Toxic Hazards of Antifouling Paints

ABSTRACT:

THE antifouling paint coatings industry has been developing new organotin based formulations which are designed to protect ships for long periods. Studies of the acute toxicity of Bis (Tri-N-Butyltin) oxide, tributytin fluoride and triphenyltin fluoride are reviewed together with a 90 day subacute dermal study and an animal study of the carcingenicity of tributytin fluoride. Presentation of the safe application of organtin antifouling compounds in Shipyards is included in this report. Organotin antifouling paints have been used safely in shipyards in the past and they are known to irritate the skin, the eye and even the upper respiratory tract. Tin oxide, a naturally occurring mineral is the result of organotins dealkylation. Tin oxide is very much present in our environment and has no history of adverse effects on marine organisms.

INTRODUCTION:

Only a relatively small number of the plant and animal species populating the sea can give rise to the fouling. Those which can tolerate the wide fluctuation in the environmental conditions, such as temperature and salinity and which have the ability to attack the surfaces quickly and firmly followed by very rapid growth dominate as ship bottom foulers(1).

Plant fouling is the more intractable problem and unfortunately the mode of operation of modern shipping predisposes the vessels to colonisation by algae. For the sake of fast transportation and efficient ship operation stationary periods of ships reduced which has resulted in plants growth rather than animals on the hulls of the ships(1).

It is very important to achieve optimum performance of ocean-going vessels for the minimum fuel consumption through the control of fouling(2). At the same time serious questions must be answered regarding the effects of the new underwater antifouling coatings on man and his environment.

TYPES AND SELECTION OF ANTIFOULING PAINTS:

The need for greater economy in ship operating has given a tremendous stimulus to the study of methods by which new coatings might reduce drag on a ship and lessen the time that has to be spent on cleaning in dry-dock. The four different types of antifouling paints are Conventional Coating, Chlorinated rubber, vinyl and self polishing (3).

CONVENTIONAL COATINGS:

These can be applied by airless spray, brush or roller and dried by solvent evaporation. They are one-pack systems. The solid contents varies from 50-60 % by volume.

VINYL COATINGS:

These can also be applied by airless spray, brush or roller and dried by solvent evaporation. The materials are one-pack systems. The solid content varies from 37-42% by volume.

CHLORINATED RUBBER COATINGS :

These are also applied by airless spray and are two-pack systems. The solid content is above 40% by volume.

SELF POLISHING COPOLYMER COATINGS :

These are always applied by airless spraying techniques. They are one-pack systems and the solid content is about 37% by volume. They contain organotin (Tributyltin oxide and Tributyltin fluoride or triphenyltin fluoride) together with cuprous oxide or curpous Thiocyanate.

At present the organotins are the most promising active ingredients available (4) as they are extremely effective as antifoulants and safe in their intended use by man if the proper instructions are followed. They are known as eye and skin irritants and will cause irritation of the upper respiratory tract.

COMPOSITION OF ANTIFOULING PAINTS :

They are composed of toxic or potentially toxic materials including solvents like white spirit, xylol and ketones; and metallic compounds like Copper, Mercury, Arsenic, Lead and Organotin (5). Other components of antifouling paints include :-

Vinyl resin, Chlor rubber, inert substances such as iron oxide, Titanium dioxide and thickening agent (5).

Organotin based paints are now the most significant and the general formula for organotin compounds is Rn Sn Y4-n where :-

R : Represents and alkyl group containing one to eight carbon atoms covalently bonded to tin atom.

N : Represents the number of alkyl group covalently bonded to the tin atom, n can have a value between one and four.

Y : Represents a singly charged anion or anionic organic group bonded to the tin atom.

SN : Is the chemical symbol for the elemental tin.

Table 1 (6) lists selected physical and chemical data for important compounds.

METABOLISM OF ORGANOTIN COMPOUNDS :

In general organotin compounds are more readily obsorbed from the gut than inorganic tin compounds. Trialkyltin compounds are also well absorbed through the skin and the lungs (7). As far as distribution is concerned, organotin compounds are concentrated mostly in the liver and the brain. Transformation apparently is occuring in the liver. The excretion of organotins is slow and mostly via urine while a small amount may be found in milk, bile or faeces.

POISONING :

Experimental local application of tributyltin chloride produced skin irritation and/or burns within one to eight hours of contact. After immediate washing, no lesion developed (8). A more diffuse but less rapidly healing lesion was caused by contact with clothes which have been moistened by vapours or liquid compounds. It also caused eye irritation and conjunctival suffusion after brief contact. Immediate eye wash did not prevent the development of irritation and/or conjunctivitis. A 20% solution of Triphenyltin acetate produced irritation of the skin and the mucous membranes of the upper respiratory tract. The signs disappeared rapidly after the cessation of exposure.

