INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH & DEVELOPMENT

ISSN: 2278 – 0211 (Online)

Environmentally Friendly Antifouling Paints And Painting Schemes

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Abstract:
Since the 1970's Tributyl tin based antifouling paints were widely used to control fouling on ships hulls. These coatings offered up to 5 years of foul-free hulls and were the most effective antifouling paints ever produced. However, due to serious environmental effects, these paints have been banned since 2008 and have been replaced by copper based antifouling paints with some success. However, the extensive use of copper based antifouling paints has led to the accumulation of cooper and its compounds in the marine environment particularly in the vicinity of ports and harbors and is beginning to pose a serious environmental problem. This paper explores the possibility of incorporating environmentally friendly biocides in antifouling paints that exhibit a low persistence in the marine environment particularly those biocides that are available in the Indian context. Another serious problem facing the marine environment is the issue of Invasive species. In recent years the issue of invasive marine species has been receiving considerable attention due to the fact that introduction of non indegenous species or non-native species transmigrated from other areas to coastal waters often results in the reduction and even extinction of the native species and thereby severely disrupts the natural marine ecosystems. The predominant vector for the transport of nonindigenous species in marine environments has been shipping. While ballast water receives the most attention, hull fouling is now considered to be the most significant means for translocation of these organisms. Certain niche areas of the vessel such as bow thrusters, sea chest, stern tube, rudder etc. are the likely areas to be heavily fouled. Although this fouling does not effect the overall performance of the vessel, would however, be a vector for the transportation of Invasive species. In addition, the other areas that are likely to be fouled are on locations where antifouling paint has been worn of due to excessive shear and bending of the hull. This paper attempts to identify such areas using CFD simulations and suggest that special paint schemes must be incorporated in these niche areas.

1.Introduction

Paint coatings or other coatings that tend to prevent or inhibit the growth of marine organisms on submerged surfaces can be broadly categorized into biocidal and non-biocidal coatings. As the name suggests, biocidal coatings release a biocide or a combination of biocides at the substrate water interface under controlled conditions. There are very few biocides that are effective antifouling properties and at the same time have an acceptable environmental risk. In the recent past, organotin (in particular TBT) based antifouling paints were widely used by the shipping industry. These paints were highly cost effective and efficient way to control fouling and offered up to five years of foul free hulls. However, organotins have been described as the most harmful substance introduced in to the marine ecological system and the International Maritime organization (IMO) placed a worldwide prohibition of organotin-bearing coatings on ocean-going vessels, requiring they be phased out by 2008. Copper based antifoulant coatings soon replaced TBT-based coatings following the worldwide controls on organotin (IMO 2002). In addition, to improve the effectiveness of copper based coatings a number of additional biocides also called as "booster biocides" which include cuprous thiocyanate, chlorothalonil, diuron, dichloro-octyl isothiazolin, thiram, zinc oxide, zinc and copper pyrithione, zineb, sea nine, irgarol etc all of which have varying degrees of environmental risks.

2.Environmental Effects Of Copper

There is a growing concern over the water quality impacts from copper. Copper has been shown to be toxic to aquatic organisms, to accumulate in filter feeders, such as mussels, and to damage larval stages of aquatic invertebrates and fish species Dissolved copper in excess of 3.1 μg/l, is reported to be toxic to mussels, oysters, sea urchins and crustaceans (Carreau and Pyle 2005, Calabrese et al. 1984, Coglianese and Martin 1981, Damiens et. al. 2006; Gould et al. 1988, Granmo et. al. 2002, Krishnakumar et al. 1990, Lee and Xu 1984, Lussier et al. 1985, MacDonald et al. 1988, Martin et al. 1981, Redpath 1985, Redpath and Davenport 1988, Rivera- Duarte et. al. 2005, Stromgren and Nielsen 1991, VanderWeele 1996) and it affects phytoplankton communities (Krett Lane 1980,).

In california, dissolved copper as high as 29 μg/l has been observed at Newport bay and as high as San Diego bay in California (USEPA 2002). Copper content in many other areas in California also exceeds the limits set by the California toxic rules (USEPA

2011). It is estimated that 95 percent of this copper comes from pleasure craft antifouling paints due to leaching.

