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FUNGAL-RESISTANT ORGANOTIN RESINS

By

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June 1976

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A series of alkyd resins were prepared that had tin chemically bonded to them. These resins had more resistance to fungal growth than did the original alkyd resins from which they were prepared. This resistance does not appear to be lost as readily by leaching with rain as that of a resin to which bis (tri-n-butyltin) oxide is added as a preservative.

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A series of alkyd resins were prepared that had tin chemically bonded to them. These resins had more resistance to fungal growth than did the original alkyd resins from which they were prepared. This resistance does not appear to be lost as readily by leaching with rain as that of a resin to which bis (tri-n-butyltin) oxide is added as a preservative.

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INTRODUCTION

Fungal defacement and deterioration of organic coatings occur at Naval installations around the world. It is especially severe at tropical and sub-tropical locations. Economic losses caused by microbiological attack on paints and paint films in the United States have been estimated to exceed one million dollars annually [1]. This does not include damage to substrate, such as communication equipment, utilities, etc., which would greatly increase this figure. Thus, the total annual damage may exceed several million dollars annually.

In order to control fungal growth on exterior paints, additive preservatives containing mercury have in the past been widely used. Their use has now been restricted because of safety and ecological considerations. Thus, the Naval Facilities Engineering Command requested the Civil Engineering Laboratory to investigate the use of organotin resins as an alternative method of controlling fungal growth. Such a method might be much safer and could possibly provide longer protection than those using additive preservatives.

BACKGROUND

Microbiological deterioration of paint has been classified into two basic categories [2]. The first category is spoilage of liquid paint (usually emulsion paint) generally by bacterial attack [3], resulting in putrefaction and general breakdown of the paint. The second consists of microbiological attack on cured paint films. The present investigation is restricted to the latter category.

Fungal growth on painted surfaces is highly dependent upon the nature of the substrate [4]. This is believed to be related more to the effect of the substrate on the environment (i.e., pH and retention of moisture) than providing nutrient for growth. Thus, fungal growth is generally greatest on painted wood, which has the high moisture retention and no adverse effect on pH of surface moisture, and is the least on painted metal and concrete. The infrequent occurrence of fungal growth on painted concrete is related to the alkalinity the concrete imparts [4], because fungal growth is greatly restricted where the pH of the environment exceeds 8.5.

The nature of paint is also an important factor affecting fungal growth. The solvent evaporates on curing, and so is not a factor on dried films. The pigment may inhibit growth by being toxic or by producing an alkaline environment, and the organic binder may serve as a source of nutrient. There have been many reports [1] of fungal metabolism of paint binders containing drying oils.

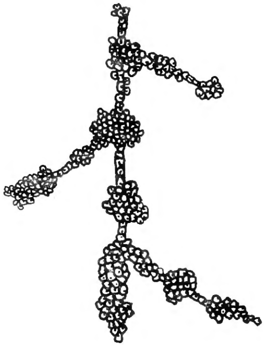

Figure 1.
Hyphae and groups of conidia (spores) on young colony of *Aureobasidium pullulans*.

Many different species of fungi have been associated with defacement of organic coatings. However, one species, *Aureobasidium pullulans* (formerly reported as *Pullaria pullulans*) has been reported [1] to predominate. This species (Figure 1) is, thus, the one most frequently used in laboratory studies.

SYNTHESIS OF ORGANOTIN PRODUCTS

The synthesis of the organotin products was a modification of the method used by Dyckman and Montemarano [5,6] in preparing tin-containing acrylic resins. In this modification bis (tri-n-butyltin) oxide, henceforth called TBTO,[a] was reacted with the carboxyl groups in free acids or in drying oil alkyd resins.