Systemic effects after both dermal and inhalation exposure include general malaise, nausea, gastric pain, dryness of the mouth, visual disturbances and dyspnoea. Hepatomegally and increased levels of transminase activity have been reported. Recovery has generally been completed, but liver damage reported to persist for upto two years (8). In 1954 over 200 cases of intoxication were reported, 100 of which were fatal, due to the ingestion of an oral medication used to treat furunculosis, anthrax, osteomyelitis and acne (7,9). The prescribed capsules contains organotins. At autopsy and decompressive surgery cerebral oedema of the white matter was found.

A six month study of carcinogenic potential of tributylin Fluoride in male white mice showed no carcinogenic effects (9). There is no evidence that organotin compounds are corcinogenic or teratogenic apart from the reported effects of triphenyltin hydroxide on the testes and ovaries of rats which require further confirmation.

ENVIRONMENTAL SURVEY :

Reviewing the four different reports (10, 11, 12, 13) concerning an atmosphere survey for Falmouth Shiprepair limited carried out by the occupational hygiene units of the north of England Institute Health Service and the TUC Centenary Institute of Occupational Health, at the docks Falmouth, and concentrating on their conclusions, it is confirmed that, provided the proposed code of practice is implemented the application of antifouling by airless spray presents an insignificant health risk to the dockyard employees when carrying out their duties. The findings also confirm that access and egress to and from the ship should be facilitated by two gangways, either one each side or one at each end of the vessel.

WORK PRACTICES :

With the basic knowledge that antifouling paints will cause eye and skin irritation on contact and that the spray mist will cause irritation of upper respiratory tract, in addition to possible absorption which may happen from inhalation of paint droplet and via absorption following skin contact with the paint, it is not difficult to provide the proper instructions for their safe handling (9). Airless spraying equipment is recommended primarily to minimize the amount of overspray. The spray man must be adequately covered to preclude the possibility of eye and skin contact and inhalation of the spray mist. A full face air supplied respirator is recommended. Other men should be similarly protected if they must be working within a 25 foot radius of or within 100 foot downwind of the spray. Obviously the extent of the wind force on a given day will cause some variation in the direction. Similar precautions should be taken in blasting and welding or burning operations on ships coated with antifouling paint (14). For blasting, wet blasting is more desirable than dry one in that it provides a method of dust control. Prior to welding or burning operations, it is desirable to remove the coatings in an area of

approximately six inches on either of the section being either welded or burned.

In considering the shipyard operations one should also include the stirring of coatings prior to application. While mixing these coatings precaution should be taken to avoid both eye and skin contact. Safety goggles and other protective clothing are important.

Education of operating personnel in shipyards or at any location that handles these coatings is important to assist in obtaining a general understanding of these materials. Care in removing protective clothing and masks, frequent washing and showering where warranted and good house-keeping are all essential components of a safe handling programme for these just as for other chemicals.

A booklet entitled 'Personal Protection Advice for the Use of Marine Paints and Composition' (Known as the PPA) has been produced by the Paintmakers Association of Great Britain in 1976 (15). It describes a classification, labelling and recommendation to users, the personal protection advice they should afford to their operatives when they are applying various types of paints and compositions in different work situations.

MEASURES TO BE TAKEN IN CASE OF ACCIDENTS

The skin stained by the paint shall be washed off with soap and water immediately but never use solvent (16). If a paint splash or dust flies into an eye, the eye should be repeatedly cleaned in tap water immediately for not less than 5 minutes. If a paint splash and/or dust is inhaled an immediate gargling should be performed with tap water, spat out and repeated many times. If concerned feel indisposed physically one should consult a doctor as soon as possible.

BIOLOGICAL MONITORING :

There is no form of biological monitoring by which the exposure to antifouling paint can be supervised. This is because of the many different constituents of antifoulings and the painters themselves can be in contact with paints other than antifoulings. Moreover information on the rate of absorption of organotins from the gut and lung is insufficient as well as no precise information available on the biotransformation and route of excretion of several organotin compounds (7).

Nowadays Aresenic, Organic lead and Organic Mercury Compounds are not used because of strict legislation and availability of organotin compounds which are much safer. There is neither available nor any called for when considering white spirit, or methyl isobutyl ketone (MIBK) or copper. This leaves us with xylol and other minor constituents of antifouling paints.

However, the practice in shipyards is to identify people from past sickness prolong absence net (A month or more) to undergo some blood examination (Haemoglobin estimation number and shape of erythrocytes, erythrocyte sedementation rate, full white cell counts and differentiation), routine microscopic urine examination and determination of organotin or methylhippric acid concentration (17). Physical examination and psychological assessment may be the prime matter to depend upon.

ENVIRONMENTAL SAFETY

Since the organotins are either liquids or solids under ambient conditions, the environmental questions are, for the most part, reduced to soil and water. The level of tin oxide reported in soil in various regions of the earth varies from 1 to 250 PPM while the level in Ocean sediment has been reported between 1-5 PPM (9).

