changing seawater conditions and ship speeds experienced by real ocean-going ships, a simulation performed using an approximate sail service is discussed. In the simulations presented all paints are assumed to be unreacted at time equal to zero.

Step Changes in Seawater Temperature

The temperatures of the world oceans vary between –2 and 30°C.[21] Therefore, ocean-going ships can experience quite rapid temperature changes when sailing from cold areas (such as northern Europe during winter time) to tropical regions in a matter of days or weeks. *Figure* 2 shows how the rate of movement of the polymer and pigment fronts varies with step changes in temperature. The thickness of the leached layer, which represents the distance between the two moving fronts, is also shown. In the figure, one day equals 24 hours. It can be seen that an instant temperature reduction from 30 to 15°C decreases the rate of polishing and dissolution and causes the thickness of the leached layer to start growing. It takes about two months to reach the maximum leached layer thickness of about 14 µm. The reason why the leached layer grows in size when the temperature is reduced is because the activation energy for the rate of pigment dissolution is smaller than that of the rate of hydrolysis.[9] It should also be noted that it takes about 100 days, following the temperature change, for the leached layer to reach a stable thickness. This is important when performing ship tests, because a paint present on a ship that experiences a temperature reduction over a short period of time probably does not reach the stable leached layer thickness, which corresponds to the lower temperature, in the test period. It can also be seen in the figure that a sudden temperature increase from 15 to 30°C reduces the leached layer thickness from just below 14 to about 7 µm, but this only takes 20-30 days. Thus, the paint behavior stabilizes more rapidly from a temperature increase than from a temperature reduction. This is because reaction rates increase with an increase in temperature.

Figure 3 shows the effect of step changes in temperature on the release rates of Cu^{2+} and TBTCl. It is evident that the biocide release rates drop instantly to about half their values when the temperature is reduced from 30 to 15°C. Furthermore, the release rates become stable at the new level after about 80 days with most of the changes taking place during the first 50 days. A temperature increase from 15 to 30°C results in an initial peak in the TBTCl release rate, but it levels off quite rapidly and reaches a stable value after about 30 days. The peak in the TBTCl release rate can be attributed to the reduction of the leached layer thickness when the temperature is increased. Keeping the temperature-independence of X_{max} in mind,[9] it is evident that the TBT-groups, present in that part of the leached layer that is rapidly removed upon the tempera-

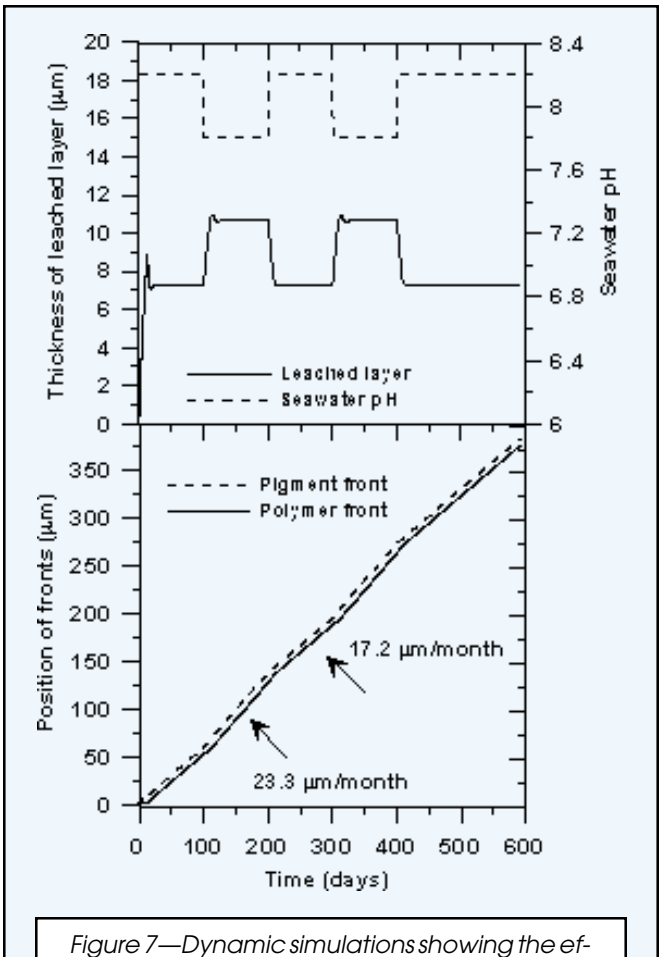

Figure 7—Dynamic simulations showing the effects of step changes in seawater pH on the rate of movement of the pigment and polymer fronts, as well as the thickness of the leached layer. Two points of stable polishing rates are indicated with arrows. Other parameters are given in Table 1.

