

HJR

23

SENATE COMMITTEE REPORT

FURTHER:

4/23/87

DATE TURNED INTO OFFICE \_\_\_\_\_

Mr. President:

RESOURCES Committee considered HJR 23

relating to tributyltin.

and recommended:

- replace with \_\_\_\_\_ CS FOR \_\_\_\_\_ )  same title
- or adopt \_\_\_\_\_ CS FOR \_\_\_\_\_ )  new title

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JOHN SUND, REPRESENTATIVE

2504 2nd Avenue  
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To: Senator Coghill  
Chairman, Senate Resources Committee

From: Representative John Sund

Date: April 28, 1987

Subj: HJR 23 - Relating to TBT  
Scheduling Request

While in Juneau  
P. O. Box V  
Juneau, Alaska 99811  
(907) 465-4919

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I would appreciate your consideration in scheduling House Joint Resolution 23 relating to TBT, a hazardous chemical found in marine paints.

Tributyltin, commonly referred to as TBT, is a highly toxic pesticide added to marine paint and coatings to prevent the growth of barnacles and algae on vessel hulls, buoys and fishing nets. It has caused fatalities and deformities in marine life.

Bills and resolutions addressing this potential threat to the marine environment and fisheries have been encouraged and even coordinated by the Pacific Fisheries Legislative Task Force made up of legislators from the Pacific coastal states. The Task Force's strategy is to support legislation banning TBT in the Pacific states while urging Congress to take national action. The Alaskan members are: Senator Eliason, Senator Zharoff, Representative Herrmann and myself.

Research conducted at the National Marine Fisheries Service Auke Bay Laboratory in Juneau was largely responsible for calling attention to the TBT threat in Alaska and the nation. Scientists there discovered that sufficient accumulation of TBT can kill salmon, especially smolt. Other studies have documented that TBT causes mortality and deformities in crabs, oysters and other mollusks.

In October, the Pacific Coast Federation of Fisherman's Associations called for a ban on the use of TBT stating they "were willing to suffer the inconvenience of using other bottom paints and hauling-out more often to prevent this substance from entering the water and killing fish and shellfish." In Alaska two fishing organizations have voluntarily stopped using TBT. The United Fishermen of Alaska testified in support of the House Bill 138 and SB 131, banning the use of TBT marine paints in Alaska. The Alaska Mariculture Association supports banning the use of TBT treated nets.

The United States currently lags behind other nations in imposing controls on TBT. So far, the toxic compound has been limited or banned in France, England, Japan, Switzerland and Germany.

JOHN SUND, REPRESENTATIVE

2504 2nd Avenue  
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HOUSE BILL 138  
AN ACT BANNING THE USE OF TBT

While in Juneau  
P. O. Box V  
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WHAT IS TBT AND WHAT IS IT USED FOR?

TBT, or Tributyltin, is a tin based pesticide added to paint used on vessel bottoms and hulls to repel barnacles and algae. It is also used on fish net pens to retard marine growth. TBT has been called one of the most toxic substances ever deliberately introduced into natural waters.

ARE OTHER MARINE PAINTS AVAILABLE?

Yes. Copper-based antifouling paints.

IS ALASKA ALONE IN ITS EFFORTS TO BAN TBT?

No. France, England, Germany (freshwater) and Switzerland (freshwater) have already banned or restricted the use of TBT based bottom paints. Japan has restricted its use in other products. In the United States, Virginia has recently passed a law restricting the sale and use of TBT based paints and Maryland is considering identical legislation. North Carolina has instituted maximum TBT concentration limits in their water quality regulations.

On the West Coast, California, Oregon and Alaska, member states of the Pacific Fisheries Legislative Task Force, have introduced bills to ban TBT after reviewing the issue at their fall meeting. Washington and Hawaii are also taking action to limit the use of TBT-based marine paints.

TBT MAY BE TOXIC, BUT THERE'S A LOT OF WATER OUT THERE. IN ALASKA, WE PROBABLY WILL NEVER NOTICE ANY IMPACT FROM ITS USE.

Not true. Research right here in Southeast Alaska has increased national and international concern about the potential economic and biological impact of TBT on fisheries. Scientists for the Auke Bay Lab (NMFS) determined that high death rates of juvenile chinook salmon at Little Port Walter Fish Hatchery were the result of TBT treated net pens. Further research showed that some chinook salmon died in all doses of TBT oxide tested.

Finally, a subsequent study by Auke Bay Lab on adult salmon in Seattle and Portland markets found that TBT had accumulated and persisted in the flesh of fish reared in TBT treated pens and could not be destroyed by cooking.

I JUST PUT TBT PAINT ON MY HULL. DOES THIS BILL MEAN I HAVE TO HAUL MY BOAT OUT OF THE WATER AND SCRAPE IT ALL OFF?

No. Absolutely not. House Bill 138 specifically states that TBT based marine paint need not be removed. However, after July 1st, 1987 you will not be able to apply new TBT paint on your boat. (This date may be changed back to December, 1987).

I'VE BEEN USING TBT MARINE PAINT FOR YEARS. WHAT HEALTH HAZARDS HAVE I BEEN EXPOSED TO BY USING IT.

According to OSHA, the major health concern is the potential for liver, kidney, heart and central nervous system damage at low concentrations. Skin problems, eye irritation and respiratory problems have been associated with inhalation of or contact with TBT. Increased sensitivity may occur with repeated use. Ingestion of Tributyltin Chloride has been found to cause progressive weakness, tremors and brain damage.

HAVE THERE EVER BEEN ANY DOCUMENTED ENVIRONMENTAL IMPACTS FROM THE USE OF TBT PAINT IN ALASKA?

No. However, consider the location of Deer Mountain Hatchery and the release of juvenile hatchery salmon into the Thomas Basin Boat Harbor for rearing purposes. Given the fact that juvenile salmon are extremely sensitive to TBT poisoning and are more susceptible to death and disease when exposed to the chemical coupled with evidence that shows that salmon rapidly accumulate higher concentrations in their tissues, it is obvious that potential problems do exist.

I OWN AN ALUMINUM BOAT. I CAN'T USE COPPER OXIDE PAINT BECAUSE OF ELECTROLYSIS. WHAT AM I GOING TO DO?

Owners of aluminum boats do have a special consideration. The sponsors of the legislation recognize this and will try to address this problem in the committee process. A provision to allow aluminum boat owners to use slow-leaching TBT paint may be considered.

I UNDERSTAND THAT THERE ARE TWO KINDS OF TBT PAINT.. FREE ASSOCIATION PAINTS AND COPOLYMER PAINTS. WHAT'S THE DIFFERENCE?

Copolymer paints generally release the TBT toxicant slower than the free association paints which have a quicker release. Although slow leaching paints are considered the less evil of the two, both are considered harmful.

IF TBT IS BANNED. WON'T THE PAINT MANUFACTURERS JUST BE ABLE TO SUBSTITUTE ANOTHER PESTICIDE IN THEIR PRODUCTS?

Amendments are being considered to tighten up the definition to prevent this from occurring.

WHAT'S THE BIG DEAL ABOUT BANNING TBT IN ALASKA?

The potential threat of a TBT scare cannot be over stated. TBT has been called the new DDT. We have the advantage of preventing an environmental problem today and avoiding a costly action later.

MY PAINT DEALER HAS A STOREROOM FULL OF TBT PAINT. WHAT IS HE OR SHE SUPPOSED TO DO WITH IT? DRINK IT?

Given the serious health effects, absolutely not!

In order to allow paint dealers to either move the paint off their shelves and/or return it to the distributors a phase-in approach is being considered by the sponsors. The date banning the sale of TBT-based paints may be changed to December, 1987 to allow stores to take care of their inventories and plan for the future.

TRIBUTYL TINS/TBT

Tributyltins (TBT) have been called the most toxic compounds ever deliberately introduced by societies into natural waters.<sup>1</sup> A growing body of scientific research indicates that TBT may seriously affect non-target organisms and have unknown effects on humans who eat marine organisms containing TBT or are exposed to it in the workplace.

In the United States, many bodies of water have concentrations of TBT that have reached levels which may cause lethal and sublethal effects in non-target organisms. For example, TBT levels in San Diego Bay have been measured at levels which could cause lethal effects in fish, mollusks, crustaceans, and algae.<sup>2</sup>

TBT is used in antifouling paints and is primarily applied to boat and ship hulls to control the growth of fouling organisms such as barnacles, tubeworms, algae, bacteria, and sponges. These organisms increase hull friction and weight, which in turn increases fuel consumption by reducing vessel speed. The antifouling paints are also used to control fouling organisms on docks, buoys, and other marine structures. TBT has been used in antifouling paints for almost 10 years and replaced the copper-based antifouling paints. The paints with tributyltins last approximately 5-7 years, whereas the copper-based paints last approximately two years.

There are two types of antifouling paints containing TBT: copolymer paints and free association paints. The copolymer antifouling paints contain TBT which is chemically bonded to the paint polymer and is released through a chemical bond breaking process called hydrolysis. New TBT molecules are exposed and released by the gradual erosion of the paint as the vessel moves through the water. The release rate is slow except during the initial one month "conditioning" period and can be controlled by

altering the paint's water absorption characteristics. The free association paints contain TBT which is physically incorporated into the paint matrix; the TBT is released through diffusion as surface paint particles dissolve. This type of paint has a short time period of protection and is characterized by a high initial release.

Antifouling paints containing TBT are registered, in the United States, for use on aluminum, steel, fiberglass, wood and cement hulls.<sup>3</sup> These paints are used on commercial and recreational vessels and some military ships. However, the Navy is the major domestic user of antifouling paints. The Navy is planning to replace the copper-based paints it is currently using on its steelhulled vessels with antifouling paints containing TBT compounds. This Navy conversion would take approximately 5 years and add an additional 90,000 pounds of TBT active ingredients to the environment. Economically, if all the Navy ships are painted, it would annually save the Navy \$150 million.<sup>4</sup> However, this cost does not include the cost to the marine environment.

Currently, there are 340 Federally registered antifouling paints containing TBT active ingredients. U.S. domestic usage of TBT in antifouling paints range from 250,000 to 300,000 pounds.<sup>5</sup> In addition to antifouling paints, TBT compounds are registered for use as disinfectants, textile biocides, wood preservatives, paper and pulp mills, leather processing and as plastics stabilizers, etc. In the United States, total usage of TBT pesticides (for all uses) ranges from 730,000 to 860,000 pounds of active ingredients.<sup>6</sup>

In 1981 France banned the use of TBT paints on all vessels less than 80 feet in length because of shellfish deformations, particularly in Arcachon Bay.<sup>7</sup>

England researched and then combined their studies with France's experience and banned the use of free association paints and copolymer formulations with more than 7.5 percent TBT on January 1, 1986.<sup>8</sup> Germany and Switzerland have banned TBT paints for fresh water usage. Japan has banned the use of TBT compounds in household products such as house paints and textiles, but has not restricted its use in vessel antifouling paints.<sup>9</sup>

In the United States, Senators Cohen and Tribble introduced Senate Resolution 272 in December 1985 calling for "public hearings to determine if further action is warranted with respect to the future use of TBT compounds" and "urging EPA to accelerate its investigation into the environmental and health effects of organotin bearing paints...." The resolution has been referred to the Senate Committee on Environment and Public Works.

On June 11, 1986 Congressman Parris introduced HR 5015, calling for a temporary ban on TBT-based paints on the hulls for commercial and recreational vessels until, "EPA has completed their ongoing studies to determine the safety of such paints and their impact on the aquatic environment.

Currently, only North Carolina has limited the input of TBT into its waters. North Carolina instituted regulations on January 1, 1985 to limit discharges from industries to 2 ppt for salt water and 8 ppt for fresh water.<sup>10</sup> These regulations were initiated because it was determined that hundreds of North Carolina companies were using TBT to control odor-causing bacteria in textiles or to control slime in piping. Some of the discharges from the textile mills were high enough to kill aquatic organisms.

On January 8, 1986, EPA commenced a special review of the nine most common TBT antifoulant paint formulations. EPA's support

document indicates that EPA is concerned about the acute and chronic toxicity potential of tributyltin compounds to nontarget aquatic organisms. Water samples have been found to contain TBT levels that may have direct effects on aquatic organism populations (mollusks). The TBT compounds may bioaccumulate in aquatic habitat and may pose a hazard to the food chain. Absorption of tributyltin compounds to sediment may have long-term toxicity effects on benthic browsing organisms such as crustaceans and snails. Contamination of estuarine areas at sublethal concentrations can influence the reproduction of several aquatic groups from fish to plankton, thus impacting the marine environment. The present use of tributyltin in antifouling paints presents a potential hazard to nontarget aquatic organisms.

The Pacific Fisheries Legislative Task Force, working in coordination with the Pacific Coast Federation of Fishermen's Associations, has passed three task force resolutions offered by Assemblyman Dan Hauser, the Task Force Vice Chairman, regarding TBT. The resolutions:

1. Urged and encouraged the Environmental Protection Agency to take the lead in creating a public information education brochure about TBT that could be distributed to every boat owner in America. The pamphlet concept is based on a similar project done in the United Kingdom entitled, Don't Foul Things Up. Short of a Congressional ban on the use of TBT, a nationwide public information awareness program is thought to be the next best alternative for controlling the amount of TBT introduced into the marine environment. It is thought by some scientists that this type of education program could reduce the amount of active TBT in the marine environment by 50%.<sup>12</sup>

2. Memorializes the Food and Drug Administration, the Environmental Protection Agency and the National Marine Fisheries Service to impose an immediate ban on all salmon imported into or produced in the United States in pens treated with TBT. This is important because TBT levels for safe human consumption have not been established. TBT was found in the flesh of salmon that were pen-reared in TBT-treated pens. Moreover, the study found that cooking does not remove the TBT from the fish.<sup>13</sup>
3. Memorializes Congress to enact an immediate ban on the use of TBT-based bottom paints on all military, commercial, and recreational vessels until such time, and if, methods of use of TBT-based bottom paints or derivatives of organotin paints are developed that pose no threat to the marine environment.