In order to study the basic reaction, experiments were first conducted with phthalic acids. In separate experiments 0.1 mole of ortho-, iso-, and terephthalic acid were dissolved (as far as possible) in hot, dry benzene (200 ml) in a 1,000-ml, 3-necked flask, and 0.1 mole of TBTO dissolved in dry benzene was then added through a separatory funnel. An immediate reaction was noted by rapid boiling of the benzene, increased solution of the phthalic acid, and collection of water distilled azeotropically from the reaction flask. The 0.1 mole of water removed by such distillation was collected in a calibrated distillation receiver. Removal of benzene by distillation allowed crystallization of the iso- and tere- reaction product. The melting point of the tere- product was near that ($78^{\circ}C$) reported by Dunn and Norris [7], and the iso- product was $50^{\circ}C$ after recrystallization from benzene. These authors report that the ortho- product was a liquid but did not report preparation of the iso- product.

Five alkyd resins with varying acid numbers and the free fatty acids from linseed oil were reacted separately with TBTO using the above procedure to yield the products listed in Table 1. The acid numbers were first determined by Federal Test Method 5072 [8] (ASTM D1639-70 [9]), and the total solids were determined by Federal Test Method 4041.1 [10] in order to determine the calculated amount of TBTO for complete reaction. In all cases, the calculated amount of water formed in the reaction was collected by azeotropic distillation. The total solids content and the percent tin (determined by atomic absorption spectrophotometry) of each product were consistent with the calculated tin values in Table 1. Also, analyses by M and T Chemicals, Inc. of reaction

[a] TBTO is the registered name of M and T Chemicals, Inc., for this product.

products indicated that no unreacted TBTO was present. A film of each organotin resin was cast on an Irtran 4 plate, and the spectrum of each was recorded on a Beckman IR-7 Spectrophotometer. Each spectrum was quite similar to that of the unreacted resin from which it came except that a new absorption peak occurred for each near 1650 cm^{-1}. Cummins and Dunn [11] report that liquid organotin carboxylates have an infrared absorption peak near 1640 cm^{-1}. A comparison of spectra of the two original alkyd resins with those of the phthalic acids used, as well as those published for phthalic acids [12], was used to identify each alkyd resin as to the type of phthalic acid present.

Table 1. Organotin Products Synthesized

No.	Type of Product Reacted	Original Acid Number	Percent Tin in Product
1	ortho-phthalic alkyd	54.7	9.2
2	isophthalic alkyd	25.7	4.8
3	ortho-phthalic alkyd	6.6	1.4
4	isophthalic alkyd	5.7	1.2
5	fish oil isophthalic alkyd	4.8	0.9
6	linseed oil acids	198.0	21.0

LABORATORY TESTS ON RESISTANCE TO FUNGAL GROWTH

It has long been recognized [13] that limitations exist on laboratory testing of paint films for resistance to fungal growth, but at least two standard tests [14,15] are currently finding use. Their findings cannot be translated into effectiveness in the field, but they can still provide valuable basic information on resistance of materials to fungal growth.

The laboratory test used in this study was a modification of Federal Test Method 6271.1 [14]. All three species of fungi listed in the Federal Test Method, *Aureobasidium pullulans, aspergillas niger,* and *aspergillus oryzae,* were used. The resins tested were both the original and the modified resins of Table 1. They were run with metal driers alone and with metal driers plus pigmentation.

The paint tested was applied to a sheet of mylar (polyethylene terephthalate) plastic at a wet film thickness of 0.003 inch (0.008 cm). After the paint had dried hard, the sheet was cut into several 4 cm squares. These squares were then placed on sterile culture plates containing a mildew test medium (Table 2). Inoculation was achieved by aseptic addition of one ml of a fungal spore suspension onto the paint film and the agar surface. Incubation was carried out in an environmental chamber set at 30 to 32°C with a relative humidity of approximately 85%. The culture plates were incubated upside down for 14 days before observing the paint films. All tests were run at least in duplicate, and the organotin resins were compared with the original resins.