In Denmark copper mean cooper concentrations of 13 μg/L were observed in the pleasure craft harbour of Marselisborg (Jensen and Heslop 1997). Similar high copper concentrations were observed in the skerries of Stockholm (Bard, 1997). These elevated copper levels were observed in the proximity of pleasure craft harbours and pleasure craft traffic. Alarmingly high copper concentrations were also observed in aquatic plants. Measurements of copper performed by the French in the Arcachon bay showed an increase in copper content in oysters (Claisse and Alzieu 1993).

As a result of alarmingly high copper levels, the United States, (particularly the states of California and Washington), Sweden, Denmark and few other countries have begun to restrict the use of copper based antifouling paints. It is likely that in the near future, many other countries would also floow suit and restrict these types of coatings. Therefore in the present scenario, alternatives for copper and tin appear to be biocides that have the following characteristics

- The biocide concentration must be such that it is effective as an antifouling agent and yet their concentrations in the aquatic environment must be such that it is not toxic to non-target organismns
- They must exhibit low persistence in the marine environment.

Among all the biocides available, natural biocides or biocides that are not synthesized appear to hold promise as safe alternatives to copper and tin for use in antifouling paint formulations.

3.Natural Product Antifoulants(NPA)

Today, the search for new antifouling substances shares many of the features experienced by the pharmaceutical industry .For example , scientific knowledge in biology, development of a control release system, production costs and how to prove the product safe for the end consumer, independent of man or nature. Natural antifoulants have been proposed as one of the best replacement options for the most successful antifouling agent, tri-n-butyl tin(TBT),which due to its ecological incompatibility, is currently facing total global ban imposed by International Maritime Organization . Research on NPAs is going on since last two decades.. The NPAs are advantageous over conventional toxic biocides in that they are less toxic, effective at low concentrations, biodegradable, have broad spectrum antifouling activity and their effects are reversible.

The aquatic fouling organisms in seawater are marine lives such as corals, sponges, marine plants, dolphins, etc., which prevent the surface of their bodies with antifouling substances without causing serious environmental problems. Therefore, these substances may be expected to be used, as new environmentally friendly antifouling agents. Many of the antifoulants are also found in terrestrial plants. The natural product antifoulants in 10 kinds of compounds of terpenes, acetylenes, polycyclic compounds, steroids, phenols, isothiocyanates, nitrogen containing compounds, glycerol derivatives, higher fatty acids, and enzymes is reported. Various NPAs have been tested for potential industrial applications including halogenated furanones, triterpinoids. Data has been collected on many natural products which seem promising as a natural antifoulant as they show bactericidal/insecticidal/pesticidal properties.

In Table 1 ,various publication based on natural products are given whose active ingredient is given.

Sl. No.	Source	Active Ingredient	Reference
1	Pongamia Pinnata (karanja oil)	Karanja oil, Furan, o-flavones, pongapin, kanjone and pongaglabrin	Meher et al (2004)
2	Leea Indica(Burm.f.) Merr. Flowers	Essential oils(esters of phthalic acid,Di-isobutylphalate(>75%),di-n-butylphthalate(>7%)n-butylisobutylphthalate(>6%),butylisohexylphthalate(>3.5%).Monobutyl carbonotrithioate	Srinivasan et al (2004)
3	Pongamia glabra	polyesteramide	Sharif et al (2004)
4	Pongamia pinnata	Karanjin,a furano-flavonoid	Vismaya et al (2010)
5	Pongamia	triglycerides, flavanoids, pongamia and karanjin	John De Britto and P.Peter Baskaran (2010)

