International Journal of Researches in Biosciences, Agriculture & Technology | January 2014 Issue-2, Volume-1 | ISSN No. (Online) 2347-517X

SYNTHESIS OF GREEN POLYMERIC MATERIAL AND ITS APPLICATION IN DEVLOPMENT OF ECOFRIENDLY ANTIFOULING COATINGS.

B. C. Burande and B. B. Gogte*

Dept. of Applied Chemistry, *Priyadarshini Indira Gandhi College of Engineering, Nagpur.*

* Shri. Shankarprasad Agnihotri College of Engg, Ramnagar, Wardha-442001, India.

ABSTRACT

The maintenance of ship bottom by using antifouling coatings is of great economic importance. Organisms settling and growing upon the hull destroy its smooth, streamlined contour which marine architects have designed with imagination and skill. After having dry dock, a ships underwater surface progressively become rough, which is responsible for friction, with the result that fuel consumption increases to maintain a given speed.

Accordingly, new antifouling paints featuring organometallic polymer (OMP) toxicants have been developed at a U.S. Government laboratory in response to these requirements. Tributyltin (TBT) is the active chemical reagent present in conventional antifouling paints which prevent the growth of fouling organism. Later it was found that TBT containing paints have toxic effect on human beings, wildlife and aquatic life. Due to these toxic effects the use of TBT is now restricted.

In this research paper the toxicity of TBT has been studied and alternative eco-friendly substitutes for TBT are proposed. Several naturally occurring bio-compounds such as cashew nut shell liquid (CNSL), rosin based alkyd resin and lemon grass oils have an excellent antifouling activities.We have prepared two types of resin,alkyd and CNSL, several formulation of antifouling paints based on above resin has been prepared. We have also compared these formulations with commercial tin acrylate paint. Prepared formulations are free from tin and also exhibit excellent physicochemical and anti microbial property.

Keywords: Tributyltin, antifouling coatings, alkyd resin, ecofriendly, CNSL resin etc.

Introduction

Marine biological fouling, usually termed marine biofouling, can be defined as the undesirable accumulation of microorganisms, plants, and animals on artificial surfaces
immersed in sea water. In the case of ships, the adverse effects caused by this biological settlement are well known High frictional resistance, due to generated roughness,
which leads to an increase of weight and subsequent potential speed reduction. To compensate for this, higher fuel consumption is needed, which causes increased emissions of harmful compounds.

Shipping industry is as old as human civilization. Ship is perhaps the instrument of adventure. This is the era of supertankers, container ships and bulk ore carriers.

In the case of large supertankers or bulk carriers, speed losses are very expensive because of the high running cost. Consider an example of the economics of the speed loss of an average of 1.5 km/hour on a 25 km/hour Vessel. The fouling organisms grown at the bottom reduce the efficiency to 82 % of the original. If we count 300 working days per annum the loss will be 6% of 300 days means 18 days will be lost. The earning capacity of larger carrier or tanker is about 30,000 $ per day, therefore each knot of the lost speed is worth 18 x 30,000 means 5,40,000 $ per year per vessel. For this reason shipping industry is very conscious about the use of specialty antifouling paints(Marine paints). An increase of the frequency of dry-docking operations, i.e. time is lost and resources are wasted when remedial measures are applied. A large amount of toxic wastes is also generated during this process.

The uses of eco-friendly silicon based fouling release coating systems have increased in recent years. This is a good sign, but the erosive systems containing biocides still dominates the antifouling market. Thus, we also have to do more research on the traditional systems.

Review

Fouling : Fouling is the settlement and growth of marine plants and animals on man made structure in the sea, such as ship. Fouling can seriously affect the roughness of the ship bottom and lead to either to a reduction in speed or to an increased fuel consumption in order to maintain a normal operating speed in either case the ship operating costs are increased.

Fouling organisms : Barnacles, hydroids, algae, molluses & tuberous are some organisms involved in fouling.

Antifouling Paints : Antifouling paints are similar to most surface coatings consisting of pigments dispersed in a resin with additives that are toxic to marine organisms.

The antifouling agent: the biocide, is a chemical substance, which is released at very low rates and which kills or inhibits growth.