Table 2. Composition of Culture Media

Chemical Compound	Amount (g)
Sodium nitrate	3.0
Dipotassium hydrogen phosphate	1.0
Magnesium sulfate	0.25
Potassium chloride	0.25
Sucrose	30.0
Agar	10.0
Distilled water (to make 1,000 ml)	-

Gross examination of the paint film revealed the level of fungal growth. Zones of growth inhibition were also examined, measured, and recorded. The plates were then examined under a light microscope at 40X magnification. The photographs (Figures 1 to 3) in ASTM D3274-73T [16] were used to distinguish spores (spherical reproductive bodies, gray to black, occurring singly or in clusters) from dirt particles and to determine the amount of growth of hyphae (thread or filamentous structures, gray to black, making up the mycelium or vegetative form of fungi). From these examinations, one of the following ratings depicted in Figure 2 was assigned to each test plate:

5 - No growth on resin film; large zone of inhibition on agar.

4 - No growth on resin film; growth on agar up to edge of film.

3 - Sparse mycelial growth on resin film; no production of new spores.

2 - Moderate mycelial growth on resin film; slight production of new spores.

1 - Heavy mycelial growth on resin film; heavy production of new spores.

0 - Little distinction between growths on resin film and on agar.

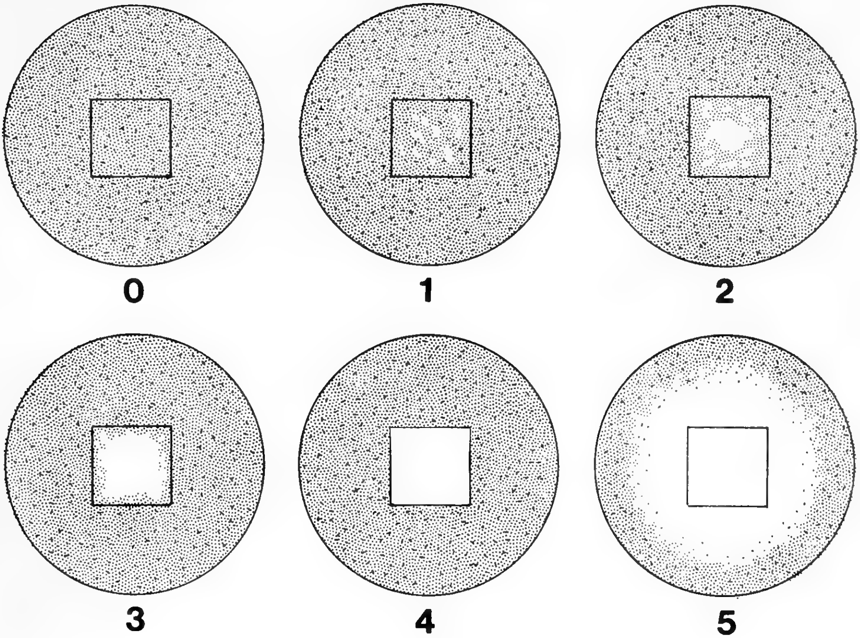

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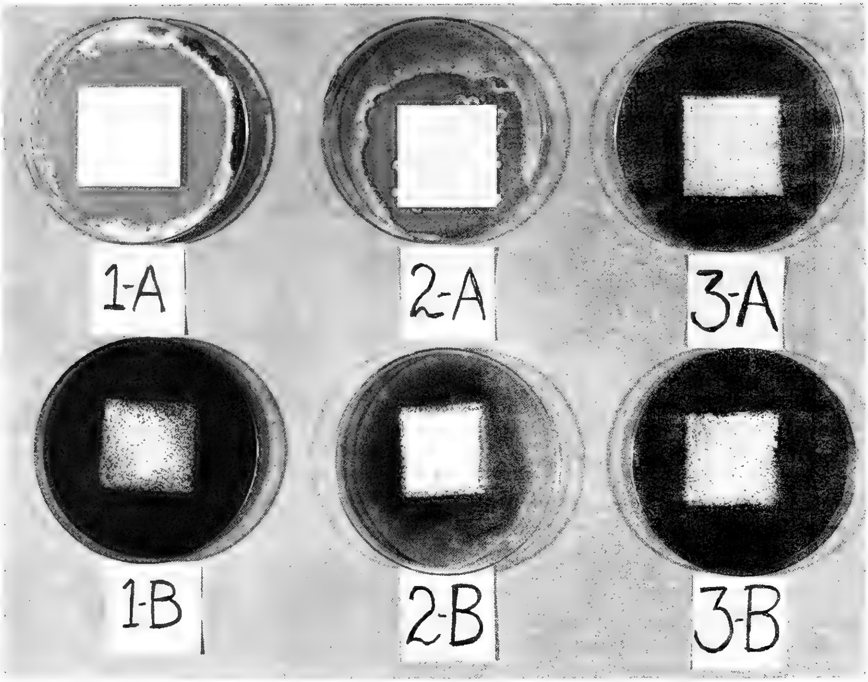
Figure 2. Representations of growth ratings.