Sl. No.	Source	Active Ingredient	Reference
6	Pongamia Pinnata	alkaloids demethoxy-kanugin,gamatay, glabrin, glabrosaponin, kaempferol, kankone, kanugin, **karangin**, neoglabrin, pinnatin, pongamol, pongapin, quercitin, saponin, β-sitosterol and tannin	Savita et al (2010)
7	Dysdercus koenigii Fab. (Hemiptera :Pyrrhocoridae)	anonin (1 %),karanjin (2 %), achook (0.15%), econeem (1%) andimidacloprid (17.8 %)	M.H. Kodandaram et al (2008)
9	Pongamia glabra, azadirachta indica and Chrysanthemum cinerariifolium	azadirachtin (10 –25%) , Active ingredient :esters Pyrethin I and II,cinerin Iand II,Jasmolin I and II insect growth.	Roman Pavela et al (2009)
10	Pongamia pinnata	pongamol	Md. Abdullahil Baki et al (2007)
11	Cladiella krempfi, Sinularia kavarattiensis and Subergorgia reticulata	(l'E,5'E)-2-(2',6'-dimethylocta-l',5',7'-trienyl)-4-furoic acid 1, (-)-6-α-hydroxy polyanthellin A 2, (+)-(7R,10S)-2-methoxy calamenene 3, (+)-(7R,10S)-2,5-dimethoxy calamenene 4 and (+)-(7R,10S)-2-methoxy,5- acetoxy calamenene 5).	T.V. Raveendran et al (2011)
12	Distaplia nathensis (Chordata)	Crude extract of Distaplia nathensis	A.Murugan&M.San thana Ramasamy (2003)
13	Helicoverpa armigeraHub. head polypeptides	Azadirachtin, tetranortriterpenoid	N. K. Neoliya et al (2007)
14	Lobophora variegata	lobophorolide	Kubanek et al (2003)

Sl. No.	Source	Active Ingredient	Reference
15	French marine seaweeds	Organic extracts of the marine seaweeds	Vonthron-Senecheau et al 2011
16	Ralfsia verrucosa, Petalonia fascia and Scytosiphon lomentaria (Phaeophyceae, Scytosiphonales)	Methanol and ethanol extracts of the algaes	Thabard et al (2009)
17	Capsaicin	Alkaloid capsaicin(N-Vanillylamide of trans-8-methyl-6-nonenoic acid)$(CH_2)_4CH{=}CHCHMe_2$	G.Ya.Legin et al (1996)
18	Marine cyanobacterium Lyngbya majuscula	Dolastatin 16, hantupeptin C, majusculamide A, and isomalyngamide A	Bi Lik Tong Tan et al (1996)
19	Marine algae	Fatty acids, lipopeptides, amides, alkaloids, terpenoids, lactones, pyrroles and steroids	Bhaduri P,Wright PC(2004)
20	Canistrocarpus cervicornis,Richardo Rogers, Valeria Laneuville Teixeira and Renato Crespo Pereira	Antifoulant diterpenes	Bianco et al (2009)
21	Haliclona koremella	ceramide N-docosanoyl-d-erythro-(2S,3R)-16-methyl-heptadecasphing-4(E)-enine (C22 ceramide)	Hattori et al (1998)
22	Mediterranean Seagrass Posidonia oceanica (L.) Delile	Aqueous and lipid extracts from the rhizomes of Mediterranean sea grass	P. Bernard and D. Pesando (1989)

Sl. No.	Source	Active Ingredient	Reference
23	Palauan Sponge, Haliclona sp.	hexapeptide, waiakeamide, and a new sulfone derivative	Dahms et al (2003)
24	Haliclona	new peptides, Haliclonamides C, D, and E.	Yutaka et al (2002)
25	Phyllogorgia dilatata Esper(octocorollia ,Goroniidae)	diterpene 11β,12β-Epoxypukalide	Mora et al (2006)
26	Chili pepper	capsaicin ,zosteric acid	XuQ et al (2005)
27	dictyota sp.(brown algae)	cyclic diterpenes and a carotenoid	Armstrong et al (2005)
28	Mediterranean Brown Alga Dictyota sp.	Diterpenoids	Camps et al (2009)
29	Red Alga Sphaerococcus coronopifolius	Terpenes	Veronica et al (2000)
30	marine sponge Acanthella cavernosa	Terpenoids	Hirotaa et al (1996)
31	Andrographis paniculata	Terpenoids	Sarala et al (2011)
32	Root of Ceriops tagal	Diterpenoid	Chen et al (2011)
33	Azadirachta indica	Nortriterpenes	Nicoletti et al (2010)
34	Azadirachta indica	azadirachtin	G K Karnavar (1987)
35	Azadirachta indica	Neem Triterpenoids	Rob J. Aerts and A. Jennifer Mordue (Luntz) (1997)
36	Azadirachta indica	azadirachtin	Mondal et al (2007)
38	mediterranean sponge Reniera Sarai(Pulitzer-Finali)	3-alkylpyridinium salts (poly-APS)	Fainali et al (2003)
39	Pongamia glabra	Triterpenes, flavonoids	Nirmal et al (2007)
40	Pongamia pinnata	pongamol and karanjin	Tamrakar et al (2008)