In addition to the resolutions passed by the task force, it is anticipated that the participating states may introduce state legislation to further regulate TBT usages in their states. Currently, efforts are underway to explore legislation to monitor dry docks, set water quality standards, ban or restrict the uses of TBT, or regulate the amount of TBT used in antifouling paints.

TRI-N-BUTYLTIN CAUSED MORTALITY OF CHINOOK SALMON, ONCORHYNCHUS  
TSHAWYTSCHA, ON TRANSFER TO A TBT-TREATED MARINE NET PEN

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ABSTRACT

The median lethal concentrations (LC<sub>50</sub>'s) of tri-n-butyltin oxide (TBTO) to juvenile chinook salmon, Oncorhynchus tshawytscha, adapted to seawater were determined in a static renewal bioassay. LC<sub>50</sub>'s were 54, 20, and 1.5 µg TBTO/l after exposures for 6, 12, and 96 h, respectively. LC<sub>50</sub>'s decreased logarithmically with time for exposures between 12 and 96 h. Average tri-n-butyltin (TBT) concentrations in liver, brain, and muscle tissues of salmon that died during the bioassay were 7.0, 3.5, and 0.52 µg TBT/g wet weight tissue, respectively. TBT concentrations in liver, brain, and muscle tissues of salmon that survived until day 4 of the bioassay were 4,300, 1,300, and 200 times exposure concentrations, respectively. Average TBT concentrations in liver, brain, and muscle tissues of salmon surviving transfer to a TBT treated marine net pen that killed 8.5% of the salmon transferred were 9.56, 3.44 and 1.24 µg TBT/g wet weight tissue, respectively. Our results indicate TBT exposure was the cause of death of chinook salmon exposed to TBT-treated marine net pens at one aquaculture facility.

INTRODUCTION

Tri-n-butyltin (TBT) compounds are widely used in the salmon aquaculture industry to retard fouling of net pens by marine organisms. Salmon at aquaculture facilities are raised to market size in marine net pens for 1 to 3 years, during which they gain most of their body mass. Nets must be periodically cleaned or chemically coated to retard fouling by marine organisms; fouling will reduce seawater exchange and result in fish kills. Antifoulants are much more economical than manual cleaning and are therefore preferred by the industry. Several antifoulant formulations are used to treat nets, but TBT compounds are among the most effective active ingredients. These compounds have low solubility in seawater<sup>1</sup>, are exceptionally toxic to marine fouling organisms<sup>2</sup>, and can be formulated for slow release.

On several occasions, we observed high mortalities in groups of chinook salmon, Oncorhynchus tshawytscha, after transfer to newly TBT-treated marine net pens at an aquaculture research facility. The facility, operated by the National Marine Fisheries Service, is located at Little Port Walter (LPW), Alaska, near the southern end of

Baranof Island. Affected fish were examined for disease agents, but none were found. Exposure to TBT was therefore suspected as the cause of the mortalities.

To determine whether exposure to TBT could cause mortalities such as those observed at LPW, we determined the median lethal concentrations (LC<sub>50</sub>'s) of TBT to juvenile chinook salmon at several exposure periods, and the TBT concentrations in liver, brain, and muscle tissues of juvenile chinook salmon that died during the bioassay. These results are compared with those of juvenile chinook salmon that had survived transfer to a TBT treated net pen at LPW that was suspected of killing some of the transferred fish due to TBT poisoning. Comparisons indicate TBT exposure as the cause of the mortalities observed at LPW.

METHODS

Bioassay Animals

Chinook salmon used in the bioassay tests were raised for 1 year in fresh water and acclimated to seawater for 4 months before testing. Fish were transferred to tanks supplied with seawater (salinity, 28‰; temperature, 4°C; flow rate 23 l/min), and were fed a diet of 3 mm Oregon Moist Pellet at a rate of 4% body weight daily until 5 days before the bioassay. Average wet weight of salmon used in the bioassay was 24.5 g (standard deviation = 16.43 g), and average fork length, 25.1 cm (standard deviation = 12.1 cm).

Bioassay

The bioassay was static, i.e., no water was replaced during the exposure period. Each of six 550 l fiberglass tanks contained one dose of TBT oxide (TBTO) and 10 randomly selected juvenile chinook salmon. A seventh 550 l fiberglass tank contained 10 similar chinook salmon, but no TBTO, and served as a control. The average ratio of wet weight of tissue to exposure volume was 0.0445 g/l. The seawater temperature was 4 ± 1°C throughout the exposure period. Solutions were aerated slowly to ensure adequate oxygen concentrations (above 80% saturation).

A solution of TBTO dissolved in 5.0 ml glacial acetic acid was mixed with seawater in the six exposure tanks, and 5.0 ml glacial acetic acid was mixed with seawater in the control tank. Salmon

were then transferred by dip net to the tanks. Dead and stressed salmon were noted at 6, 12, 24, 48, 72, and 96 h of exposure. Following 96 h of exposure, clean seawater was flushed through the exposure tanks at a rate of 23 l/min, and the survivors were observed for five additional days to determine any subsequent mortality. LC<sub>50</sub>'s were calculated using the method of Spearman and Karber<sup>3</sup>.

The solutions of TBTO in glacial acetic acid were prepared to give nominal TBTO concentrations of 2, 4, 8, 16, 32, and 64 ug TBTO/l exposure water. These doses were selected on the basis of trial exposures that determined approximate lethal doses. TBTO concentrations in exposure water were measured with atomic absorption spectrophotometry (AAS) immediately before salmon were placed in the solutions and, subsequently, once every 24 h. TBTO dose concentrations decreased to about 63% of those initially measured after 48 h of exposure; therefore, TBTO dissolved in 2 ml glacial acetic acid was added to each lobe to increase the concentration to the original level. The 2 ml aliquot was added dropwise to the intake of a submersible pump in the exposure tank to minimize high localized concentrations of TBT. The TBTO dose concentration was measured just before and just after this addition of TBTO. We used the average of all measurements for each dose and exposure period to calculate the LC<sub>50</sub> for each exposure period.

TBTO concentrations were measured by estimating the tin concentration of hexane extracts in the exposure water. One 50 ml aliquot of seawater was taken from each dose and extracted twice with two successive aliquots of 25 ml hexane each. Hexane extracts were combined and evaporated to dryness at 25°C on a rotary evaporator. The residue was taken up in 2 to 10 ml concentrated nitric acid and analyzed on a Perkin-Elmer model 5000 atomic absorption spectrophotometer equipped with a Zeeman background corrector. Concentrations of TBTO were estimated by comparison with standard concentrations of TBTO dissolved in hexane and processed similarly. With this method, recovery of TBTO from a TBTO concentration of 3 ug/l seawater was determined to be 95%.

#### Animals Surviving a Suspected TBT Poisoning Incident at LPW

Chinook salmon were hatched in January 1985 and reared for 15 months before they were mistakenly transferred to a TBT coated net pen on 3 May 1986. Four hundred fish were transferred, having an average weight of 49 g. These animals had no known prior exposure to TBT. Within three days of transfer the fish displayed poor feeding response, darkened pigmentation, and tended to hang listlessly near the corners of the net pen. Thirty-four of the fish subsequently died. Personnel at LPW suspected TBT poisoning and verified that the net material actually was treated with TBT by tracing invoice records. On 20 May 1986 these fish were transferred to an untreated net pen, and no further mortalities occurred. Six of these fish were killed, frozen whole and sent to

the Auke Bay Laboratory where they were stored frozen until analysis. Also sent were five cohorts of the TBT exposed fish that had never been exposed to TBT treated net pens as controls.

#### Tissue Sampling and Analysis

Salmon that died during the bioassay were removed and stored frozen in glass jars. After thawing, all of the liver and brain and approximately 1 g of muscle tissue were dissected for analysis. Each tissue was mechanically homogenized and then extracted with hexane, and the tin concentration of the hexane extract was measured by AAS. Results are reported as if all the tin in the hexane extracts were tri-n-butyltin, although possibly some of the tin may be di-n-butyltin. This method is more fully reported in Short and Thrower.<sup>4</sup>

#### RESULTS

Chinook salmon died in all doses of TBTO tested, but none died in the clean water control tank during or immediately after the bioassay. Only five salmon in the lowest exposure dose survived the bioassay; of these, three died within the next 24 h in clean seawater. The logarithm of the LC<sub>50</sub> decreased linearly with time between 12 and 96 h of exposure (Fig. 1). The natural logarithm of the LC<sub>50</sub> fits the following equation for a straight line for this exposure time period, using linear regression analysis:

$$\ln(\text{LC}_{50}) = -(0.031078)(T) + 3.363289 \quad (1)$$

where *T* is the exposure time in hours. The measured 96-h LC<sub>50</sub> was 1.5 ug TBTO/l seawater, whereas the measured 0-h LC<sub>50</sub> was 54 ug TBTO/l seawater.

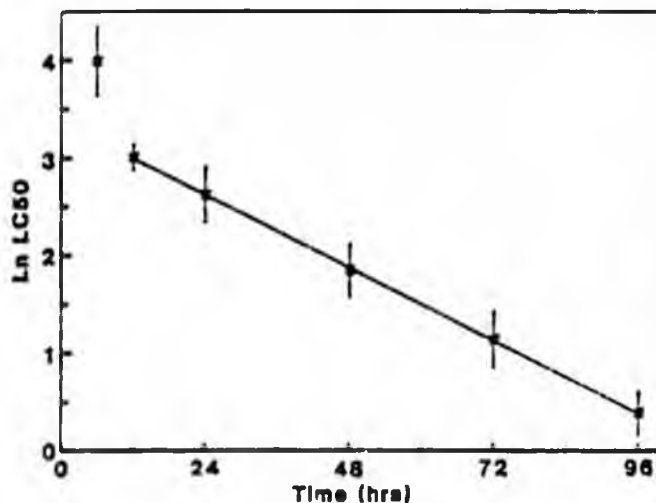


Fig. 1. Natural logarithm of TBT LC<sub>50</sub> to juvenile chinook salmon, adapted to seawater, as a function of exposure time. Upper and lower ends of vertical bars indicate 95% confidence intervals. The solid line is derived from the linear regression of the natural logarithm of the LC<sub>50</sub> with the exposure time.

All salmon that died during the bioassay displayed the same series of progressive signs: darkened pigmentation, apathy, loss of stability, hemorrhage of the gills and fin insertions, defecation, and finally death. Salmon in the lowest doses did not display any symptoms until near the end of the bioassay period. Death usually occurred within 24 h of the onset of darkened pigmentation. The two survivors in the lowest exposure dose had darkened pigmentation at the end of the bioassay, but they returned to normal pigmentation within 24 h after being placed in clean seawater and apparently recovered from TBTO intoxication.

Concentrations of TBTO tended to decrease at all dose levels with time (Fig. 2). Dose levels declined to an average of 80% of the initially measured levels after the first 24 h of the bioassay and to an average of 63% after the first 48 h. Dose levels resumed their decline after TBTO was added to restore the desired concentrations.

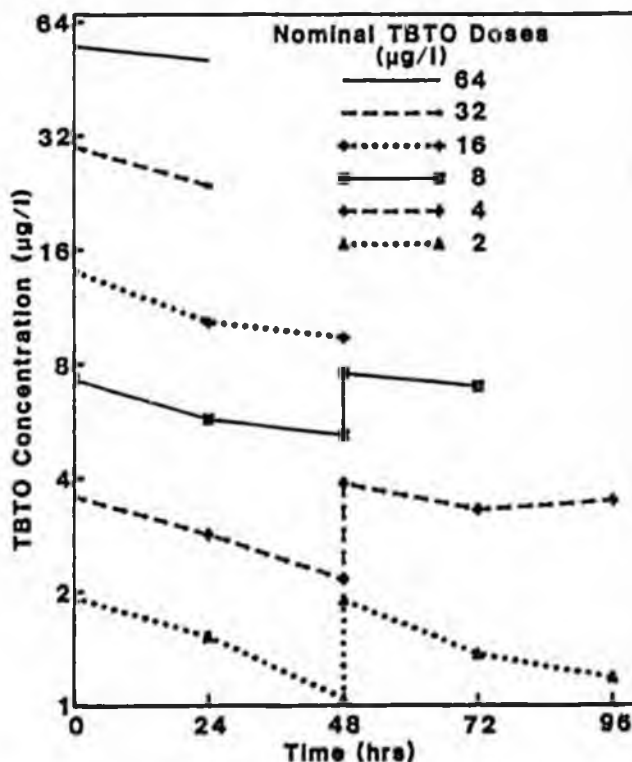


Fig. 2. TBT concentrations measured in bioassay doses as a function of time. TBT measurements were terminated in the higher doses after all the salmon in those doses died. The increase in measured TBT concentrations of the lower doses at 48-h of exposure is due to the addition of TBT to those doses at that time.

Average concentrations of TBT in tissues of salmon that died during the bioassay were highest in liver, intermediate in brain, and lowest in muscle tissues (Table 1). In liver and muscle tissues, the highest concentrations of TBT were in salmon killed by exposure to intermediate doses for intermediate exposure periods, and were about twice the concentrations found in salmon exposed to

either high doses for brief periods or low doses for longer periods. In contrast, brain tissue concentrations of TBT were highest in salmon killed by exposure to high doses for brief periods.