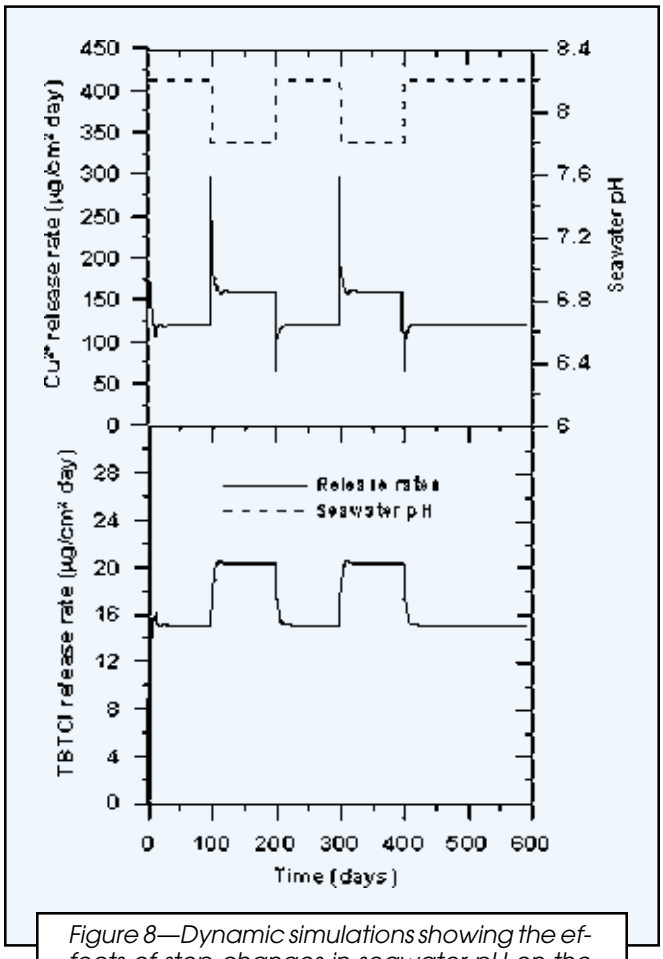

Figure 8—Dynamic simulations showing the effects of step changes in seawater pH on the release rates of TBTCl (aq) and Cu^{2+}. Other parameters are given in Table 1.

ture increase, must be released as TBTCl. The Cu^{2+} release rate, however, does not show a peak initially when the temperature is increased. This is because the Cu^{2+}-ions all originate from Cu_2O dissolving at the pigment front, whereas the hydrolysis reaction takes place in the entire leached layer.[9]

Step Changes in Ship Speed

The speed of large ocean-going ships can vary from zero to about 30 knots, depending on whether the ship is in port or at open sea. This large variation in speed can have a pronounced influence on the behavior of self-polishing antifouling paints.[22] *Figure* 4 shows the effects of dynamic changes in ship speed on the rate of movement of the polymer and pigment fronts and the thickness of the leached layer. It can be seen that a sudden reduction in ship speed from 20 to zero knots initiates a growth of the leached layer. This is because the polishing stops completely for 20 days following the speed reduction. At a speed of 20 knots, the value of the surface conversion at which the active polymer is released, X_{max}, is 0.75, whereas at zero speed it is about 0.96.[9] Therefore, the 20 days of no polishing corresponds to the time it takes for the hydrolysis reaction to increase the surface conversion of the active polymer from 0.75 to 0.96. Following the 20 days, the polishing is reactivated, though now at a smaller rate, leading to a reduction in the leached layer thickness from 12.5 to 9.3 µm. The total time elapsed from the speed reduction to the establishment of a new stable leached layer thickness is 80 days. When the speed is increased again from zero to 20 knots, the leached layer thickness is decreased momentarily from 9.3 to 3.8 µm. The reason for this is that the value of X_{max} now changes from 0.96 to 0.75. Therefore, a portion (about 60%) of the leached layer is washed away down to the position in the layer at which the conversion of the active polymer is equal to the new value of X_{max} (i.e., 0.75). From this point on, the leached layer thickness begins to grow again until a stable thickness of 7.2 µm is reached after about 30 days. Consequently, the paint behavior stabilizes more rapidly from a speed increase than from a speed reduction. Whether the above-mentioned rapid removal of part of the leached layer that follows a speed increase helps to also remove fouling is not known.