The reason for this extremely low levels in sea water is obvious since tin oxide is relatively insoluble. As the organotin leaches slowly from the surface of the coating, under condition of maximum dilution, it is dealkytated in sea water by hydrolysis and natural stress factors to inorganic tin oxide. Organotin and inorganic tin chemicals being highly substantive to soil and cellulose materials, will accumulate in the slime and muds on the Ocean floor. The dealkylation process will continue on the ocean floor. This effect minimizes the potential contact of these chemicals with aquatic life (9).

ACKNOWLEDGEMENT

I would like to thank Dr. H.A. Waldron, Dr. J.F. Wollaston, Dr. F. Rose, Mr. A.J. Woolley and Mrs. Batool.

Table I
Selected Physical Properties and Products uses of Selected Organotin Compounds (a)

	Appearance	*Solubility*		*Product Uses*			
Compound		*H_2O*	*Organic Solvents*	*Catalyst*	*Stabilizer*	*Biocide*	*other*
Monomethyltin-tris (isooctylmer-captoacetate	Liquid				X		
Monobutyltin-tris (isooctylmer-captoacetate)	Liquid				X		
Dibutyltin-bis (laurylmer-captide)	Clear pale	Insol.	Sol.		X		
Dibutyltin dilaurate	Liquid or low m.p. solid	Insol.	Sol.	X	X		5
Dibutyltin-bis (isooctyl-maleate)	White powder	Insol.	Insol in almost all	X	X		5
Di (n-octyl) tin-S,S'-bis-(isooctylmer-captoacetate)	Clear yellow liquid	Insol.	Sol.		X		
Di (n-octyl) tin maleate polymers	Powder	Insol.	Sol.		X		
Bis (tributyltin) oxide	Yellow liquid	Insol.	Sol.	X		X	1,2,3, 4,5,6.
Tributyltin fluoride	White powder	Insol.	Sol.			X	
Dibutyltin-bin (2-ethyl hexoate)	Waxy white Solid	Insol.	Sol.	X		X	

Other Use Code :
1. Flame resistant polymer
2. Wood preservative
3. Spreading coefficient of solder
4. Water repellent coating
5. Antioxidant or corrosion inhibitor
6. Adhesives preservative.

(a) **Source :** Taken from Midwest Research Institute, 1977, which used the following references :
NIOSH, Occupational Exposure to Organotin Compounds, U.S. Department of HEW, No. 77 - 115, Nov. '76.

Kirk-Othmer Encyclopedia of Chemical Technology, 2nd ed., Vol. 20, John Wiley & Sons, New York, '69.
MQT Chemicals, Inc., Rahway, New Jersey.
Tin Research Institute, Greenford, Middlesex, ENGLAND.

REFERENCES

1. Byrne O., Hull., Roughness of ships in service, "Paper presented at the Feb. 1979 meeting of the North East Coast institute of engineers and shipbuilders".

2. Townsin A.L., The Economic Consequences of Fouling and Roughness. "Paper presented at the 1974 international ship painting and corrosion conference".

3. Christie A.O., Recent Development in Antifoulings. J. Oil Chem. Assoc., 1977, 60, 348 - 353.

4. ASRY News, Cost savings from paint developments, published by Lloyd's of London Press Ltd. on behalf of Arab Shipbuilding & Repair Yard Co., Bahrain, 40, Oct. 1981.

5. Health and Safety Committee. Paint Research Association, Antifouling Paints undated.

6. Federal Registrar, Volume 45, No. 229, Tuesday November, 25, 1980, Notices.

7. WHO, Tin and Organotin Compound, Environmental Health Criteria 15.

8. Lyle W.H., (1458) Lesions of the skin in process workers caused by contact with

bytyltin compounds B.J. Ind. Med. 15, 193 - 196, - 1958.

9. Sheldon A.W., Effects of Organotin Antifouling Coatings on Man and his Environment, J. of paint technology, 47, 54 - 58, 1975.

10. Ellis R.W., Woolley A.J., An Atmospheric Survey for Falmouth Shiprepair Limited, the Docks Falmouth, 1814/15/81 - Feb. 1981.

11. Ellis R.W., Woolley A.J., Sutherland D., An Atmospheric Survey for Falmouth Shiprepair Limited, The Docks Falmouth 1885/86/81 - Sept. 1981.

12. Ellis R.W., Sutherland D., An Atmospheric Survey for British Shiprepairing Limited, Falmouth, 1898/99/81. Oct. 1981

13. Ellis R.W., Sutherland D., An Atmospheric Survey for British Shiprepair Limited, The Docks Falmouth 1935/1/82. Jan. 1982.

14. Paint Department, Production Rationalisation Committee, The Shipbuilders Association of Japan "Working Standards of Safety and Health on Job Using Antifouling Paints of Organotin leneage. Sept. 1978.

15. Paintmakers Association of Great Britain, Personal Protecton Advice for the Use of Marine Paint and Composition "PPA Booklet" - 1976.

16. Waldron H.A. Lecture Note on Occupational Medicine, 2nd edition, occupational skin diseases, 172 - 173, - 1981.

17. WHO (1980b) Study group on health based occupational exposure limites for selected organic solvents, Geneva, 17 - 23, June, 1980. □□