Sl. No.	Source	Active Ingredient	Reference
41	Pseudognaphalium robustum	Flavonoid	Cotoras et al (2011)
42	Pongamia glabra	Isopongaglabol and 6-methoxy isopongaglabol	Talapatra et al (1982)
43	Azadirachta indica	azadirachtin	A. Mordue (2004)
44	Azadirachta indica	2',3'dehydrosalannol,nimbolide,salanin & azadiradione	S Gunasekaran and B.Anita(2010)
45	Anacardium Occidentale	cashew nut shell liquid or (CNSL)-Anacardic acid	Asogwa et al (2007)
46	Azadirachta indica	Azadiracthin	Xie et al (1995)
47	Pongamia pinnata	70% ethanol extract of Pongamia pinnata leaves	Srinivasan et al (2003)
48	Pongamia pinnata	Karanjin	Akanksha et al (2011)
49	Azadirachta indica	azadirachtin	Schaaf et al (2000)
50	Azadirachta indica	azadirachtin	Wana et al (1997)

Table 1

From above table, we can see that most of the active ingredient are terpenoids, flavonoids, polyphenolic ,halogenated polyketides compounds.

3.1.Potential Antifouling agents available locally

Some of the natural products that have potential for being used as a biocide and have not been fully investigated are listed below

<u>3.1.2. Pongamia Pinnata (Karanj) seed oil</u>

Pongamia Pinnata (Karanj) seed oil contains karanjin ,a bioactive molecule with important biological attributes

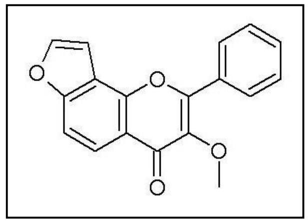

Figure 1:Karanjin

Antibacterial activity of this oil was demonstrated against Bacillus, E.Coli, Pseudomonas,Salmonella, Staphylococcus and Xanthomonas.

3.1.3. Äzadirachta indica (neem)

Compounds of neem (Äzadirachta indica) contain Azadirachtin which is a tetranortriterpenoid .

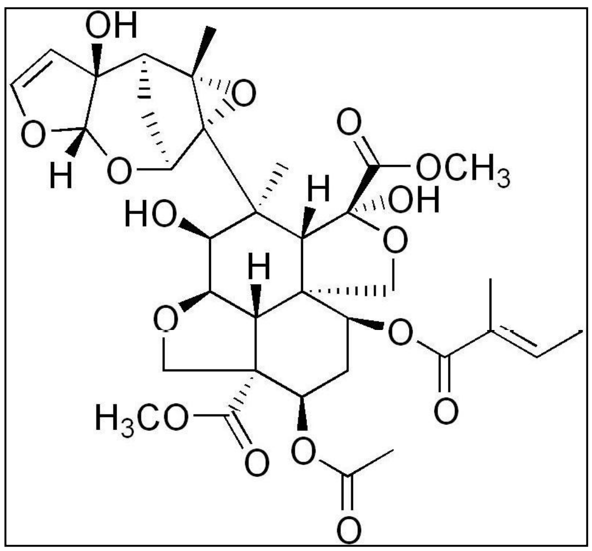

Figure 2: Azadirachtin molecule

The LD_{50} value of Azadirachtin is found more than 5000mg/kg both in male and female rats if a single oral dose of Azadirachtin(5000mg/kg)was given to male and female rats.(Raizada et al 2001)

3.1.4. Cashewnut Shell oil

Cashew nut shell oil contains anacardic acid which acts as repellent to pest insects. It is traditionally used by fishermen to protect the hulls of country boats and is claimed to have antifouling properties

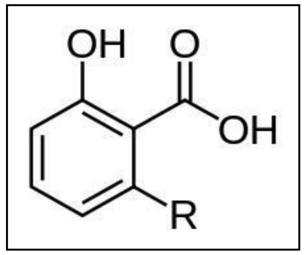

Figure 3: Anacardic acid

Cashew nut shell oil contains anacardic acid which acts as repellent to pest insects. Work is being done to determine antifouling property for these terrestrial natural products.