In order to illustrate the changes in polishing rate (i.e., the temporal derivative of the position of the polymer front) in more detail, the polishing rate obtained from *Figure* 4 has been plotted in *Figure* 5 as a function of time. Here, it can be clearly seen that the polishing rate varies between 0 and about 32 µm/month. At a ship speed of 20 knots, the stable polishing rate is 17.2 µm/month, whereas at 0 knots it is 8.5 µm/month. It can also be seen that the polishing rate is 0 µm/month during the very first 13 days of seawater exposure, corresponding to the time it takes for the hydrolysis reaction to increase the surface conversion from 0.0 to 0.75. The maximum polishing rate is reached at the point at which the surface conversion first reaches X_{max} (i.e., 0.75). The reason for this can be attributed to the shape of the Sn-conversion profile in the leached layer[9] (not shown), which is less steep near the paint surface at this point compared to all other times, whereby the hydrolysis reaction can rapidly react a substantial portion of the TBT-polymer near the surface to a conversion of X_{max}. It should also be noted that the (hypothetical) infinite polishing rate, corresponding to the instant removal of a portion of the leached layer when the speed is increased from 0 to 20 knots, is excluded from *Figure* 5.

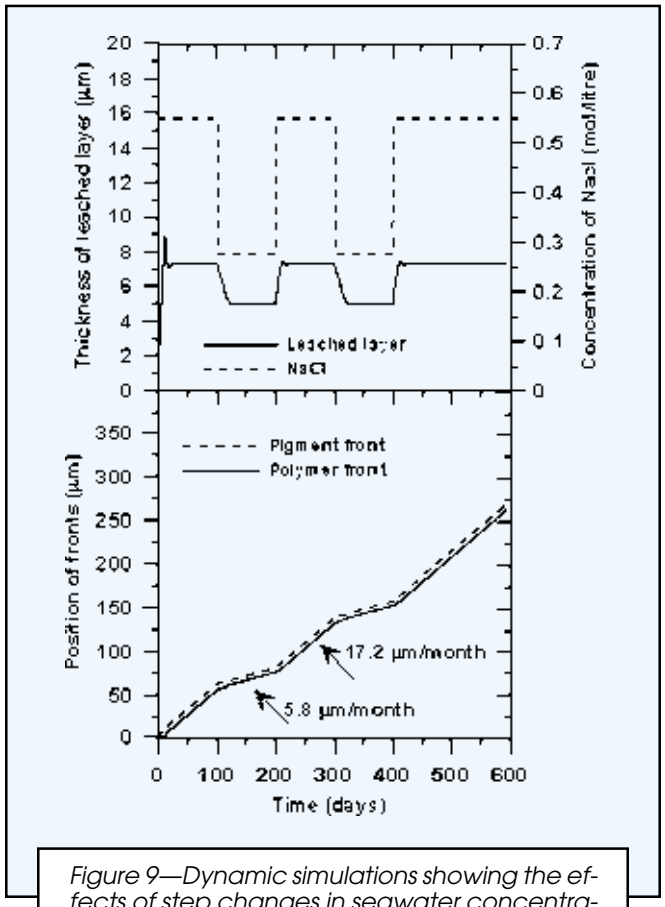

Figure 9—Dynamic simulations showing the effects of step changes in seawater concentration of NaCl on the rate of movement of the pigment and polymer fronts, as well as the thickness of the leached layer. Two points of stable polishing rates are indicated with arrows. Other parameters are given in Table 1.

The release rates of Cu^{2+} and TBTCl during step changes in the ship speed are shown in *Figure* 6. It can be seen that the release rates of biocides drop rapidly when the speed is decreased and become stable after about 80 days. When the speed is increased again to 20 knots, peaks in the release rates are observed. These are due to the aforementioned sudden reduction in the leached layer thickness, which provides a short diffusion path for TBTCl and Cu^{2+}. It should be noticed that the peaks are of a short duration (a few hours or less). It is also evident that even during the periods of a polishing rate of 0 µm/month (see *Figure* 5) there is still a release of TBTCl. This is because the hydrolysis of TBT-polymer takes place throughout the leached layer even when the polymer front is not moving.