We calculated apparent bioconcentration factors of liver, brain, and muscle tissues for salmon that died between 72 and 96 h of exposure to the lowest bioassay dose. These factors were 4,300 for liver, 1,300 for brain, and 200 for muscle tissues, calculated as the ratio of the TBT concentration in tissue to the average exposure concentration of the lowest bioassay dose (1.49 µg TBT/l).

Average concentrations of TBT in tissues of salmon that survived transfer into the TBT treated net pen at LPW are not significantly different from concentrations in corresponding tissues of salmon that died during the bioassay (Table 1). In contrast, much lower average TBT concentrations were found in tissues of salmon that were cohorts of the LPW salmon exposed to the TBT treated net pens (Table 1).

#### DISCUSSION

Juvenile chinook salmon are very sensitive to TBT poisoning in seawater. We found the 96-h LC<sub>50</sub> of 1.5 µg TBT/l to be lower than any reported for fish in a recent survey of the literature on acute toxicity of organotins.<sup>2</sup> The most significant difference between bioassay conditions in our experiment and those reported in Hall and Pinkney<sup>2</sup> was that in ours, water temperature was lower (4°C), which may be the cause for some of the sensitivity observed.

TBT concentrations in salmon that died during the bioassay were nearly constant for all doses, suggesting that TBT continues to accumulate until a threshold concentration is reached in critical tissues and causes death. This conclusion is supported by our observation that salmon exposed to low doses of TBT displayed no intoxication symptoms until late in the bioassay. The linear relationship between the logarithm of the LC<sub>50</sub> and the exposure time (cf. Equation 1) indicates that significant mortalities may occur in salmon exposed for longer than 96 h to TBT concentrations lower than 1.5 µg/l.

The bioconcentration factors we measured are not equilibrium factors. Bioconcentration factors for salmon exposed to sublethal doses of TBT would be higher if the accumulation time was longer than in our study. However, our 96-h bioconcentration factors indicate that relatively brief exposure to TBT results in the accumulation of appreciable concentrations in salmon tissues.

The similarity of tissue TBT concentrations in salmon that died during the bioassay and salmon that survived transfer to the TBT treated net pen at LPW indicates that the transferred salmon were exposed to a nearly lethal dose of TBT. These results, together with the similarity of distress signs displayed by salmon tested in the bioassay and those transferred to the TBT treated net pen at LPW, indicate that TBT poisoning was the cause of death of the thirty-five salmon that died after

being transferred to the TBT treated net pen at LPW. The salmon that died represent the most sensitive individuals of the transferred group to TBT poisoning.

Table 1. Comparison of TBT concentrations in liver, brain, and muscle tissues of juvenile chinook salmon, adapted to seawater, that were killed by TBT exposure during the TBT bioassay, with survivors of a suspected TBT poisoning incident at LPW and with salmon from LPW that were not exposed to TBT. Concentrations are given as  $\mu\text{g TBT/g}$  muscle tissue (wet wt.), together with 95% confidence intervals. N = number of individual salmon analyzed.

Tissue	TBT of	N	Trans-	N	Control	N
	fish killed		ferred to TBT		fish at	
	during bioassay		net pen at LPW		LPW	
Liver	7.44 $\pm$ 0.84	54	9.56 $\pm$ 2.91	6	0.13 $\pm$ 0.24	5
Brain	3.46 $\pm$ 0.33	53	3.44 $\pm$ 2.54	6	0.12 $\pm$ 0.18	4
Muscle	0.52 $\pm$ 0.21	49	1.24 $\pm$ 0.25	6	0.012 $\pm$ 0.007	5

TBT leaching from treated marine net pens may cause adverse effects that are more subtle than intoxication symptoms or death. Growth in salmon could be affected by TBT; Chliamovitch and Kuhn<sup>5</sup> have suggested that TBT inhibits metabolic pathways in rainbow trout, *Salmo gairdneri*. Chinook salmon exposed for prolonged periods to sublethal doses of TBT in treated marine net pens may therefore grow more slowly than those in untreated net pens due to the additional energy required to compensate for such stress. A similar effect has been demonstrated in salmon exposed to prolonged sublethal doses of the water-soluble fraction of crude oil.<sup>6</sup> Low doses of TBT can impair the immune system of rats,<sup>7</sup> which suggests that salmon raised in TBT-treated marine net pens may be more susceptible to disease.

In summary, our results show that juvenile chinook salmon are very sensitive to TBT poisoning in seawater, that they rapidly accumulate TBT to high concentrations in tissues, and that lethal effects are dose and time dependent. For these reasons, TBT-treated net pens for salmon aquaculture applications should be used with caution.

#### ACKNOWLEDGEMENTS

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ACCUMULATION OF BUTYLINS IN MUSCLE TISSUE OF CHINOOK SALMON  
REARED IN SEA PENS TREATED WITH TRI-N-BUTYL TIN

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ABSTRACT

Muscle tissue of chinook salmon, Oncorhynchus tshawytscha, reared for 3 to 9 months in sea pens treated with an antifouling biocide, tri-n-butyltin (TBT), contained organotin concentrations of 0.28-0.90  $\mu\text{g/g}$  (as TBT). Organotins are present in some pen-reared salmon sold in the United States: Eleven of 15 salmon advertised as aquaculture products and purchased from public markets contained organotin concentrations of 0.081-0.20  $\mu\text{g/g}$ . Preliminary analyses by GCAA indicate that these organotin concentrations are TBT. Most common cooking practices do not effectively destroy or remove butyltins from salmon muscle tissue. We believe this is the first evidence of entry of organotins into the human diet in the United States.

INTRODUCTION

Tri-n-butyltin (TBT) compounds are emerging as the leading compounds in the effective control of marine fouling of sea pens, a serious problem in the salmon farming industry. Fouling organisms restrict water flow through the sea pens and increase the risk of dangerously low oxygen levels occurring as a result of poor water exchange in the sea pens. TBT compounds have a low solubility in seawater<sup>1</sup>, are exceptionally toxic to marine fouling organisms<sup>2</sup>, and can be formulated for slow release. The recent increase in the use of TBT compounds could result in an environmental hazard in marine waters. Continued uncontrolled use is being debated; the U.S. Congress has prevented the U.S. Navy from implementing plans to begin using TBT compounds as bottom paint for their fleet in 1986. Their use is banned in some countries and states.

Following the industry practice, TBT-treated sea pens were used beginning in 1983 at Little Port Walter (LPW), near the southern end of Baranof Island in Southeast Alaska, where research on improving fish farming methods is carried out by the National Marine Fisheries Service. At that time, the intent was only to minimize marine fouling of the pens and any potential effects of TBT on salmon were not considered. On several occasions, unusually high mortalities were observed in populations of chinook salmon, Oncorhynchus tshawytscha, after transfer to newly TBT-treated sea pens. In one instance, 5555 (over 50% of the

population) yearling chinook salmon died within 2 weeks of transfer. These fish were carefully examined for disease agents, but none were found. As part of an effort to determine the cause of these mortalities, the survivors were analyzed for organotins. Also analyzed were the fish food and local seawater. Our results prompted us to look in the marketplace for organotin-contaminated salmon and, subsequently, to determine whether normal cooking processes destroyed these compounds.

In this paper, we present evidence that pens treated with TBT may contaminate the flesh of salmon with TBT and its metabolite di-n-butyltin (DBT). The butyltins may persist in the flesh to the marketplace, and most will not be destroyed by cooking.

METHODS

Four groups of chinook salmon reared at LPW were examined for organotins after mortalities associated with transfers to TBT-treated sea pens were observed in two of the groups, 1981 and 1982 brood-year salmon. LPW is a pristine area, unaffected by pollutants from industrial or urban sources: The only population centers within a 75 km radius are fishing villages of less than 500 people each, and less than 100 000 people live within a 1000 km radius. The 1981, 1982, and 1983 brood-year fish had different histories of exposure to TBT. The fourth group, cohorts from the 1983 brood, was a control group which had no exposure to TBT.

The 1981-brood fish had been placed in newly TBT-treated sea pens in May 1983 and subsequently transferred to newly TBT-treated sea pens in October 1983 and May and August 1984. The 1982-brood fish had been placed in newly TBT-treated sea pens in October 1983, and again in May and August 1984. The 1983-brood fish had been placed in used TBT-treated sea pens in October 1984. The control group had been reared in ordinary, untreated sea pens.

On 6 November 1984, two salmon were randomly taken for organotin analysis from each of two sea pens containing 1981-brood fish (average body weight 1700 g) and from each of four sea pens containing 1982-brood fish (average body weight 1200 g). Seven 1983-brood fish (average body weight 20 g) were randomly sampled from a single sea pen on 28 January 1985.

Twelve control fish (average body weight 160 g) were randomly taken for organotin analysis on 1 November 1985.

Muscle tissue samples were analyzed for organotin compounds. The sampled salmon were killed, frozen whole, and stored at  $-20^{\circ}\text{C}$  for up to 2 months. One to 5 g of muscle tissue was dissected from each, and care was taken not to include any skin, fat tissue, or portions of the lateral line. The dissected tissue was homogenized with a glass homogenizer in 10 ml of pH 7.5 phosphate buffer solution ( $[\text{PO}_4^{3-}] = 1.0 \text{ mM}$ ), and the homogenate was extracted with two 25 ml aliquots of hexane. Hexane extracts were combined and centrifuged at  $10\,000 \times g$ , and supernatant was evaporated to dryness under reduced pressure on a rotary evaporator at  $25^{\circ}\text{C}$ . The residue was taken up in a solution of 0.1 ml concentrated nitric acid diluted to 5.0 ml with glacial acetic acid.

Tin concentration in the acetic acid solution was measured by flameless atomic absorption (AA) on a Perkin-Elmer model 5000 spectrophotometer equipped with a Zeeman background corrector and an electrodeless discharge tin lamp. The manufacturer's suggested conditions and instrument settings were used for the analysis of tin in the acetic acid solutions. For the purpose of calculating organotin concentrations, we assumed that all tin found in the hexane extracts was present as TBT.

The method of standard additions was used to estimate organotin concentrations in muscle tissue. Our method is similar to that of M&T Chemicals Ltd. for the analysis of butyltins in fish tissues (Standard Test Method AA-33, M&T Chemicals, Inc., Rahway, NJ 07065). The M&T method involves hexane extraction of a hydrochloric acid digest, followed by solvent resolution of individual butyltins. The M&T method finds that only TBT and DBT are extracted by the hexane. Our method differs in that mechanical homogenization was used instead of acid digestion, the pH of our homogenate was higher (7.5), and we did not attempt to separate TBT from DBT. Use of mechanical homogenization may significantly lower the extraction efficiency of TBT and DBT, causing butyltin concentrations to be underestimated. Salmon muscle tissues spiked with 0.60  $\mu\text{g}$  TBT/g and with 0.52  $\mu\text{g}$  DBT/g have recoveries of 55% and 37%, respectively. The limit of detection was 0.013  $\mu\text{g}$  TBT/g muscle tissue.

To determine whether organotins were inorganic tin complexed with ligands, three salmon from the control group were selected, and a 2 g portion of muscle tissue from each fish was processed using the modified M&T method described above, except that the buffer solution contained 20  $\mu\text{M}$  (as  $\text{SnCl}_2$ ), and the homogenate was allowed to rest at room temperature for 4 h. This procedure was repeated using Sn (IV) (as  $\text{SnCl}_4$ ). No organotins were detected in either case. This rate of addition of inorganic tin is equivalent to 10  $\mu\text{g}$  Sn/g muscle tissue, which is more than 10 times higher than the highest organotin concentrations found in the muscle tissue of LPW salmon reared in the TBT-treated sea pens. It is therefore very

unlikely that the organotins were derived from inorganic tin.

To verify the source of the organotins in LPW salmon, we analyzed the fish food and the seawater inside the sea pens. We extracted one 1.5 l. seawater sample from each of six TBT-treated sea pens with 0.5 l. methylene chloride and analyzed the tin content of these extracts. The extracts were all evaporated to dryness, and the residue was taken up with 5 ml of the acetic acid solution, which was analyzed by flameless AA as previously described. In seawater recovery experiments, 15 ng TBT/l. gave an average response of 0.009 absorbance-seconds on our instrument. We also analyzed three surface-seawater samples from Chatham Strait, Alaska, about 2 km east of LPW and, using the modified M&T method, analyzed muscle tissue samples from 10 wild chinook salmon caught by hook and line near Auke Bay.

To determine whether pan frying, boiling, or using a microwave oven destroys accumulated butyltins, we cooked a single 20 to 30 g portion of muscle tissue from a single LPW 1981 brood-year chinook salmon that had been analyzed for organotins, using each cooking method. Muscle tissue was cooked to an internal temperature of  $100^{\circ}\text{C}$ . Each cooked portion was subsampled five times for organotins and analyzed by the previously described method.

## RESULTS AND DISCUSSION

All samples from the three groups of fish reared in TBT-treated sea pens, but none from the untreated sea pen, contained readily detectable concentrations of organotins (Table 1). Organotin concentrations (0.70-1.1  $\mu\text{g}/\text{g}$ ) in the 1981 and 1982 brood-year salmon were not significantly different ( $P = 0.81$ ) as determined by analysis of variance comparing all results from the 1981- and 1982-brood fish, suggesting that the time scale for accumulation in these fish is less than a year. The average organotin concentration in the 1983-brood fish was 0.28  $\mu\text{g}/\text{g}$ . This lower concentration may result from the relatively brief exposure to the TBT-treated pen, which had in fact been soaking in seawater for more than 6 months before the 1983-brood fish were transferred to it. In contrast, no organotins were detected in the muscle tissue of the control group.