The function of antifouling

- To prevent or reduce the growth.
- To provide better fuel economy over the sailing period.
- To avoid growth penetration through the coatings, and thus extend corrosion protection.

The most important change in the growth of marine transport

- Turn round times reduced from 10 to 14 days to 24-48 hours.
- Dry docking intervals increase from 12 to 30 months. Due to this turn round of 24 to 48 hrs. there is a insufficient time for settlement & adhesion of animals, algae fouling etc.
- The conventional marine antifouling coatings contain TBT, cuprous oxide, copper, silicon, cuprous thiocynate, organic compounds like DDT (Dichloro diphenyl trichloroethane).

Tributyltin as a antifouling agent

- Tributyltin $(C_4H_9)_3$ Sn, a biocide used in ship antifoulant paints for preventing the growth of fouling organisms on ships (e.g. barnacles).

- They are formulated in such a way that the control agents gradually leach out so that film of water nearest to the hull becomes toxic to organisms and in this way control biological growth (fouling) on ship hulls, piping system and other submerged structures. Due to this, it has been extensively used on the hulls of almost every seagoing vessels in the world.
- However, it was found that tributylin tin is toxic. Due to this toxic effect all aquatic animal and plant life is in danger.
- Studies have shown that these chemicals, particularly tributyltin which can be toxic at minute concentrations (1-2ng/litre^{-1}) are evident in fresh and saltwater, sediments, the blubber, liver and kidney of marine mammals including killer whales and common dolphins, and have resulted in the thickening of oyster shell and imposex (the development of male genitalia) in female dog whelks and other gastropods.
- The marine Conservation Society also believe that organo-tins may act concurrently with other pollutants.
- These agents, though effective are toxic and face restrictive regulations to limit its use and reduce its environmental concentrations.

Toxicological Assessment of Tributyltin

The studies presented assess the potential risks posed by tributyltin (TBT) to

1. Workers commercially applying antifouling paints
2. Sea otters feeding on bivalves containing TBT
3. A shorebird (the oystercatcher) that may forge on invertebrate with TBT residues.

Composition Of Conventional Antifouling Paint

Ingredients	Super tropical antifouling paint (Soluble matrix type)	Antifouling paint (Contact type)
Cuprous oxide	24.0	57.4
Zinc oxide	5.0	--
Tributyltin oxide	2.0	--
Red iron oxide	8.0	--

Paris white	9.0	--
Talc	6.0	--
Benton 38	0.3	--
White Sprit	4.6	
Rosin		16.1
Asbestine		2.4
n- Butanol	0.1	--
Limed rosin/boiled linseed oil, 3:1 60% in naphtha	41.0	--
Modified phenolic/linseed oil 1:2 60% in 90/190 solvent naphtha	--	9.0
Chlorinated plasticizer	---	5.4
solvent naphtha 90/190	--	9.7

Alternative Solutions

One alternative is to use the naturally produced antifouling agent. Many marine organisms such as corals, sponges, and seaweed produce chemicals with antifouling properties research has shown that some marine bacteria are also capable of producing antifouling agents. The inhibition by agents produced by bacteria in fouling control have been studied. There is a need to utilize nonconventional, renewable vegetable sources like Castor oil, Rosin, C.N.S.L. liquids, lemon grass oil etc.

- Castor Oil, CNSL , Rosin, lemon grass oil also possess antifouling activity.
- These natural products will be extracted from beans of castor plant, pine tree, cashew nut tree and lemon grass by different method of extraction. Our idea is to develop antifouling character in the paint based on phenolic binders like CNSL and Novel alkyd resin.
- Cashew nut shell liquid is phenolic in nature therefore this itself have antifouling activity.
- Several paint compositions will be formulated using ZnO, lithophone (which contains Zn-sulfphide) and lemon grass oil.

The lemon grass oil is known to have an excellent antifouling character. Thus a new combination of pigments, Novel binders and plant extracts which can be used successfully in developing tin free antifouling ship bottom paints

Method

Experimentation:

Synthesis of Alkyd Resins COA 10

Compositions Novel alkyd resins were investigated in this research work based on castor oil, rosin, glycerol, Pentaerythritol, sorbitol, maleic anhydride, phthalic anhydride and Benzoic acid.