Step Changes in Seawater pH

Typical values of pH for surface seawater are between 8.0 and 8.2,[21] but in polluted waters or near river mouths in areas with low limestone contents of the underlying

rock, the pH may attain values down to 7.8 or lower.[1] In *Figure* 7 the effects of dynamic changes in pH on the rate of movement of the polymer and pigment fronts and the thickness of the leached layer are shown. The latter increases from 7.2 to 10.6 μm in about 30 days when the pH is reduced from 8.2 to 7.8. The reason for this behavior is that the rate of dissolution of Cu_2O is proportional to the concentration of H^+.[23] Thus, when the concentration of H^+ is increased, the rate of movement of the pigment front is increased. This also leads to a faster rate of movement of the polymer front, because the movements of the two fronts are coupled. An increase in pH from 7.8 to 8.2 reduces the leached layer thickness to its original value in about 14 days. Therefore, the paint behavior stabilizes only somewhat more rapidly when exposed to a pH increase than to a pH reduction.

In *Figure* 8 are shown release rates of Cu^{2+} and TBTCl when the paint is exposed to step changes in pH. The release rates reach stable values in about three weeks when the pH is either increased or decreased. It can be seen that the rate of release of TBTCl is increased when the pH is lowered, even though the thickness of the leached layer increases. In the case of Cu^{2+} an initial peak in the release rate of more than twice the number of the original level is seen when the pH is decreased. This is because the rate of dissolution of Cu_2O, as discussed previously, is increased when the pH is lowered, initially allowing more Cu^{2+} to be released. At the same time, the pH decrease leads to a faster rate of movement of the pigment front, thereby increasing the thickness of the leached layer, which eventually leads to a slower rate of effective diffusion and a lower release rate of Cu^{2+}.

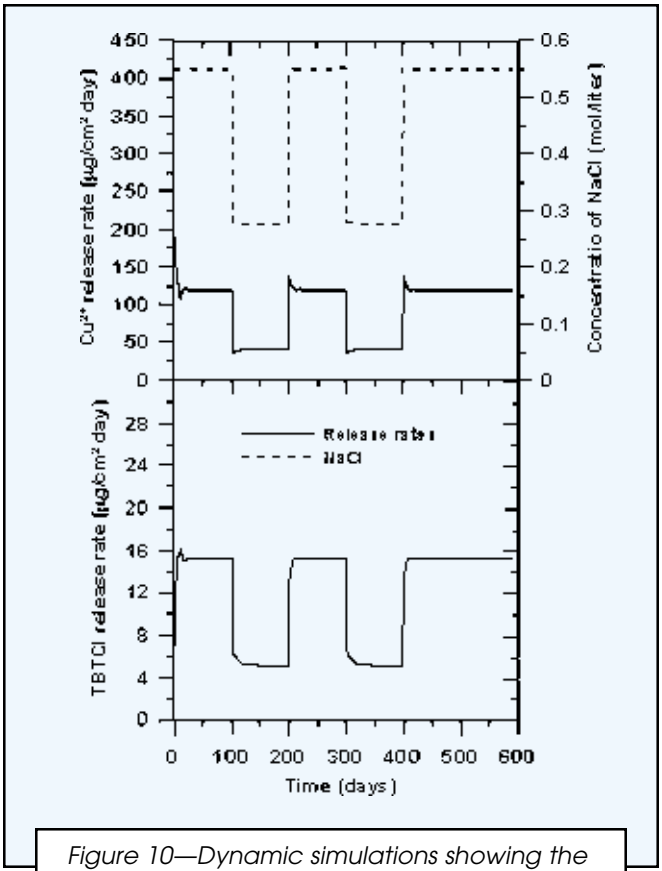

Figure 10—Dynamic simulations showing the effects of step changes in seawater concentration of NaCl on the release rates of TBTCl (aq) and Cu^{2+}. Other parameters are given in Table 1.

Step Changes in Seawater Concentration of NaCl

The salinity of the world oceans is fairly uniform with an average of about 3.5 wt%[21] (corresponding to about 0.60 M if all salts are taken to be NaCl). However, there may be local variations in the salinity near, for instance, river mouths. The relative amounts of the various salt components in seawater are practically constant with NaCl being the most abundant species.[21] The latter salt influences the behavior of self-polishing antifouling paints[9] (and the extent of fouling[1]) and dynamic simulations of changes in the concentration of NaCl is therefore of interest. In *Figure* 9 the effects of dynamic changes in the concentration of NaCl on the rate of movement of the polymer and pigment fronts and the thickness of the leached layer are shown. In the figure, it has been chosen to reduce the concentration of NaCl down to 0.28 M, which is an estimate of what the concentration could be in estuarine waters. However, the concentration of NaCl could indeed be different from this depending on the location under study. Lowering the concentration from 0.55 to 0.28 M reduces the thickness of the leached layer from 7.2 to 4.9 μm in about 30 days. Re-establishing the concentration of 0.55 M also results in a response time to reach stable values of about 30 days. Thus, the paint behavior stabilizes at equal rates when the paint is exposed to an increase and a reduction in the concentration of NaCl.