Table 1. Concentrations of butyltins in the muscle tissue of 1981, 1982, and 1983 brood-year chinook salmon reared in TBT-treated and untreated sea pens at Little Port Walter, Alaska. Butyltin concentrations, together with 95% confidence intervals, are based on wet tissue weights. Each fish was analyzed in triplicate. NT = none detected (detection limit is <0.013 µg TBT/g muscle tissue).

Brood year	Duration of residence in TBT-treated sea pens (months)	Muscle tissue concentration of butyltins, as TBT (µg/g)	Number of salmon analyzed
1981	19	0.90 ± 0.10	4
1982	13	0.82 ± 0.05	8
1983	3	0.28 ± 0.04	7
1983	0	ND	12

No organotins were detected in the fish food samples or in any of the 10 wild salmon caught by hook and line near Auke Bay, nor were any organotins detected in the three surface-seawater samples from Chatham Strait. However, organotins were detected in all six seawater extracts from the sea pens, at concentrations of 18-65 ng TBT/l.

Our results indicate that the source of the organotins in muscle tissue of LPW salmon was the TBT-treated sea pens. The only naturally occurring organotin compounds are methyltins<sup>3</sup>, and their concentrations in unpolluted seawater are probably less than 1 ng/l.<sup>4</sup> If naturally occurring or anthropogenic organotins from sources remote from LPW were significant, we would have expected to detect them in the control group or in the 10 wild chinook salmon. A local source is indicated because organotins were detected in all the marine water samples from inside the sea pens, but in none of the samples from Chatham Strait. At LPW, organotin compounds were only used to treat the sea pens.

The organotins present in our hexane extracts probably include TBT and DBT. The half life of TBT in water exposed to the environment is about 3 months.<sup>1</sup> Juvenile chinook salmon rapidly accumulate TBT immediately upon exposure to low concentrations: We have observed that juvenile chinook salmon exposed to 2 µg TBT/l. seawater for 72 h accumulated 0.3 ± 0.1 µg TBT/g muscle tissue (wet wt).<sup>5</sup> It is therefore likely that the salmon were exposed to only TBT and not to significant concentrations of any TBT degradation products. Once absorbed, TBT may be catabolized to DBT.<sup>6</sup> The organotins in our hexane extracts of muscle tissue from LPW salmon are therefore probably TBT and DBT (See footnote).

Our results imply that TBT is bioconcentrated to a great extent in the muscle tissue of chinook salmon. We cannot determine a bioconcentration factor with any precision from our data because LPW salmon were probably exposed to TBT concentrations higher than those found in the seawater samples. The leaching rate of TBT is highest when the treated nets are first placed in seawater and decreases roughly exponentially with time.<sup>7</sup> By the time we sampled the seawater in the sea pens at LPW, the nets had already been in seawater for at least 5 months. The 1981 and 1982 brood-year groups, on the other hand, had been repeatedly transferred into newly TBT-treated sea pens. However, chinook salmon probably bioconcentrate TBT in their muscle tissue to a greater extent than do sheepshead minnows, *Cyprinodon variegatus*, which bioconcentrate TBT by factors ranging from 740 to 1600.<sup>8</sup> Greater bioconcentration factors for chinook salmon are expected, because their muscle tissue is relatively high in lipids<sup>9</sup> and TBT has a high octanol-water partition coefficient.<sup>1</sup>

#### Market Survey

The readily detectable TBT concentrations found in the 1983 brood-year salmon, after a relatively brief exposure to a used TBT-treated sea pen, caused us to speculate whether organotins are present in aquacultured salmon in the U.S. marketplace. TBT compounds are widely used as a sea pen antifoulant in the salmon aquaculture industry. Therefore, we thought it likely that salmon reared in commercial aquaculture operations using TBT-treated sea pens may be subjected to a TBT exposure similar to that of the 1983-brood salmon reared at LPW.

We purchased eight salmonids from four markets in Seattle, Washington, and seven from one market in Portland, Oregon, in February 1985. All the Seattle fish, consisting of chinook salmon; silver salmon, *Oncorhynchus kisutch*; and Atlantic salmon, *Salmo salar*, were advertised as imported products of aquaculture. The seven fish from Portland were silver salmon reared in the United States at a facility that used TBT-treated sea pens. Fish were analyzed for organotin concentrations in muscle tissue, using the previously described method; concentrations were 0.072-0.20 µg/g in four of the eight fish from the Seattle markets, and 0.059-0.10 µg/g in all seven Portland fish (Table 2). Fish from the Seattle markets that did not contain organotins were probably not reared in TBT-treated sea pens. Although the exact history of these market fish is unknown, our results from the LPW fish suggest that the market fish acquired their organotin burdens while being reared in TBT-treated sea pens (See footnote)

Table 2. Concentrations of organotins in salmonids purchased from fish markets in Seattle, Washington, and Portland, Oregon and advertized as products of aquaculture. Organotin concentrations, together with 95% confidence intervals, are based on wet tissue weights. Each fish was analyzed in triplicate. ND = none detected (detection limit is <0.013 µg TBT/g muscle tissue).

Species	Number of fish analyzed	Muscle tissue concentration of organotins, as TBT (µg/g)
Seattle Market		
Silver salmon	1	0.20 ± 0.11
Silver salmon	1	ND
Chinook salmon	2	ND
Atlantic salmon	3	0.081 ± 0.031
Atlantic salmon	1	ND
Portland Market		
Silver salmon	7	0.081 ± 0.009

Three common cooking methods for salmon did not eliminate butyltins from the cooked portions. Average percentages of butyltins remaining were 55%, 67%, and 76% for the microwave, pan frying, and boiling methods, respectively. These percentages are corrected for the loss of water that occurred during cooking. Results indicate that cooking is ineffective in eliminating butyltin concentrations in food.

#### SUMMARY

Rearing salmon in sea pens treated with antifoulant containing TBT compounds resulted in the accumulation of organotins in the muscle tissue of salmon. Organotins were detected in several fish from different countries purchased from the marketplace and advertized as products of aquaculture. Additionally, cooking was found to be ineffective in destroying or removing accumulated organotins. We believe this is the first evidence of entry of organotins into the human diet in the United States.

#### Footnote

Analysis of the samples on which the results presented in this paper are based have recently been repeated by one of us (JWS) using a gas chromatograph interfaced with an atomic absorption spectrophotometer (GCAA). Results of the GCAA analyses showed TBT concentrations in chinook salmon muscle tissues that were quantitatively similar to the organotin concentrations (expressed as TBT) presented in tables 1 and 2. In particular, DBT accounted for less than 2% of the TBT found by GCAA. A manuscript reporting these results more fully is in preparation.

#### ACKNOWLEDGEMENTS

We thank R. James Maguire, Vernon Hodge, and Stuart C. U'ren for their review of the manuscript and helpful discussions, and A. Moles and W. Whelan for their technical assistance.

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# COOPERATIVE EXTENSION SERVICE

UNIVERSITY OF ALASKA  
FAIRBANKS ALASKA 99701

Marine Advisory Programs  
2651 Providence Avenue  
Anchorage, Alaska 99504  
(907) 263-1890

June 29, 1981

## MEMORANDUM

TO: Brian Paust, Agent  
FR: John Ball, Safety Specialist *John*  
RE: Tributyl-Tin-Fluoride (TBF)

This is a response to your question about the toxicity and special handling of this anti-fouling compound. Since it is not uncommon and is a nasty item, I am taking the liberty of circulating this information to other friends in MAP/CES/Sea Grant.

For more information on this or other compounds there are several places to turn to in the future:

- ① Carl Harmon, Environmental Engineer with the State Department of Environmental Conservation in Anchorage (the person who helped me with this)--phone: 274-2533.
- ② Environmental Protection Agency (EPA)--phone: 271-5083.
- ③ Poison Center at Providence Hospital in Anchorage--phone: 274-6535.
- ④ Chemical Transportation Emergency Center (CHEMTREC)  
Phones: (800) 424-9300 (supposedly toll free)  
(202) 483-7616 (call collect 24 hours a day).

I did not have the occasion to call the Coast Guard on this, but on materials that are recognized hazardous materials, the Coast Guard does have some references.

① Well, basically this is a substance not unrelated to 2,4-D and agent orange. ② It operates as an anti-fouling agent by breaking down the cell walls of living tissue. It will do this in people too. ③ It can be absorbed through the skin, inhaled, ingested, etc. ④ If it gets into the eyes and remains there for any appreciable period of time, it can affect vision and cause blindness. ⑤ Using this material in a confined space can lead to unconsciousness and presumably death. ⑥ For physical as well as health reasons this material should not be applied in a spray. It should be painted onto the surface to be protected (and I would go try to find my worst enemy to do the work).

Brian Paust  
Page 2  
June 29, 1981

⑦ The material collects in fatty tissue and therefore has a considerable impact upon kidneys and livers.

⑧ If one is going to use it, it is recommended that the application be done under controlled conditions, in open air (so others can share in the bounty?), with a respirator, protective clothing, gloves, etc.

I did not get the recommended solvent, but at all cost one ought to avoid getting this material in contact with the skin and it might be a good idea to be prepared with the recommended solvents and eye washes.

Basically, the stuff sounds almost too dangerous to use. The only other thing to add is that several brands have been removed from the market, and one ought to check with the CHEMTREC number above to see if specific brands are even allowed in the market anymore. Apparently, many of the earlier editions have been recalled. Keep the stuff in Petersburg, eh?

Hope this helps.

ee

January 8, 1987

~~University of Hawaii Sea Grant Extension Service would like to contact~~  
anyone in the Sea Grant network familiar with the environmental and  
biological effects resulting from use of organotin (i.e., tributyltin or TBT)  
antifouling paints. US Navy plans to experiment with TBT application on ship  
hulls at Mayport, Florida, and Pearl Harbor, Hawaii. Purposes of the study  
are to track and measure leaching of TBT into marine environment and assess  
environmental effects. USN claims TBT would be more cost-effective than  
copper-based paints. US Environmental Protection Agency is presently  
conducting a lengthy review of TBT use on vessels, triggered by recent ban of  
TBT in United Kingdom and France due to "malformations" observed in  
shellfish.

~~State Department of Health is presently reviewing existing information~~  
and obtaining views of local agencies including NMFS, USFWS, state CDM  
program, and UH Sea Grant. A meeting is being planned for January 15, 1987  
in Honolulu, at which the US Navy will brief local agencies about their plans  
and address concerns.

~~If there is any researcher or extension agent/specialist familiar with~~  
TBT, please contact Ray Tabata, marine extension specialist, UH Sea Grant  
Extension Service, 1000 Pope Rd., MSB 205, Honolulu, HI 96822; phone -- (808)

946-8191.

*Simon -  
Donk You  
Have and please  
send me the  
copy of the  
SGNET computer  
network to  
Hawaii -  
Thanks:  
Keller*

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### **EPA Warns Vessel Owners of TBT Paint**

The Environmental Protection Agency has begun a special review of the use of the pesticide tributyltin (TBT) in antifouling paints to determine whether it should be banned or restricted because of its toxicity to fish and shellfish. Between 250,000 and 300,000 pounds of TBT is used in vessel paints each year. Water samples taken in several U.S. ports contained relatively high concentrations of TBT prompting the investigation. While no decision has been made, EPA is advising all vessel operators that:

"It would be most prudent to use copper-based antifouling paints containing no TBT."

WFE - Fishes

March 1986

### HEARING HELD ON TRIBUTYLTIN

The use of tributyltin (TBT) in antifouling marine paints was the subject of a U.S. House of Representatives, Merchant Marine and Fisheries Sub-Committee hearing on Sept. 30. Three expert panels from academia, the TBT and TBT paint producing industries and the Environmental Protection Agency provided testimony. The objective of the hearing was to explore the facts about TBT, issues requiring further study and possible action to be taken.

Scientists from John Hopkins University and VIMS presented data indicating that TBT levels in water samples taken from several sites in in-shore Maryland and Virginia waters were higher than those levels found to be toxic to shellfish larvae in laboratory experiments. ~~They further noted that shellfish are known to bioaccumulate TBT.~~ Although acknowledging the existence of certain data gaps, including some in the area of public health implications, the researchers recommended immediate restrictions on TBT paint use.

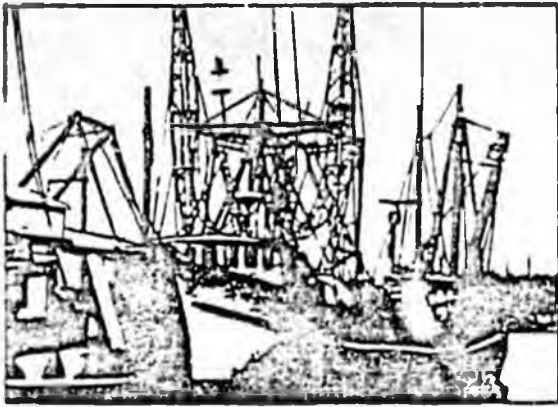
Testimony from industry representatives pointed out that no real problems have been observed that can be directly attributed to TBT. It was noted that two types of TBT-based paints are produced and marketed: a "copolymer" type, ~~which has been observed to leech TBT very slowly,~~ and a "free associated" type, which has a quicker release. It was suggested that the latter could be restricted or banned, alleviating much of TBT release into waters.

The EPA representative testified that the EPA is currently undertaking a complete review of TBT antifouling paints. While completion of the entire study may require three to five years, EPA could rule on restrictions regarding usage of high release paints by spring 1987. Congressman William Carney (NY) noted that there is little chance that legislative action on TBT use could be taken before June 1987, and requested that the EPA official keep the Committee advised on the progress of its review.