COMPOSITION OF ALKYD RESINs BASED ON CASTOR OIL

Composition % by weight

Ingredients	COA10
Castor Oil	35.89
Rosin	37.62
Glycerol	6.0
Pentaerythritol	4.25
Sorbitol	-----
Maleic Anhydride	5.40
Phthalic Anhydride	9.84
Benzoic acid	1.00
Sodium bisulphate	1.5
Sodium bisulphite	0.5
% Yield	95.0

ANALYSIS OF ALKYD RESINS

Name of Alkyd Resin	Acid Value	Iodine Value	Peroxide Value	Hydroxide Value	% Solids
COA10	30.0	42.0	1.02	120.3	95.14

The resin composition suitable for preparing antifouling paint was developed.

CNSL Resin

The cashew nut shell liquid consists chiefly of the two naturally produced phenolic compounds - anacardic acid - about 90% and cardnol - about 10%

Anacardic acid is a derivative of salicyclic acid. This acid is easily decarboxylated by heat during the roasting process which is employed to obtain cardnol. Cardnol is a monohydroxy phenol. Cardol is a resorcinol derivative having a long unsaturated hydrocarbon chain. CNSL due to its many of the advantage over phenolics it is widely used in surface coating

Polymerization of CNSL : - The CNSL resin was procured from small scale industry in which following process of polymerization was adopted.

CNSL - 70% Hexamine - 5% Solvent for thinning: - 20% mineral turpentine oil and 5% butanol.

Charge CNSL oil into the reactor, heat up to 100^{O}C add slowly Hexamine and solvents. Control the frothing by slowly and steady increase of temperature. Take the temperature to 150^{O}C and maintain for 2 hrs. The final product should have viscosity of 90 sec. by ford cup no.4 at 25^{O}C.

Table No. 01: COMPOSITION OF ANTIFOULING PAINTS BASED ON BLENDS OF NOVEL AIKYD COA 10 & CNSL RESIN. (Composition % by weight)

Components	E1	E2	E3	E4	Tin Acrylic paint
TiO_2	21.08	20.96	20.65	20.24	24.91
ZnO	9.83	9.73	9.64	9.44	8.97
Al. Stearte	0.19	0.188	0.186	0.18	0.19
Alkyd (COA 10)	22.37	21.24	21.92	21.47	------
CNSL Resin	12.22	12.19	11.97	11.73	--------
*Tin acrylic Resin	------	-----	-----	-------	22.84
LGO	---------	0.99	1.96	3.84	---------
Cobalt octate	0.94	0.93	0.92	0.902	----------
Lead octate	1.89	1.87	1.83	1.82	----------
Xylene	22.4	22.27	21.95	21.51	29.81
Mineral Turpentine	8.96	8.87	8.78	8.60	12.49
Butanol	0.64	0.63	0.627	0.62	0.89
Pigment Binder Ratio	0.89	0.89	0.89	0.89	1.50

* Tin acrylic Resin -Tin Acrylic Resin (AF:435) , was obtained from Jotun A/S Norway.

TABLE NO. 02: PHYSICOCHEMICAL & FILM PROPERTIES OF ANTIFOULING PAINTS BASED ON BLENDS OF NOVEL AIKYD COA 10 & CNSL RESIN .

Analysis	E1	E2	E3	E4	Tin Acrylic Paint
Viscosity by Ford cup No.4 at 30°C in Seconds	60	60	60	60	60
Density (G/cc)	1.431	1.398	1.410	1.396	1.371
Hiding power (Sqm/L)	21.94	19.87	20.11	18.36	14.34
% Solids	67.83	65.21	66.78	65.11	61.76
Surface Dry (In Min)	90	95	95	110	10
Hard Dry (In Min)	320	330	345	365	100
Scratch Hardness (Gms)	>1000	>1000	>1000	>1000	>1000
Finish	Semigloss	Semigloss	Semigloss	Semigloss	Semigloss
Adhesion Test	Excellent	Excellent	Excellent	Excellent	Excellent
Stability Test (3 Month)	Excellent	Excellent	Excellent	Excellent	Excellent

TABLE NO. 03 :RESISTANCE PROPERTIES OF ANTIFOULING PAINTS BASED ON BLENDS OF NOVEL AIKYD COA 10 & CNSL RESIN .