4.Painting Schemes

The commercial shipping industry primarily uses self-polishing copolymer paints (SPC) paints as anti-fouling coatings. These paints were introduced in the mid-1970s and in this class of paints, the biocide is chemically bonded to a copolymer (Anderson, 1993, Hunter and Cain, 1996). The leaching rate of the biocide is very controlled due to the fact that biocide is released when sea water reacts with the surface layer of the paint. The SPC paints allow the application of thicker coatings with the biocide chemically bonded throughout the coating. This results in the slow and uniform release of biocides to the surface. The biocide release for these coatings is only a few nanometres deep and the spent layer is slowly eroded away and a new active layer develops. The popularity of these AF coatings was primarily due to a controlled chemical dissolution of the paint film capable of long dry-dock intervals, typically between five to seven years; predictable polishing, enabling tailor-made specifications by vessel/operation; thin leached layers, making it easy to clean and recoat; good weather ability, quick drying, and extremely good value for money.

The extent of polishing action in these types of coatings depends primarily on the hydrodynamic forces at the paint-seawater interface. The higher the hydrodynamic forces, the higher are the polishing rates. Conversely, lower hydrodynamic forces at the paint-seawater interface imply lower polishing rates. This implies that at locations where the hydrodynamic forces are high, the polishing rates would be high and this would result in premature depletion of the antifouling coating. Conversely, when the hydrodynamic forces are low, low polishing action would result and this would lead to insufficient biocide release at the paint-water interface. In both the preceding scenario's, the paint film does not offer antifouling protection and there is a tendency for fouling to take place at these locations.

The practice of application of antifouling coating is that an uniform coating of a specified pre-calculated thickness is applied on the underwater hull of the vessel taking in to account the average speed of the vessel, its trading routes, length of stay in port, etc. However, shipbuilders/owners etc they do not account for the fact that there non-uniform polishing rates along the vessels hull in certain niche areas in the proximity of bow thrusters, sea chest, stern tube, rudder, shoulder, water line, etc that are prone to premature fouling. Although these areas are less than five percent of the total underwater area of the vessel and therefore have negligible effect as far as the operational parameters of the vessel are concerned, they are the primary vector for the transmigration of invasive species.

Invasive species also called as alien species or non-native species are introduced in the marine environment by human activities threatens biological diversity and ecological integrity worldwide. They can cause irreversible reduction in biodiversity by preying on or by competing, or causing or carrying diseases, or altering habitats of native species. They can also cause serious economic and ecological damage. Some can damage shorelines, man-made marine structures, equipment and vessels. The UNEP has declared that the invasive species are the most serious environmental issue only next to habitat loss. Many studies show that hull fouling the primary vector for invasive species. (Rainer 1995; Coutts 1999; Hewitt and Campbell 2001; Gollasch, 2002; Ashton *et al* 2006). Even the best maintained vessels are fouled to the extent of at least three percent of the hull area and are more than sufficient to cause the transmigration of alien species (Gollasch, 2002).

The issue of invasive species can therefore be best addressed if fouling is elimanted and further reduced/eliminated in the niche areas of the vessel. This could be best accomplished if these areas are accurately identified and appropriate paint schemes are applied at these regions. To locate these nice areas, hydrodynamic forces at the paint-water interface could be analyzed. Figures 1 and 2 shows the wall shear stresses of a 200 meter long tanker using computational fluid dynamics (CFD) techniques and figures 3 and 4 show the computed stresses of a 100 meters long passenger vessel operated by the Andaman and Nicobar administration. In all the figures shown below there is a variation in the wall shear stresses throughout the hull, which depends on the speed, the draft and the vessel profile. For both the tanker and the 100 passenger (PAX) vessel, the computed shear stresses at the waterline and the stern have lower than average hydrodynamic forces which indicates low polishing rates, the extent of which depends on the draft, speed and type of vessel. In these areas insufficient biocide delivery results which is likely to result in premature fouling. On the other hand, for the tanker in particular, the shoulder of the vessel (below the bow) experiences high wall stresses which result in higher polishing rates in comparison to the rest of the vessel. This would lead to the premature depletion of the antifouling paint and would again result in fouling much ahead of the bulk of the surface of the vessel.