*Source: National Fisheries Institute "Flasher"  
October 1986*

*W. H. Mauldin (Cal. Sea Grant)*

*35(6).3*



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# Commercial Fishing Newsletter

VIRGINIA SEA GRANT COLLEGE PROGRAM AT  
VIRGINIA INSTITUTE OF MARINE SCIENCE

Vol. 5, No. 4

Fall 1985

## VIMS Contest's Navy Plan to Use TBT Until Scientific Studies Prove Its Safety

by Susan Schmidt

Dr. Frank Perkins, director of the Virginia Institute of Marine Science (VIMS), recommends against the use of tributyltin (TBT) to paint Navy ships until better data on environmental effects are assembled.

The Navy says that mixing organotin with copper-based paint to kill barnacles and retard algal slime could save \$150 million a year in maintenance and fuel costs. VIMS is concerned that there is insufficient scientific data on the environmental impacts of TBT and has started testing toxic effects of this chemical on oysters and clams.

VIMS is charged with advising the Commonwealth on protecting estuarine resources, and in particular, species for commercial and recreational harvest in the Chesapeake Bay. At the same time, VIMS is uniquely qualified to study a toxic chemical, because of the experience of chemists at the Institute and their sophisticated testing equipment.

Dr. Robert Huggett, head of the chemical oceanography department at VIMS, says TBT is one of

"We believe that the protection of human health and the high economic value of recreational and commercial fishing warrant the postponement of this program until the risks can be fully assessed."

### Virginia Protests Naval Plan

In an environmental assessment released in June 1985, the Navy said that TBT is 7 to 40 times more toxic than the copper-based paint now in use. After consultation with VIMS, the Virginia Council on the Environment responded to the Naval proposal in August, requesting more research.

Keith Buttleman, administrator of the Council, said,



Surf breaking over the VIMS Ferry Pier during the November 4th storm washed away several scientific experiments.

In August a Virginia Congressional delegation wrote a letter protesting the Naval plan to use TBT. In September Sen. Paul Trible set up a meeting with Navy Secretary John Lehman, attended also by Sen. John Warner, and Reps. Herbert Bateman, William Whitehurst, and Norman Sisisky. They asked the Navy to stop its plan to use paint containing TBT until VIMS' intensive study of environmental effects could be completed. Dr. Perkins and Dr. Huggert of VIMS attended the meeting.

Citing VIMS' concerns, in October the U.S. House of Representatives Appropriations Committee has encouraged the Navy to postpone fleetwide implementation until impacts on estuarine marine life and on human health are determined.

### Risks to Environment and Human Health

One of VIMS' concerns is the effect of TBT on shellfish. Several vessels that have visited nearby harbors, one of which is Norfolk, Va. Norfolk Naval facilities and the Newport News Shipbuilding and Dry Dock Company are within a tidal cycle of major oyster seed beds in the James River and crab spawning areas in the mouth of the Chesapeake Bay. The Navy report does not list the effect of TBT on shellfish species near Norfolk harbor.

The Virginia Department of Health says TBT accumulates in aquatic organisms. In oysters, TBT can be magnified 1000 to 6000 times, and in mussels, 2700 times over water concentrations. Experimental tests on rats indicate TBT causes skin sores and severe eye damage. Possible effects on workers exposed to TBT are problems with eyes, skin, lungs, liver, nervous system, abdominal pain, nausea, headaches, and unconsciousness. Because of the risk to workers, the Newport News Shipbuilding and Dry Dock Company says it will not use TBT in the future until its effects on workers and the environment are known.

### History of Anti-foulants

Three thousand years ago Phoenicians used copper on their ships. In the 19th century arsenic and mercury enhanced the activity of copper until environmental concerns banned their use.

Fifteen years ago organotins were added to marine paint, because they were thought to be less toxic than mercury and arsenic and more effective than copper. This paint is efficient at protecting against fouling because the poison is released slowly over time. In some of the newer co-polymer paints, hulls do not have to be scrubbed or repainted for years. Furthermore, a layer of paint sloughs off when the vessel is underway. In fact, the Navy says

no better alternative exists to the co-polymer mixture of tin and copper.

### Naval Readiness

By increasing fuel efficiency with cleaner hulls, the Naval fleet can travel farther and faster. By reducing time in drydock, the Navy can respond more quickly in an emergency. Initial Naval tests say that ships may be able to stay out of drydock for five years. In addition to using TBT to kill barnacles and algal slime that retard ship speed and increase fuel consumption, the Navy says it needs to use TBT on aluminum hulls to avoid corrosion caused by copper-based paints.

The Navy started using TBT in the late 1960s, discontinued use in the mid-1970s and resumed use again in 1977. So far 19 Naval vessels have been painted with TBT. On a continuing test basis, the Navy wants to paint two to five more ships with TBT in the next year. The Navy proposes that all 550 vessels would be painted with TBT marine paint by the 1990s.

### Recreational and Commercial Use of TBT

For about 10 years TBT has been used on private and commercial boats in the United States. However, in France and Great Britain its use is restricted on pleasure craft. France has banned use of marine paints with more than 3 percent organotins on boats less than 25 meters (about 80 feet). Great Britain forbids TBT on small, shallowdraft vessels, and Japan bans TBT on household textiles and paints.

TBT is a biocide, which literally means killer of life. Besides marine paints, the other uses of TBT are on textiles to kill fungus, in cooling water to kill slime on plastics and foam to control mildew, and on food preservatives and disinfectants.

### Standards and Testing

The Navy sets allowable levels at 50 parts per billion (ppb) in salt water and 3 ppb in freshwater. VIMS scientists found a potentially dangerous level of 60 ppb as TBT in a water sample from a small, private pleasure craft marina. VIMS scientists found a potentially dangerous level of 60 ppb as TBT in a water sample from a small, private pleasure craft marina. VIMS scientists found a potentially dangerous level of 60 ppb as TBT in a water sample from a small, private pleasure craft marina. Elizabeth River near the Norfolk Naval Base had concentrations exceeding the Navy's proposed standard of TBT.

Over the next year VIMS scientists will conduct an intensive study of the impacts of TBT on the environment, so that the assessment as to whether it is advisable for the Navy to paint its fleet with TBT is based on accurate scientific evidence.

## Government studying TBT-paint hazards

The U.S. Environmental Protection Agency has begun a review of some tributyltin (TBT) pesticide compounds after determining they may endanger mussels, clams, oysters and fish. There is no evidence that TBTs harm humans who eat seafood containing TBT residues, and the EPA has not banned their use.

TBTs have been used for 20 years in the manufacture of antifouling paints applied to the hulls of boats to inhibit the growth of barnacles, tubeworms and other marine life considered harmful to vessels. Small quantities of TBT paints also are used in lobster pots and buoys.

The EPA's review was prompted by laboratory studies showing that TBT at minute levels is highly toxic and potentially lethal to marine and freshwater organisms. Data measuring TBT in the Great Lakes and coastal waters show levels at concentrations that adversely affect laboratory animals.

Until the EPA investigation it concluded that copper-based antifouling paints containing no TBT, even though copper-based paint, were effective against the same organisms as TBT-based paint, tended to be corrosive to metal, especially aluminum.

Protect as long as the aluminum hulls of boats. Such hulls eventually lose the TBT treatment, however.

## TBT bottom paints face EPA action

Lawmakers in the U.S. House of Representatives have agreed to consider imposing restrictions on the use of popular tin-based bottom paints that contain tributyltins, or TBT. Such anti-fouling coatings are believed to pose serious environmental threats, particularly to shellfish.

In a hearing Sept. 30, House members agreed to ask the Environmental Protection Agency (EPA) to decide if TBT paints should be restricted or banned from use while further scientific studies are performed.

Two scientists from the Virginia Institute of Marine Science (VIMS) and Johns Hopkins University told a House Merchant Marine and Fisheries subcommittee that early scientific analysis showed that highly toxic TBT residues from the boat paints are increasingly being found in the sediment and water column of productive estuaries like Chesapeake Bay. These scientists, whose testimony was disputed by representatives of two marine paint companies, recommended immediate restrictions on the use of TBT paints.

Since the 1970s, TBT paints have become very popular, with estimates showing that upwards of 70% of all recreational vessels and more than 80% of all commercial vessels now use the product.

In the past six years, however, scientific studies have shown that the TBT paints are leaching into the environment, par-

ticularly in areas of heavy boat traffic. In Europe, where the pesticide is used to ward off aquatic growth on boat hulls, it has been found to impede the growth of shellfish, particularly oysters.

In this country, EPA opened a massive national study into TBT's effects just last January (see NF March '86, p. 10). The investigation is expected to continue through the end of the decade.

But Thomas J. Gibbons, director of marine marketing for International Paint Co. in Union, N.J., said significant questions about the allegedly harmful effects of TBT use must be answered before any restrictions are imposed.

He noted that two forms of TBT paints are currently being used: one is a "free-association" mix, which has a higher rate of release into the water, and the second is a copolymer, which leaches very little into the environment.

"A ban on all TBT-based paints in U.S. waters would create economic havoc as well as great enforcement problems," said Gibbons, "since some 70% of all oceangoing vessels are coated with TBT copolymer anti-fouling paints."

John A. Moore, assistant administrator for pesticides and toxic substances at EPA, said the agency might take interim steps — such as imposing limited restrictions on TBT use — before its lengthy federal studies are completed.

— Christopher Simpson

# Toxic chemical detected in farm salmon

A spokesman for B.C.'s ministry of the environment confirmed Nov. 7 that there are no controls in this province on the use of a toxic anti-fouling agent that has been detected in farmed salmon.

The substance is called tributyltin, or TBT, and is one of the most toxic substances known to man. Popular as an anti-fouling paint for boat bottoms, it has been banned in a number of European countries because of the damage it inflicts on the environment.

Now TBT has been detected in pen-reared salmon sold in U.S. seafood markets. According to *Friday*, the publication of the Pacific Coast Federation of Fishermen's Associations, aquaculture products from Puget Sound and Norway purchased in public markets contained concentrations of .28 to .9 micrograms per gram of TBT.

TBT, sometimes used to treat netting used in salmon pens, can be toxic in levels as low as five parts per trillion. Two scientists working for the National Marine Fisheries Service found the substance in baby coho sold in public markets.

"We have no controls on the use of anti-fouling agents," B.C. environment ministry spokesman Michael Coon told *The Fisherman* Nov. 7. "We're in the process of collecting samples. We're trying to assess the problem. It's something we don't know very much about."

Evidently the pan-sized fish are not exposed to the TBT for long enough to die from its effects. The chemical concentrates over time in certain parts of the body.

Coon said the toxic effects of anti-fouling agents are a concern. "It's in everyone's interest to make sure fish aren't contaminated."

UFAWU secretary-treasurer Bill Procopation said the threat of TBTs is another example of the chaos surrounding the B.C. fish-farming issue. "We'll need more than a 30-day review to establish regulations to prevent this kind of damage," he said.

The two American researchers also studied the effect of low concentrations of TBT on juvenile salmon, concluding that exposure to low doses may increase susceptibility to disease.



• UFAWU secretary-treasurer Bill Procopation, (left) and Gibson's troller Gary Russell (right) were among fishermen who appeared at hearings of the B.C. Finfish Aquaculture Inquiry chaired by David Gillespie, a Kamloops lawyer.

## Province, DFO to probe TBT contamination from fish farms

Both the federal and provincial governments have undertaken studies of the impact of tributyltin anti-fouling paints on farmed salmon in the wake of a UFAWU call for a ban on the use of the chemical.

In a supplementary brief to the B.C. Finfish Inquiry, UFAWU researcher Geoff Meggs reported that tributyltin, or TBT, was in widespread use in the salmon farming industry under the brand name Flexguard.

TBT is extremely toxic, especially to marine organisms like molluscs. It has been detected in farmed fish on sale in the United States.

In a telegram to Fisheries Minister Tom Siddon, the union called

for an immediate investigation to ensure no TBT-contaminated salmon is for sale in Canada.

The union also called for a freeze on the shipment of any salmon from farms using TBT-treated pens and permanent inspection and labelling regulations to ensure that farmed fish is marked as such at the retail level.

In an interview Dec. 9, provincial fisheries branch director Gordon Halsey said "we've advised and asked individual farm sites where we think there is an impact on shellfish to stop using" TBT.

Meanwhile, the province has at last committed funds complete a study on TBT that was begun

during the summer. Halsey said the province has "general concerns about TBT" although "no one has said for certain TBT is a problem."

TBT is banned in France for use on most vessels and under strict controls in several other countries.

Rudy Chang, of the federal fisheries inspection branch, said Dec. 9 his department is developing studies to allow regular inspection of farmed fish for TBT.

He said there are no plans to require the labelling of farmed fish. Siddon told the UFAWU earlier this year the department does not believe such regulations are necessary.

# **Anti-fouling paint**

A SHOCK report by British Ministry of Agriculture, Fisheries and Food scientists that certain anti-fouling paints can be deadly to many types of fish and shellfish is causing growing concern to shellfish growers and inshore fishermen in England.

Ministry scientists have established a fatal link between anti-fouling paints containing toxic TBT (tributyl tin) compounds and the death or deformity of thousands of estuarine fish or shellfish.

South Devon fishing communities are worried that this new source of pollution is causing poor growth of oysters in the River Dart and at Salcombe — areas now used for mooring yachts.

The claim is now being made that the livelihoods of local fishermen are being threatened.