Analysis		E1	E2	E3	E4	Tin Acrylic Paint
Water Resistance	15 Days	Ex	Ex	Ex	Ex	Ex
	1 Month	Ex	Ex	Ex	Ex	Ex
Seawater Resistance	15 Days	Ex	Ex	Ex	Ex	Ex
	1 Month	Good	Good	Ex	Ex	Ex
*Algae Resistance (1Month)		Ex	Ex	Ex	Ex	Good
Alkali 3%NaOH (30min)		Ex	Good	Ex	Ex	Good
Acid 3% H_2SO_4 (48 hrs)		Good	Poor	Ex	Ex	Poor
3% Detergent (30 min)		Good	Good	Good	Ex	Good
Solvent Xylene (15min)		Good	Good	Good	Ex	Poor
Antimicrobial test by Cup Method (Diameter of inhibition zone in Cms.)						
Staphylococcus aureus		1.9 cm	2.2 cm	2.4 cm	2.6 cm	1.4 cm

EX.: FILM UNAFFECTED, GOOD : FILM SLIGHTLY AFFECTED BUT REMAINS INTACT , POOR : FILM AFFECTED

*Algae Resistance :-Ex- Film unaffected by algae deposition. Good – Film intact but slightly affected by algae deposition

Poor – Adhesion lost with deposition of algae.

Results & Conclusions:-

- A combination of alkyd with CNSL has been tried (Table No.1). A proportion of ZnO has been added to the composition. All these formulation indicate the capacity of alkyd resin, CNSL, and LGO to fight against the microorganisms.
- These formulation indicate that a combination of CNSL and alkyd give both the property i.e. antimicrobial activity as well as film resistance properties.
- The use of LGO shows excellent antimicrobial activity against S. aureus.(Table no. 2,3) Thus we have developed a tin free antifouling paints based on natural extracts which are comparable to conventional commercial tin acrylate based paints.
- The lemon grass oil plays very important role in antifouling property. The paint based on CNSL resin with 1.96% LGO gives excellent antimicrobial activity.

Conclusion:-

- Alkyd and CNSL binders are promising binders of future. They may become important binders for future ecofriendly systems, provided further studies are carried out for standardization of the compositions.
- Finally the following formulations have been adjudged as best and are technically sound and have excellent antimicrobial activity. Their performance is comparable and even better than commercial sample. **[** E3, & E4]
- Our resins are based on ecofriendly renewable resources like Castor oil , Rosin, and CNSL liquid. Based on these resins we

have developed Tin free antifouling paint, which gives excellent physicochemical and antimicrobial property.

- These compositions should be prepared on pilot plant scale and put to actual trials on Harbor testing sites. The field trials will finally establish the utility of these formulations and then only above compositions became commercially viable.

REFERENCES

Joshi, V.G. 1984. “Antifouling paints for marine application”, Paint India , 34(8), p-5.

Surface Coatings, Paints and their applications, Oil of Color Chemists Association, London, 2, p 508-514., 1984.

Morgans W.M. , 1996. " Outlines of paint technology”, 3rd edition, CBS Publishers, and Distributors N. Delhi p - 408-409.

Anderson, C.D. and Dalley, 1986. R. " Use of Organotins in Antifouling Paints" In oceans 86, 4, Organotin Symposium, Washington D.C. Sep.

Lambourne R. 1987. " Paint and Surface Coatings: Theory and Practice, Published by Ellis Horwood Limited, John Wiley and Sons, New york , p 546.

Mallik B.P., 2002. Paint India, 52, P - 44, Feb.

Marine Engineer Review, 1998. " Total Ban of TBT containing antifoulings", sept - 1998.

Laboratory methods for Blue green algae, 58.

Michel Pelezar, Jr. E.C.S., Chan, Noel R. Krieg, 1986. Microbiology, control of organism by chemical agents, p 504-506.