Release rates of Cu^{2+} and TBTCl for a paint exposed to step changes in the seawater concentration of NaCl is shown in *Figure* 10. It can be seen that the release rates reach stable values in about 30 days when the concentration of NaCl is either increased or decreased.

Combined Step Changes in Seawater Temperature and Ship Speed

To explore the effect of a combined step change in temperature and ship speed, simulations were performed with the parameter changes shown in *Figure* 11. It can be seen that a simultaneous temperature drop (from 30 to 15°C) and speed reduction (from 20 to zero knots) results in the leached layer thickness growing from 7.2 to 23.2 μm in about 300 days with most of the changes taking place during the first 100 days. Hence, the changes in the paint behavior may take quite a long time to stabilize and lead to a large thickness of the leached layer. However, the TBTCl and Cu^{2+} release rates (not shown) stabilize quite rapidly.

Construction of a Typical Ship Sail Service

In the earlier sections, the influences of step changes in relevant process parameters were considered. However, it is of interest to try and reconstruct a typical sail service in order to see the impact of the parameter changes on the paint behavior. In *Figure* 12 are shown the effects of dynamic changes in seawater temperature and ship speed

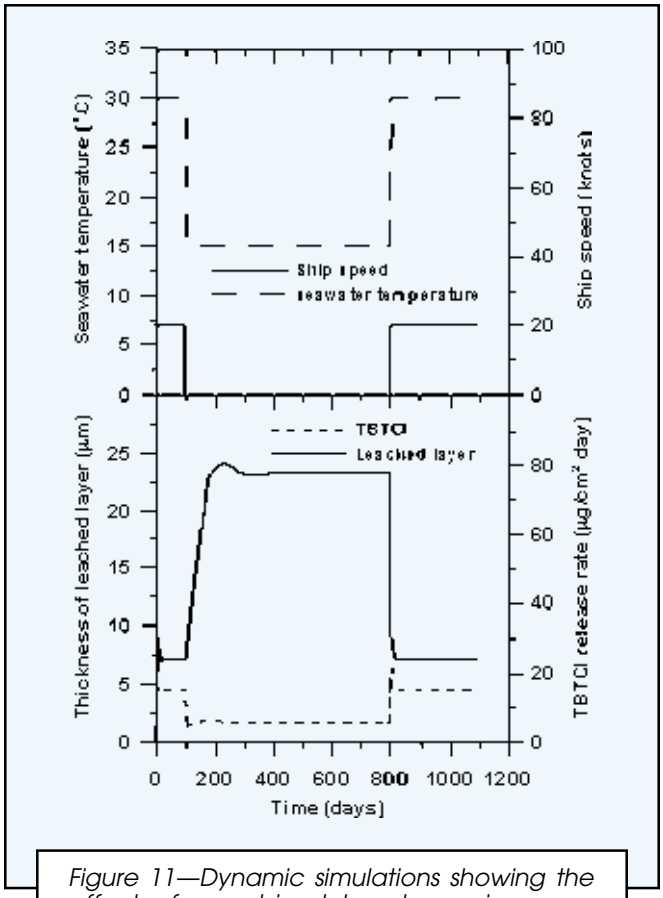

Figure 11—Dynamic simulations showing the effects of a combined step change in seawater temperature and ship speed on the release rates of TBTCl (aq) and the thickness of the leached layer. Other parameters are given in Table 1.