One shellfish farmer at Salcombe estimates that he has lost stock worth more than £25,000 and Captain Philip Gibbon of Offshore Farms, Totnes, has been moving thousands of threatened oysters to unpolluted rivers.

Local men also claim that the disappearance of winkles, cockles, mussels and shrimps from certain Devon estuaries may have been caused by the chemicals from anti-fouling paints.

Ministry experts have been quick to point out that, while small concentrations can prove fatal to marine life, it is harmless to humans when it is so diluted. But they have no doubt that it is toxic to fish and shellfish. Dr. Mike Waldoek of the MAFF Fisheries Laboratory, Burnham-on-Crouch, confirmed that even 0.1 milligrams of TBT in one litre of water can be deadly to many kinds of marine life.

Oyster samples taken from the Dart showed a high level of TBT and this might explain the poor growth rates experienced in recent years. Pacific oysters are particularly sensitive to this chemical which causes shell thickening and slows down growth, and the local oyster industry — once expanding — seems to be affected by

## **scare in** **England**

this toxic paint.

The Shellfish Association of Great Britain was hard at work last month lobbying government departments and certain MPs to ban the use of paints containing TBT. Protest letters have been sent to Westminster from river users, conservationists and anglers.

Devon Euro-MP Lord

O'Hagan is being asked to back the case for banning TBT and to investigate the case made by the French who banned its use in 1982.

British government departments concerned with fishing, pollution and the environment are holding joint talks about whether changes in the legislation are necessary

## WATCH ON TIN

THE fisheries departments in Britain recognise that there is evidence to show that tributyl tin in anti-fouling paints can inhibit the cultivation of shellfish.

Asked in the House of Commons what steps will be taken to ban tributyl tin compound in anti-fouling paints, the minister responsible for fisheries, John MacGregor, said that the Ministry of Agriculture, Fisheries and Food was considering with other government departments what action might be appropriate.

# On the shellfish scene



With Dr. Eric Edwards, Director, Shellfish Association of Great Britain

FROM January 13, boatowners in Britain are not able to buy certain types of antifouling paints which contain high levels of organo-tin compounds, including tributyl tin (TBT).

Scientists now agree that TBT — the active ingredient of many yacht paints — is one of the most toxic substances deliberately discharged by man into the marine environment.

The British government through its Department of the Environment, aware of these dangers, has introduced some curbs on the use of TBT under the Control of Pollution (Anti-fouling Paints) Regulations 1985.

It is now a criminal offence to use the worst offenders among the organo-tin paints including those copolymer paints containing more than 7.5 per cent tin.

"Free association" paints in which the tin is not bound to resin have also been withdrawn.

Until recently the case against TBT paints centred on their stunting effect on the growth of Pacific oysters (*Crassostrea gigas*), which today form the basis of commercial oyster fisheries in Britain.

Scientists from the Fisheries Laboratory, run by the Ministry of Agriculture, Fisheries and Food at Burnham-on-Crouch, Essex, carried out field and laboratory trials from 1982 to 1984.

Their work has shown conclusively that even low

levels of TBT in an estuary can cause shell thickening and malformation in Pacific oysters to such an extent that they become unsuitable for sale.

But there is growing evidence that TBT pollution has wider effects. Researchers at the University College of North Wales have found that the growth of phytoplankton is severely retarded and barnacle larvae can only survive a very short time in minute traces of TBT. (1 microgram of TBT per litre of seawater).

## Enough

Some marine larvae were affected at one tenth of this concentration and a level of 0.5 micrograms of TBT per litre — a concentration found in estuaries with plenty of pleasure craft — was enough to reduce the population of the common mussel and to kill shrimps.

Environment Minister William Waldegrave, explaining the problem to yachtsmen, said: "Less than one teaspoonful of TBT in a million gallons of water is



Concrete cages for rearing ormers off Guernsey.

sufficient to stop the growth of phytoplankton — the marine equivalent of grass."

The Shellfish Association campaigned hard to press for controls on the use of TBT in anti-fouling paints. The French, greater connoisseurs of shellfish than the British, banned the use of TBT on boats that are less than 25 metres long in 1982. Biologists there had found that oyster shells were deformed, reproduction rates were reduced, and larvae stood less chance of surviving close to marinas and boat moorings.

Despite France's three-year-old ban, Britain has decided to move slowly. But the introduction of controls under the new anti-fouling rules is a start. Mr Waldegrave has promised parliament that these levels "will be reviewed in time for the 1987 yacht painting season" and a Government seawater monitoring programme is underway.

What has disappointed me is the general lack of interest in protecting the marine environment shown by the yachting fraternity. Their main concern was to ensure that their favourite brand of paint would be on sale in their chandlery. Why should they bother if their boats kill the phytoplankton or reduce the life expectancy in mussel larvae?

## Sea dump

As I wrote last month, the sea is too often used as a dumping ground for toxic wastes. At least the UK has made some attempt to begin controlling lethal organo-tins now proven to affect the marine environment.

In tropical and warm climates gastropods such as conchs or abalones are a favourite seafood. The northern European cousin of the Californian abalone and

the Japanese awabi is the ormer (*Haliotis tuberculata*) found around the Channel Islands and parts of the north Brittany coast. In Guernsey and Jersey the ormer is a favourite seafood but unfortunately, since the late sixties, this large grey sea-snail has been mysteriously disappearing from their beaches.

Overfishing is blamed. The shore-gatherers accuse the divers of robbing islanders of their birthright by scooping up large hauls of the shellfish which are sold for high prices in France. In turn, the divers claimed that unrestricted shore-gathering had hit the shore population but there were plenty left in deep water.

In 1983 Guernsey's parliament decided to put a three-year ban on ormering and the island's Sea Fisheries Committee brought over a Japanese expert, Ikuo Hayashi, to study the biology and life cycle of this elusive gastropod.

Diving for ormers is now banned and Guernsey only allows them to be caught on 24 days in the year. But, despite these controls, *Haliotis* continues to get scarcer and some experts believe that a temperature drop in the English Channel over the past 20 years is causing ormers to retreat south to warmer areas.

Channel Islanders must have their ormers and fortunately Dr. John Mercer, of Galway University's Shellfish Research Laboratory at Carna, Ireland, is now rearing them in a pilot scale hatchery. He has supplied over ten thousand juveniles for the Channel Islands' farming trials.

## Nurseries

On Guernsey, Sea Fisheries Officer John Lintell has set up ormer nurseries at five sites and one of his routine jobs is to ensure these vegetarians have plenty of tender seaweeds to graze upon.

As far as I know, the Guernsey ormer trial has been successful and the survival rate, to edible size, is between 80 and 90 per cent. The aim now is to encourage a private investor to start farming ormers commercially. No doubt some of the farmed animals will be used to restock the island's natural population but others will be exported to France where they fetch prices of £12-14 a dozen.

This is another example of how marine farming — under controlled environmental conditions — can help boost natural stocks. Well done to the Carna Shellfish Laboratory and the Guernsey Sea Fisheries Committee for this initiative!

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TRIBUTYL TIN ANTI-FOULING AND OYSTERS

or

"There's tin on them thar hulls"

A A A A A A A A A A A A A A

Recent work in Europe and the United States has indicated that recently developed tin based anti-fouling paints may have deleterious effects on oyster larvae development and shell growth. These new paints use bis-tributyltin oxide (fluoride, sulphide) as the active ingredient. These substances are highly toxic, with a half-life in seawater of 2-3 weeks.

Alzieu et al (1982), stated that "anomalies of calcification, show an obvious correlation between the extent of malformation and the vicinity of boat concentrations". Experimental work by Waldock and Train (1983) showed C. gigas spat grew less well and exhibited pronounced thickening of the upper valve compared to controls. As well, at low concentration levels, (0.15 ug/l) bioaccumulation factors of 10000 times were recorded.

Earlier work by Waldock showed that, generally, concentrations of TBT in the water column were related to the intensity of use by boat traffic levels of organotin which resulted in growth irregularities (0.15 ug/l) were found to occur commonly while levels as high as 2.25 ug/l were recorded. Waldock suggests that levels of TBT which would have no effect on C. gigas would be below 0.08 ug/l.

Currently TBT anti-fouling paints are banned on vessels <25m in France and are also restricted in California.

In recent years, spatfall in Pendrell Sound has become less reliable than in the past and post-settlement mortalities appear to be increasing. While no accurate records are kept, Pendrell Sound is a popular stopover point for recreational boaters. During peak periods, 50-60 boats anchor at the head alone.

In light of the problems occurring in Europe and Pendrell Sound, Marine Resources carried out a small survey of anti-fouling paint use on boats anchored at the head of Pendrell. The following results were obtained:

Type of Bottom Paint:

Copper based	30
Tin based	7
Antimony based	2
Unknown	11
None used	2
	<u>52</u>

Ratio of use by percent (n=39): 77 (copper): 18 (tin): 5 (antimony).

Mean length of stay for boats with tin based anti-fouling: 1.5 days.

Water line (wetted length) for boats with tin paint: x 30 feet.

It seems unlikely that the relatively low percentage of vessels utilizing tin based paint are alone sufficient to have major deleterious effect on spatfall success in Pendrell Sound. Whether tin based paints are one of a number of interactive factors affecting spatfall is a question outside the scope of current financial and staff availability.

Robert K. Cox  
Shellfish Unit  
Marine Resources Section

B.C. Shellfish Narrative Note  
1985 5(1) : 9-10

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## Oysters in danger from paint

RECENT research at the MAFF Fisheries Laboratory in Burnham-on-Crouch, England, has shown that tributyl tin (TBT) compounds unused in anti-fouling paints can cause excessive shell thickening in Pacific oysters.

Native oysters (*O. edulis*) do not appear to be affected in this way but toxicity tests indicate that the larval stages of oysters and crustacea can be killed with low concentrations of TBT.

Reporting this in its latest newsletter, the Shellfish Association of Great Britain, says that the work has established that TBT levels in some estuaries, used for mooring pleasure craft, are at a level which can cause problems to certain shellfish.

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# Britain may move on killer paints

**TOUGHER** controls on certain antifouling paints containing tributyl tin (TBT) compounds, which can kill or retard the growth of estuarine fish and shellfish, are being considered in Britain.

Consultation is now taking place between government departments, the Shellfish Association and environmental groups. The plan is to include all antifouling paints in new pesticide regulations, and to bring in tighter screening procedures.

Manufacturers of antifoul-

ing paints would have to have them tested to ensure limited toxicity to the environment, putting them on the same footing as pesticides used by farmers.

The shellfish industry has already suffered badly from this antifouling pollution with many growers facing

financial losses due to poor shell growth in oysters and mussels.

Research has also proved that toxic antifoulants can cause a wide range of environmental problems, especially in shallow enclosed estuaries where even minute traces of TBT are known to kill the young larvae of most estuarine fish or shellfish. Tests have also shown that phytoplankton — the 'grass

of the sea' — is destroyed by TBT.

Regulations, which came into force in January, make the retail sale of most yacht antifouling paints, which contain high levels of TBT, illegal. But because of the complexity of finding acceptable antifouling replacements, it seems likely that there will be a long lead-in time before the new regulations come into operation.

## Paint curb welcome

THE British Department of the Environment's new regulations to limit the use of antifouling paints containing tributyl tin (TBT) have been well received by the shellfish industry.

The industry has suffered badly because dangerous levels of TBT in antifouling paints is accumulated by oysters and can cause shell thickening to such an extent as to make oysters unsaleable. Growth rates of oysters have been adversely affected in some estuaries.

High levels of TBT can kill the young stages of scallops, shrimps, crabs and mussels as well as oysters.

Plans to expand the UK

production of Pacific oysters, and the struggle to maintain beds of native oysters, have been seriously affected by TBT contamination. At least one specialised oyster and clam nursery in a recreational area has had to close and employment in the industry has suffered.

The Shellfish Association of Great Britain has urged both the Ministry of Agriculture, Fisheries and Food and the Department of the Environment to ban the use of TBT in antifouling paints sold in the UK. The French government took action in 1982 when it prohibited its use in boats less than 25 metres in length and reports confirm that their shellfish industry has already benefited from this control.

# Navy studies paint risks

TWO-PACK and 'coal tar' epoxy paints, which are widely used aboard ships, have recently attracted some suspicion about their possible effects on users' health. These effects may not be permanent, but they are very unpleasant and it is best to adhere strictly to the paint manufacturers' instructions.

The latest issue of the *Journal of the Royal Naval Medical Service* discusses a study of work-related symptoms and lung function in a group of painters working in a British naval dockyard. They were exposed to organic solvents and epoxy-resin-containing paints used during refitting work.

The study was triggered by complaints of asthma in another dockyard, and it was suggested that the organic solvents and epoxy resins could be a health hazard.

There are several possibilities involved. For example, the epoxy resins can cause dermatitis, and the curing agents, such as ethylene amines, aliphatic polyamines, phthalic anhydride and trimellitic acid anhydride, have been associated with occupational asthma. Also, chronic low exposure is thought to have produced harmful neuropsychiatric effects.

These possibilities are made more ominous by reports that almost three quarters of the men involved at some time had to stop work and get into fresh air. It was not surprising that smokers did not come out of the tests too well and were found to suffer more from shortness of breath, phlegm and cough. But a large proportion of almost 100 men involved said that they regularly suffered from irritations, coughing and stomach trouble while painting.

Figures show that 65 per cent suffered from eye irritation, 70 per cent lightheadedness, 50 per cent throat irritation and 40 per cent nausea. Also 71 per cent complained of a taste of solvents in their mouths, and many suffered from a combination of these unpleasant effects.

The critical symptoms affecting the men who were forced to stop work were

lightheadedness and sore or runny eyes.