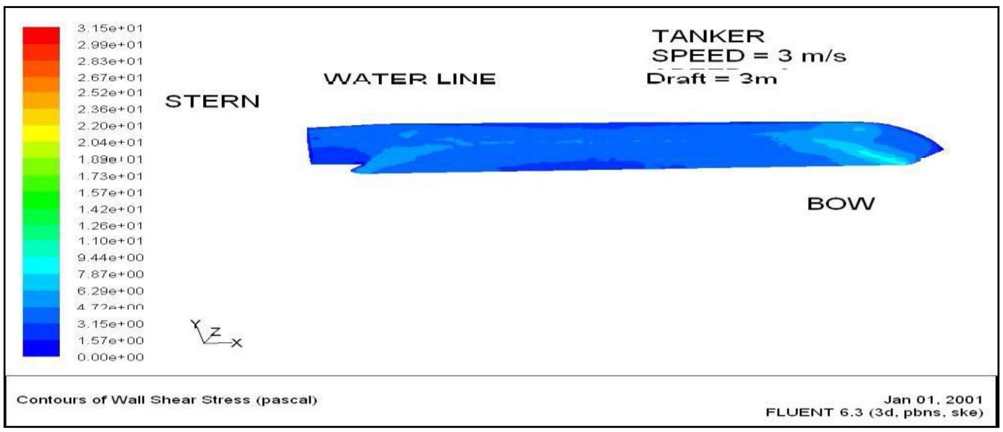

Figure 4

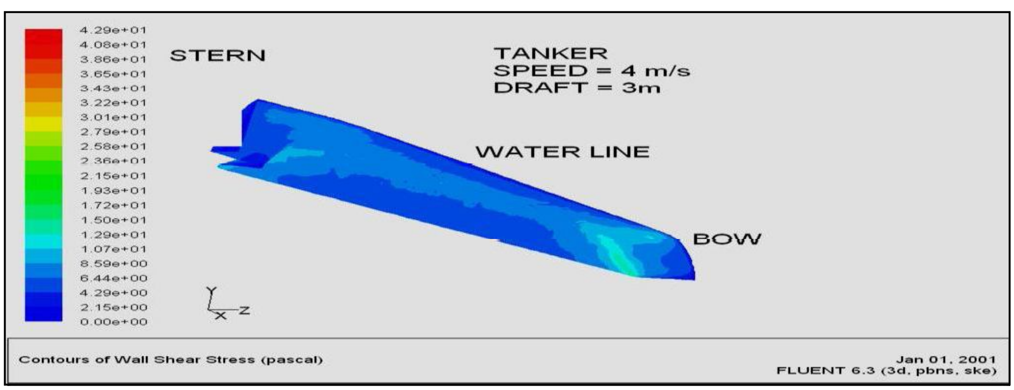

Figure 5

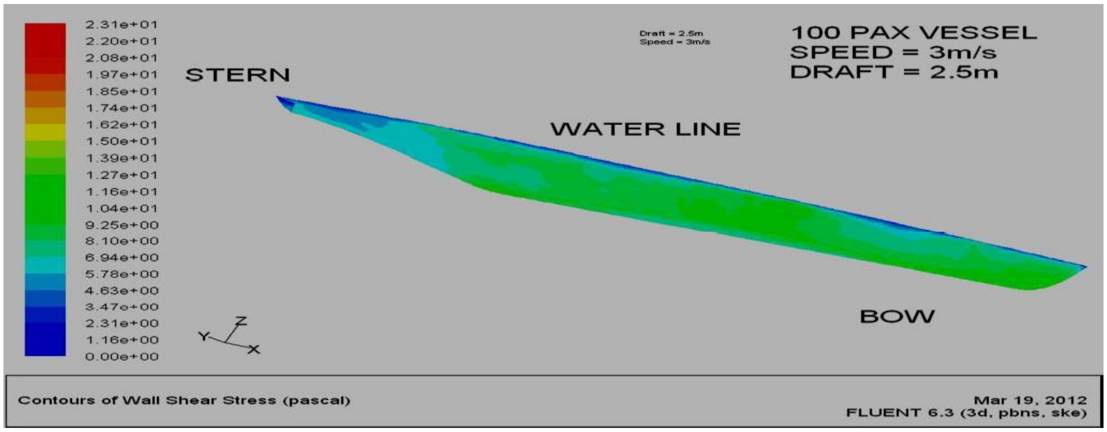

Figure 6

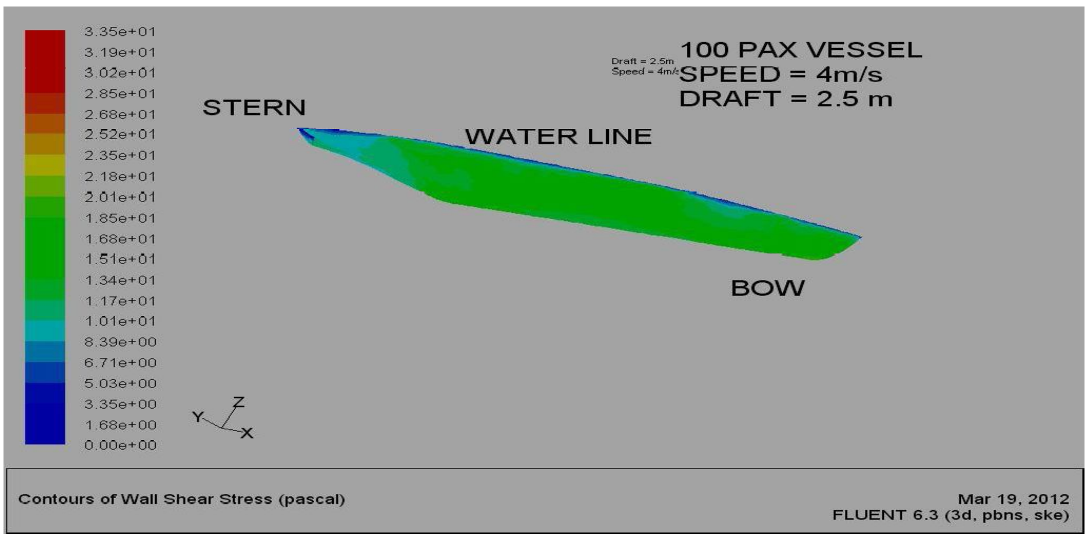

Figure 7

As self-polishing coatings have the unique advantage that they could be tailor made to produce variable polishing rates, the niche areas prone to premature fouling could be could be coated with antifouling paints with pre-calculated polishing rates which could significantly reduce the risk of invasive species.

5.Conclusion

Metallic antifouling coatings are of serious environmental concern. Since the banning of TBT based AF coatings, copper is widely used in AF formulations. However, there is growing evidence that copper released from these coatings is highly detrimental to the marine environment. Natural antifoulants have been proposed as one of the best replacement options for the metallic based AF coatings due to the fact that that they are less toxic, effective at low concentrations, biodegradable, have broad spectrum antifouling activity and their effects are reversible. Several of these products have been identified for the Indian context.

CFD analysis of hydrodynamic forces around the vessel's hull shows that there are non-uniform wall shear stresses around the hull of vessels. The current practice of painting is that a coat of uniform thickness is applied over the entire hull and as self-polishing antifouling paints depend on these hydrodynamic forces for the delivery of biocides to inhibit fouling, non-uniform biocide delivery is likely to result in premature fouling in certain niche areas of the vessel. Field data indicates that although premature fouling takes place in less than five percent of the vessels surface area, this is more than sufficient to result in an exponential increase in transmigration f invasive species. In order to alleviate this problem, special paint schemes are required in these niche areas and CFD analysis of the hydrodynamic forces around the vessels hull is a useful tool to identify such areas.

6.Reference

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