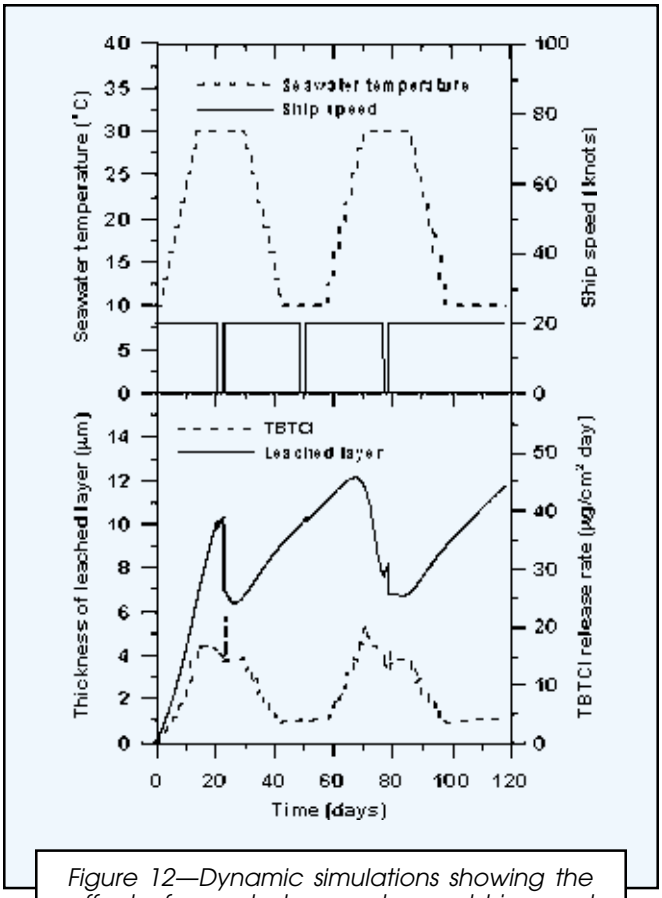

Figure 12—Dynamic simulations showing the effects of seawater temperature and ship speed changes, along an approximated typical sail service, on the release rates of TBTCl (aq) and the thickness of the leached layer. Other parameters are given in Table 1.

on the thickness of the leached layer and the rate of release of TBTCl. The sail route shown approximates the conditions a ship sailing between northern Europe (10°C) and a tropical region (30°C) would experience. The ship is assumed to be in port (zero speed on the figure) for two days only in both the tropical and the cold region. It can be seen that the thickness of the leached layer varies between about 6 and 13 µm, depending on the location of the ship. Of more importance is the observation that the release rate of TBTCl varies between about 3 and 22 µg/(cm^2/day) (disregarding the initial 10 days) and that of Cu^{2+} (not shown) between about 36 and 126 µg/(cm^2/day). Thus, according to the model the biocide release rates varies by a factor of 3-7 along the sail route. It is an advantage, however, that the release rates are at maximum in the tropical areas, where the fouling is most severe.[1]

Considering the simulations of *Figure* 12 in more detail, the following phenomena can be observed: During the first 20 days, the leached layer grows in size due to pigment dissolution. On day 20, approximately, the polymer conversion has reached X_{max} and the eroding polymer front (i.e., the paint surface) begins to polish, whereby the leached layer thickness starts to decrease. However, on day 21, the ship speed is reduced to zero knots leading to an increase in the leached layer thickness for the reasons discussed in an earlier section. On day 22, the ship speed is once again raised to 20 knots, whereby part of the leached layer is rapidly washed away. From day 30 to day 49 the temperature decreases with a growth in the leached layer thickness as the direct consequence. The two days the ship is in port at 10°C appears to be insignificant with respect to polishing and biocide release rates. Subsequently, the leached layer thickness increases for about 16 days (even though the temperature increases in this period) until the high temperature imposes a leached layer reduction, which continues until the ship is in port at 30°C. The remaining of the ship pattern shown in *Figure* 12 can be explained by similar arguments.

CONCLUSIONS

Dynamic simulations of a self-polishing antifouling paint exposed to seawater have been presented. The simulations revealed that the paint behavior rarely would reach stable conditions because of the slow response of the paint to changes in temperature and ship speed. These results are important in relation to ship (and rotary) tests, because the rate of polishing and the extent of pigment leaching are dependent on, for instance, the time a ship has been in port prior to a given polishing measurement. Simulations also showed that paints experiencing certain

combinations of temperature and ship speed may lead to leached layers of a large thickness.

The modeling tools underlying the simulations can be adapted to other self-polishing antifouling paints employing different binder and pigment phases, but kinetic expressions for the relevant hydrolysis and pigment dissolution reactions need to be determined from laboratory measurements if not available in the literature. Many of the novel tin-free paints under development use Cu_2O as one of the biocides and here the principles of this work are directly applicable.

Future work involves investigations with other soluble (such as ZnO) and insoluble (such as TiO_2) pigments present in the paint, as well as mathematical modeling of tin-free self-polishing antifouling paint systems.

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