It was very likely that the levels of solvents were quite high in the confined quarters where the paint was being applied. Most paint makers do advise that there is proper ventilation and that breathing apparatus is used when necessary.

Many of the painters disliked the full-face air-fed masks which were supplied, saying they were too heavy and bulky for comfort. When they used half-face masks they suffered problems with irritants getting into their eyes.

The survey concluded that several approaches could be made to the problem. These included making the painters aware of the risks involved in not using the face-masks, using paints with less volatile solvents, and improving ventilation.

One leading paint maker said that it would be difficult to make paints with less solvents, and the only way to cut down on curing agents would be to use heat to cure the paint. This would be unsatisfactory in a confined space.

Obviously there has not been strict enough control of painting practices in the particular dockyard concerned, and although things are now being tightened up there it is clear that other painters will also suffer unless they are very careful.

Similar problems have been found in the past with welders in dockyards. They have suffered from metal fume fever, and a study by the Institute of Naval Medicine showed that this was largely due to their reluctance to wear suitable protective masks.

According to the officer who conducted the paint survey, it is likely that the effects are only temporary, but this is not guaranteed.

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# Boat paints are killing estuaries and fisheries

by Andrea Granahan

**S**cientists are warning fishermen and pleasure boaters that the bottom paints they are using on their boats is highly toxic and is killing off life in marinas, and estuaries.

"This is not environmental red flag waving. This is serious. The compounds we are looking at are much worse than DDT and may be the environmental problem of the 1980s and 1990s," said Paul Siri, manager of the Bodega Marine Laboratory in California.

The culprit is tin. Anti-fouling boat paints have switched from a copper base to tin in recent years. Now there is evidence that the tin based paints are responsible for the death of a major oyster fishery in Europe.

Britain and France have already severely curtailed the use of the paints.

A report funded by the California Department of Water Resources and the Environmental Protection Agency has been issued by Scripps Institute of Oceanography. Dr. E. Goldberg, a leading marine chemist, studied a number of American marinas and determined tin compounds, tributyltin and dibutyltin, are turning estuaries into "sterile deserts."

A general alert has gone out to those who use the paints. Some marine suppliers have appealed to paint companies to come up with a substitute. The EPA is reviewing Goldberg's alarming report. Marine scientists are calling for a ban of the product.

# Antifoulant search takes a new turn

ATTEMPTS to find an alternative to the toxic organotins used in anti-fouling paints have taken a new turn, reports ROBIN BURTON. Scientists in the USA and Britain are beginning to concentrate on formulae which deter foulants from settling, rather than poisoning them and the surrounding water.

A British research team from the oil company Shell last year announced the development of silicone rubber coating impregnated with ordinary mineral oil. It is about 5 mm thick, and marine life is unable to get a grip on it and goes away.

It is open to question whether bacteria will develop to beat the repellent, but after six years of testing there has been no sign of the necessary genetic mutations.

The US Naval Research Laboratory has developed an experimental coating of powdered polytetrafluoroethylene, more widely known as Teflon, dispersed in fluorinated polymers. It is meant to have the same effect as a non-stick frying pan.

A sample coating was applied to the hull of a tug seven years ago, and reports say that very few sea squirts or barnacles have been able to take a grip.

This paint is said to have several advantages. Apart from being non-poisonous and long-lasting it can be

easily cleaned off underwater with a power brush.

Further research at the University of Delaware has studied the rate at which bacteria attach to various plastic, glass and metal surfaces, and how foulants protect themselves from each other. It has been found that sessile organisms, such as

sponge, which cannot move, protect themselves by producing secondary metabolites.

Several natural marine products have also been found to contain halogen elements, such as bromine, chlorine and iodine. These halogens are known as poisons, but are proving effective

as antifoulants at low concentrations which have a minimal affect on the marine environment.

Overall, scientists are hoping that their efforts at 'stealing' chemical systems from the natural world will result in better ways of controlling fouling on ships' hulls.

## **ADDITIVE MAKES PAINT SAFER**

THE Star Brite Corporation claims to have developed an ~~anti-fouling~~ ~~marine~~ paint additive which will satisfy the demands of skippers and environmentalists. Compound X increases the life of anti-fouling paints without giving off the toxic materials which can be harmful to marine life and to humans.

Despite being a very costly operation, bottom painting is important to fishing vessels as it provides a safeguard against fouling, which ultimately increases drag and fuel consumption, and reduces profits. But a constant problem with anti-foulants is that their toxic materials are not biodegradable and continue to create a menace.

Dr. Ralph Grams of the Department of Pathology at the University of Florida has been working on these problems for several years. He selected a series of compounds thought to be active underwater and added them to existing paint formulae. One of these compounds proved to be highly active, adding six or seven months to the lifespan of most anti-foulants in the tidal flow areas off Florida.

Further tests on the compound showed that what toxicity it possessed self-destructed in 12 to 24 hours, and although it does not work indefinitely it has been proved to double the life of most antifouling paints.

## Tin from paint is found in salmon flesh

**C**ONCERN is rising both in the US and in Britain over the environmental effects of tin-based antifouling paint. These paints carry an active component called tri-n-butyl tin (TBT) and are applied to marine vessels and structures to prevent incrustation by shellfish.

The paints disrupt marine ecosystems, and are particularly harmful to oysters. Other effects are less visible. Now, there are indications that TBT can enter the human food chain.

Scientists in the US have warned that salmon reared in sea-pens by fish farmers can be contaminated with poisonous organotin compounds.

Researchers from the US's National Marine Fisheries Service in Alaska found that chinook salmon can absorb the compounds from antifouling paint on the pens where the fish are reared.

Pens at an Alaskan research station run by the service were coated in 1983 to prevent them becoming clogged with marine crustaceans. This improves circulation of water and oxygen in the pen. TBT was thought to be barely soluble in sea water, so the researchers saw no risk to the fish in the pen. Yet the researchers, Jeffrey Short and Frank Thrower, soon found young fish dying for no apparent reason. Further investigations confirmed that TBT dissolving in the water was responsible.

TBT residues in the muscular tissue of the fish reached concentrations of 0.9 micrograms per gram of tissue.

In the US, it is standard practice for

salmon farmers to coat pens with paints containing TBT. So Short and Thrower bought fish sold on markets in Seattle and Portland to check for TBT contamination. They found concentrations of organic tin, including TBT, up to 0.2 micrograms per gram of salmon tissue. Only four of the 15 salmon examined contained no TBT.

The researchers warn that cooking does not destroy or remove the compounds from the fish.

Meanwhile in Britain, the government has threatened to ban the use of tin-based antifoulants altogether. A partial ban is in effect at the moment.

William Waldegrave, Britain's environment minister, announced recently that restrictions on TBT use would come into immediate effect in the Norfolk Broads. Here, the levels of waterborne TBT exceed "considerably" the government's target concentration of 20 nanograms per litre.

Quoting preliminary results from last year's TBT monitoring programme, he pointed out that TBT levels exceed the limit in six of the nine estuaries studied. The worst-affected area is the Norfolk Broads, which are congested with pleasure boats. The organotin compounds leach from paint used to coat the hulls of the vessels. This year's Broads monitoring programme will be expanded, he added.

Waldegrave delivered a sharp rebuke to Britain's Paintmakers' Association (PMA). "I have warned them that unless there is a marked improvement in the monitoring results in the first half of the year—which I am advised seems unlikely—the govern-

ment will have to consider further measures... which might include a ban on the use of some or all organotin compounds in antifouling paints intended for small boats," Waldegrave said.

The minister has asked the PMA to restrict immediately the sale of TBT-based paints in the Broads area.

In the US, TBT is causing trouble along the Pacific coast. Legislators are moving in several states to investigate its use and environmental impact. Some have already demanded a ban. Marine scientists in California say it is wiping out marine life in marinas from California to Alaska.

Tests by scientists at the Scripps Institution of Oceanography in La Jolla found traces of the substance in 60 Californian marinas. Some of the harbours were devoid of plant and animal life. "It's a potential DDT of the waterways," Edward Goldberg, a chemist at Scripps, said last week. □

## Cattle deaths warning

**A** GOVERNMENT report on the death of dozens of cattle that grazed near a Scottish waste incinerator has been attacked by some of Scotland's leading epidemiologists. They call for a new investigation.

Most of the cattle that died belonged to one farmer, John Taylor, who blamed the 50 deaths in his herd between 1978 and 1980 on pollution from a waste incinerator at nearby Bonnybridge, which closed amid public uproar in 1985.

The government study, chaired by John Lenihan, a former professor of clinical physics at Glasgow University, concluded in February 1985: "In our view, from the evidence available it was ragwort poisoning." And he dismissed suggestions that the deaths might be linked with congenital abnormalities in babies born locally.

Now, a team from the Wolfson Institute of Occupational Health in Dundee, led by Owen Lloyd, casts doubt on these findings. Writing in this month's *Chemistry in Britain*, Lloyd and his colleagues also point out that the deaths are continuing. One farmer lost 57 animals during 1986. And he quotes a veterinary report which excludes the possibility that many of Taylor's cattle died of ragwort poisoning.

Lloyd also criticises a report by G. H. Eduljee of the Chem's environmental unit, published last April. Eduljee blamed the deaths on ragwort, a poisonous plant that he said the cattle had eaten. Eduljee claims to have found a ragwort leaf bearing teeth marks, and cites this as evidence that they were chewed by cattle. Lloyd dismisses the claims. "To use the leaf of one plant in the context of massive morbidity and mortality is an extreme case of arguing from the very tenuous particular to the general," they say.

Nor does the ragwort theory explain why the cattle died only between 1977 and 1980. If ragwort has always grown in the field, then why have herds not been poisoned in the past, asks Lloyd. Also, he points out that fields on neighbouring farms—away from the incinerator—support extensive patches of ragwort, yet the cattle grazing on them are healthy. □

## Peril from dog faeces in London parks

**A** PARASITE that can blind children if it infects them has been found in high levels in the soil of London parks.

Keith Snow and colleagues from the North East London Polytechnic examined 503 samples of soil from London parks. They found that 332 contained eggs of the round-worm, *Toxocara*, the highest levels ever found by a survey in Britain.

The worm is a parasite of cats and dogs. It does not reproduce in humans but causes a condition known as visceral larva migrans. If swallowed, the eggs hatch in the gut and migrate into the blood and lymph systems. They form cysts in a variety of organs, including the eye, the lungs, the liver and even the brain.

Children aged between eighteen months and three years are most at risk. They can be infected if they play in soil contaminated with animal faeces, or if they play with infected pets.

Snow and colleagues reported in the *Veterinary Record* last week that all five parks surveyed in the East End carried high enough soil levels of living eggs in soils to pose a "significant risk of acquiring toxocarosis". They add that the eggs can survive for long periods in the soil.



Scoop! Scooters on patrol in Paris

Encouragingly, they found fewer eggs in fenced areas for children where it is forbidden to exercise dogs. Even here though, they noted an average of 4.6 eggs in each 26-gram sample of earth, compared with 12 in unfenced areas.

The findings increase pressure on the government to introduce "poop scoop" regulations. It is considering whether or not to introduce a model by-law for adoption by local authorities following a successful pilot scheme in four districts.

A simpler solution is for pet owners to treat their animals with worming preparations that kill the organism. But few are aware of the problem and even fewer owners bother. □

ANTI-FOULING PAINTS FOR VESSEL BOTTOMS AND HULLS  
CONTAINING TBT FLUORIDE

Carboline Company  
40600 Albrae Street  
Fremont, CA 94538

Carboline Super Tropical anti-fouling red 1240-18  
Carboline Super Tropical anti-fouling black 1240-1B  
Carboline Super Tropical anti-fouling 1240-31

DeSoto, Inc  
1700 S. Mt. Prospect Road  
Des Plaines, IL 60017

Sears Best anti-fouling bottom paint - gold bronze  
Sears Best anti-fouling bottom paint - red  
Sears Best anti-fouling bottom paint - copper bronze  
Sears Best anti-fouling bottom paint - white  
Sears Best anti-fouling bottom paint - green  
Sears Best anti-fouling bottom paint - blue

DeVoe Marine Coatings Co.  
4000 Dupont Circle  
Louisville, KY 40207

Navicote anti-fouling vinyl anti-fouling white MD-3095  
Navicote anti-fouling vinyl anti-fouling gray MD-3883  
Navicote anti-fouling vinyl anti-fouling black MD-3761

Gibson Paint Co.  
1199 East 12th Street  
Oakland, CA 94606

Gibson Paints Copper Bottom Paint

Hempel's Marine Paints, Inc.  
Foot of Currie Avenue  
Wallington, NJ 07057

Hempel's antifouling oceanic 0733  
Hempel's antifouling oceanic 0733-5140 red  
Hempel's antifouling oceanic 0733-3084 blue  
Hempel's antifouling nautic 7680-1999 black  
Hempel's antifouling nautic 7685-1999 black  
Hempel's antifouling nautic 7695-6464 brown

International Paint Co. (California) Inc.  
220 S. Linden Avenue  
South San Francisco, CA 94030

International red hand wide spectrum antifouling red  
Mark II 3210  
Interantioanl wide spectrum antifouling gray Mark I 3201  
International red hand wide spectrum antifouling  
Tri-Lux Vinyl-Base paint antifouling paint 64 wide spectrum  
red (TBIF) Mark I  
Tri-Lux Vinyl-Base paint antifouling paint 65 wide spectrum  
dark green (TBIF) Mark I  
Tri-Lux Vinyl-Base paint antifouling paint 66 wide spectrum  
dark blue (TBTF) Mark I  
Tri-Lux Vinyl-Base paint antifouling paint 67 wide spectrum  
black (TBTF) Mark I  
Tri-Lux Vinyl Base paint antifouling paint 68 wide spectrum  
white (TBTF) Mark I  
Interlux outboard/outdrive antifouling paint 263 white  
Interlux outboard/outdrive antifouling paint 267 black  
Tri-lux vinyl base paint antifouling paint 63 wide spectrum  
light green mark I (TBTF)  
Tri-lux vinyl base paint antifouling paint GI wide spectrum  
light blue Mark I (TBTF)

Koppers Company, Inc  
1201 Kippers Building  
Pittsburgh, PA 15219

Brolite Z-spar colortox bottom paint antifouling B-43 green  
Brolite 2-spar colortox hard-vinyl type antifouling paint  
B-43 green  
Brolite Z-spar colortox bottom paint antifouling B-42 blue  
Brolite 2-spar colortox hard vinyl type antifouling paint B-42 blue  
Brolite Z-spar colortox bottom paint B-41 red  
Brolite 2-spar colortox hard vinyl type antifouling paint b-41 red  
Brolite z-spar colortox bottom paint antifouling B-40 white  
Brolite 2-spar colortox har' vinyl type antifouling paint B-40 white  
Brolite z-spar colortox bottom paint antifouling B-44 black  
Brolite 2-spar colortox hard vinyl type antifouling paint B-44 black  
Brolite Z-spar B-70 supertox red antifouling paint  
Brolite Z-spar B-71 supertox blue antifouling paint  
Brolite Z-spar supertox hard type antifouling paint B-71 blue  
Brolite Z-spar B-90 antifouling paint semi-hard type  
Brolite Z-spar the protector hard type antifouling paint B-90 red  
Brolite Z-spar B-60 racing bronze antifouling paint  
Brolite Z-spar B-60 racing bronze hard racing type antifouling paint  
Brolite Z-spar colortox bottom paint antifouling B-45 international orange  
Brolite 2-soar colortox hard vinyl type antifouling  
paint B-45 international orange  
Brolite Z-spar supertox hard type antifouling paint B-73 brown  
Brolite Z-spar the protector B-901 blue antifouling paint semi-hard type

Brolite Z-spar the protector hard type antifouling paint B-91 blue  
Brolite Z-spar supertox hard type antifouling paint B-74 black

Porter Coatings Division of Porter Paint Co  
400 South 13th Street  
Louisville, KY 40201

Chlorinated rubber antifouling paint 1195 red  
Chlorinated rubber antifouling paint 11958K black

Pro-Line Paint Manufacturing Co  
2446 Main Street  
San Diego, CA 92113

1077 Vinyl Antifouling paint  
1088 Hi-speed antifouling paint

Sears Roebuck and Co.  
Attn. L.D. Hurse  
Sears Tower Dept. 766  
Chicago, IL 60634

Sears Marine anti-fouling bottom paint gold bronze  
Sears Marine antifouling bottom paint red  
Sears Marine antifouling bottom paint copper bronze  
Sears Marine antifouling bottom paint white  
Sears Marine antifouling bottom paint green  
Sears Marine antifouling bottom paint blue

The Valspar Corporation  
Attn. B.C. Heath,  
Technical Manager  
1101 Third Street South  
Minneapolis, MN 55415

Valspar Vinyl antifouling bottom paint 3548 bright red  
Valspar vinyl antifouling bottom paint 3537 coho blue  
Valspar vinyl antifouling bottom paint 3505 white

Woolsey Marine Industries Inc.  
183 Lorraine Street  
Brooklyn, N.Y. 11231

Woolsey Lumalast antifouling finish 678 white  
Woolsey super vinelast 723 permanent red  
Woolsey lumilast antifouling finish 679 black  
Woolsey super vinelast 724 permanent blue

**ANTI-FOULING PAINTS FOR VESSEL BOTTOMS AND HULLS  
CONTAINING TBT OXIDE**

**Carboline Company  
40600 Albrae Street  
Fremont, CA 94538**

**Carboline Super Tropical anti-fouling red 1240-18  
Carboline Super Tropical anti-fouling black 1240-1**

**Devoe Marine Coatings Co.  
4000 Dupont Circle  
Louisville, KY 40207**

**Devoe Marine Super Tropical anti-fouling ship bottom paint MD-2771  
Triple "C" Cape Cod Copper Compound MD-8024  
Devoe Marine Tropical anti-fouling ship bottom paint MD-1754  
Devoe Marine Devran 216 permanent red anti-fouling paint MD-3873  
Devoe Marine Forumula 218 Devran permanent red anti-fouling paint  
MD-3888  
Devoe Marine ABC anti-fouling coating formula 8 MD-4755  
Devoe Marine ABC Anti-fouling coating formula 2 red MD 4754  
Devoe Marine ABC anti-fouling coating formula 8 black MD-5027  
Devoe Marine Devchlor Lt. red anti-fouling paint MD-5188  
Devoe Marine Devran 222 Allseas permanent red anti-fouling paint  
MD-4312  
Devoe Marine Devchlor anti-fouling paint red MD-4366  
Devoe Marine ABC Anti-fouling coating formula 2 red MD-4754  
Devoe Marine Devran 222 Allseas light blue Anti-fouling paint  
MD-5023  
Devoe Marine ABC anti-fouling coating formula 2 black MD-4883  
Devoe Marine ABC anti-fouling coating formula 2 light blue  
MD-5100**

**Dupont De Nemours, E.I. & Co. Inc.  
Agricultural Products Department  
Attn: Billie Lynn Rach  
Barley Mill Plaza  
Wilmington, DE 19898**

**Du Pont Chlorinated Rubber anti-fouling red 360-Y-782  
Du Pont Chlorinated Rubber anti-fouling red 360-78-2  
Du Pont Extended Life anti-fouling red 360-Y-785  
Du Pont Extended Life anti-fouling red 360-785**

Glidden Coatings and Resins  
Div. of SCM Corporation  
Attn: James Woebkenberg  
16651 Sprague Road  
Strongsville, OH 44136

178-R-401 red vinyl-cote no-cop anti-fouling coating  
Vinyl-Cote no-cop anti-fouling coating 7082 red (178-R-401)  
178-B-404 Black Vinyl Cote no-cop anti-fouling coating  
Vinyl-cote no-cop anti-fouling coating 7081 black (178-B-404)  
178-R-401B Red vinyl-cote no-cop anti-fouling coating  
Vinyl-cote no-cop anti-fouling coating 7083 (DGL 3 191)  
178-W-401 White vinyl-cote no-cop anti-fouling coating  
Vinyl-cote no-cop anti-fouling coating 7080 white (178-W-401)

Hempel's Marine Paints, Inc.  
Foot of Currie Ave  
Wallington, NJ 07057

Hempel's antifouling nautic 7690-5030 red  
Hempel's antifouling nautic 7690-5111 red  
Hempel's antifouling nautic 7680-1221 gray  
Hempel's antifouling nautic 7687-4222 green  
Hempel's antifouling nautic 7685-1000 white  
Hempel's antifouling nautic 7680-1999 black  
Hempel's antifouling nautic 7685-1999 black  
Hempel's antifouling nautic 7695-5030 red  
Hempel's antifouling nautic 7695-5111 red  
Hempel's antifouling nautic 7695-1999 black  
Hempel's antifouling sleek 765U Brown 6464  
Hempel's antifouling nautic 7695-6464 brown  
Hempel's antifouling nautic 7697-5030 red  
Hempel's antifouling nautic HI 7695-5030 red

International Paint Co. (California) Inc.  
220 S Linden Avenue  
South San Francisco, CA 94080

Copper-lux antifouling paint 80 red  
Latenac high builo antifouling red extra 3022/3021  
Copper-lux antifouling paint 82 blue  
International tropex antifouling paint 1600  
Interlux antifouling 62T bottom paint red  
Interlux antifouling 62T bottom paint blue  
Intersmooth self polishing copolymer antifouling blue BFA042  
Intersmooth SPC self polishing copolymer antifouling green BFA043  
Intersmooth SPC self polishing copolymer antifouling pink BFA206  
Intersmooth SPC self polishing copolymer antifouling plum BFA 204

Interspeed special copolymer antifouling brown BHA 018  
Interspeed special copolymer antifouling red BHA017

Intersmooth spc self polishing copolymer antifouling pink BFA096  
Intersmooth spc self polishing copolymer antifouling plum BFA094  
Micron 22 organo-metallic polymer anti-fouling paint 450 blue  
Micron 22 organo-metallic polymer anti-fouling paint 451 green  
Micron 22 organo-metallic polymer anti-fouling paint 452 red  
Micron 22 organo-metallic polymer anti-fouling paint 453 black  
Micron 22 organo-metallic polymer anti-fouling paint 454 white  
Micron 33 an organo-metallic polymer anti-fouling paint for  
brush or roller application 460 blue  
Micron 33 an organo-metallic polymer anti-fouling paint for  
brush or roller application 461 green  
Micron 33 an organo-metallic polymer anti-fouling paint for  
brush or roller application 462 red  
Micron 33 an organo-metallic polymer anti-fouling paint for  
brush or roller application 463 black  
Micron 33 an organo-metallic polymer anti-fouling paint for  
brush or roller application 464 white

Pettit Paint Company, Inc.  
36 Pine Street  
Rockaway, NJ 07866

Pettit marine paint anti-fouling 1970 starline bronze  
Pettit marine paint unepoxy anti-fouling 1626 red inland formula  
Pettit marine paint unepoxy anti-fouling 1326 green inland formula  
Pettit marine paint unepoxy anti-fouling 1226 blue inland formula  
Pettit marine paint unepoxy anti-fouling 1920 bronze tropic formula  
Pettit marine paint unepoxy anti-fouling 1926 bronze inland formula  
Pettit marine paint unepoxy anti-fouling 1924 bronze pacific formula  
Pettit marine paint unepoxy anti-fouling 1324 green pacific formula  
Pettit marine paint unepoxy anti-fouling 1320 green tropic formula  
Pettit marine paint unepoxy anti-fouling 1224 blue pacific formula  
Pettit marine paint unepoxy anti-fouling 1624 red pacific formula  
Pettit marine paint unepoxy anti-fouling 1220 blue tropic formula  
Pettit marine paint unepoxy anti-fouling 1620 red tropic formula  
Pettit marine paint unepoxy anti-fouling 1126 white inland formula  
Pettit marine paint anti-fouling 1130 alumacide white  
Pettit marine paint anti-fouling 1805 alumacide black  
Pettit marine paint anti-fouling 1205 alumacide blue  
Pettit marine paint anti-fouling 1649 alumacide red  
Pettit marine paint unepoxy 1124 anti-fouling white pacific

Pro-Line Paint Manufacturing Company  
2646 Main Street  
San Diego, CA 92113

1077 vinyl anti-fouling paint  
1025-03-E red seven seas copperbottom anti-fouling paint

U.S. Paint Division/Grow Group, Inc.  
831 South 21st Street  
St. Louis, MO 63103

Awlgrip awlstar anti-fouling blue label 73134 red  
Awlgrip awlstar anti-fouling blue label 73132 black  
Awlgrip awlstar anti-fouling blue label 73133 lt. blue

Woolsey Marine Industries, Inc.  
183 Lorraine Street  
Brooklyn, NY 11231

Woolsey neptune anti-fouling 710 royal red  
Woolsey self-spraying anti-fouling for outboard lower units  
321 white  
Woolsey maxitox fiber-glass anti-fouling 775 blue  
Woolsey maxitox fiber-glass anti-fouling 774 green  
Woolsey maxitox fiber-glass anti-fouling 773 red  
Woolsey blue streak vinelast 200 sr blue

ALL TBT RESINATE

Woolsey Marine Industries Inc.  
183 Lorraine Street  
Brooklyn, NY 11231

Woolsey antifouling hard racing finish T 758 blue  
Woolsey antifouling hard racing finish T 754 white  
Woolsey antifouling hard racing finish T 755 red  
Woolsey antifouling hard racing finish T 759 green  
Woolsey antifoulin hard racing finish T 756 black

ANTI-FOULING PAINTS FOR VESSEL BOTTOMS AND HULLS  
CONTAINING TBT METHACRYLATE

Carboline Company  
40600 Albrae Street  
Fremont, CA 94538

Carboline Super Tropical anti-fouling red 1240-31  
Carboline Super Tropical anti-fouling black 1240-30

Hempel's Marine Paints, Inc.  
Foot of Currie Ave  
Wallington, NJ 07057

Hempel's antifouling nautic 7690-5030 red  
Hempel's antifouling nautic 7690-5111 red  
Hempel's antifouling nautic 7680-1221 gray  
Hempel's antifouling nautic 7687-4222 green  
Hempel's antifouling nautic 7685-1000 white  
Hempel's antifouling nautic 7680-1999 black  
Hempel's antifouling nautic 7685-1999 black  
Hempel's antifouling nautic 7695-5030 red  
Hempel's antifouling nautic 7695-5111 red  
Hempel's antifouling nautic 7695-1999 black  
Hempel's antifouling sleek 7650 Brown 6464  
Hempel's antifouling nautic 7695-6464 Brown  
Hempel's antifouling nautic 7697-5030 Red  
Hempel's antifouling nautic Hi 7695-5030 Red

Pettit Paint Company, Inc.  
36 Pine Street  
Rockaway, NJ 07866

Pettit marine paint offshore antifouling Red 1680  
Pettit marine paint offshore antifouling Black 1880  
Pettit marine paint offshore antifouling Brown 1580  
Pettit marine paint offshore antifouling Blue 1280  
Pettit marine paint offshore antifouling Green 1380