1A – *A. pullulans* on organotin Resin 1.
1B – *A. pullulans* on original Resin 1.
2A – *A. oryzae* on organotin Resin 2.
2B – *A. oryzae* on original Resin 2.
3A – *A. niger* on organotin Resin 3.
3B – *A. niger* on original Resin 3.

Figure 3. Test specimens after 14 days of incubation.

Tables 3 and 4 list results of growth resistance tests on unpigmented and pigmented resins, respectively. Table 5 presents the formulation of the pigmented resins. In all cases, the average resistance to fungal growth was greater with the reacted resin containing tin than the corresponding original resin (see Figure 3). Also, rating totals generally increased with increasing acid values for the four vegetable oil alkyds (Resins 1 through 4), both for the original and the organotin resins. This was also true for the fish oil alkyd (Resin 5) in the test with pigmented resins. This may be related to the fact that the resins with higher acid numbers had lower oil contents (shorter oil lengths); thus, their films had less nutrient for the fungi and were harder. Softer films are reported [1] to be more susceptible to fungal attack.

Table 3. Growth Resistance of Unpigmented Resins

Resin Tested	Acid No.	*A. pullulans*	*A. oryzae*	*A. niger*	Totals
1 original	54.7	2; 1	2; 3	2; 2	12
1 organotin	–	5; 5	5; 5	5; 5	30
2 original	25.7	1; 1	1; 2	1; 3	9
2 organotin	–	5; 5	5; 5	5; 4	29
3 original	6.6	0; 1	0; 1	0; 0	2
3 organotin	–	2; 2	2; 3	2; 2	13
4 original	5.7	0; 1	0; 0	0; 0	1
4 organotin	–	1; 2	2; 4	2; 2	13
5 original	4.8	0; 1	2; 2	1; 2	8
5 organotin	–	3; 1	5; 3	5; 4	21
Totals		39	52	47	138

It was expected that growth resistance ratings would be much greater overall for the pigmented than the unpigmented resins because of the pigmentation dilution of the nutrient content of all the resins and the tin content of the organotin resins. However, this did not occur in all cases. *A. pullulans* grew most abundantly and *A. oryzae* least abundantly under the test conditions. *A. oryzae* enzymes degraded the paint films even when the growth on the film was sparse. This suggests that enzymes diffused from the agar where growth was heavy onto the paint film. Large zones of growth inhibition on the agar suggest leaching of toxic tin compounds from the paint film.

In another test, blends were made of each of two organotin resins (Resins 1 and 2) with their original resins, and the resistance to growth of these blends was determined. It can be seen from Table 6 that decreasing the tin content generally decreases the resistance to fungal growth. In a final variation, blends of the organotin linseed oil ester in Table 1 and two of the organotin resins (Resins 1 and 3) were tested for resistance to growth of *A. pullulans*. It can be seen from Table 7 that the addition of 10% organotin linseed oil ester to organotin Resin 1 and 20% to organotin Resin 3 completely inhibited growth on the paint film and produced a large zone of inhibition on the agar.

Table 4. Growth Resistance of Pigmented Resins

Resin Tested	Acid No.	Growth Resistance Ratings for –			
		A. pullulans	*A. oryzae*	*A. niger*	Totals
1 original	54.7	1; 3; 3	3; 4; 3	3; 2; 2	24
1 organotin	–	5; 5; 5	5; 5; 5	5; 5; 5	45
2 original	25.7	1; 1; 3	2; 1; 2	1; 2; 3	16
2 organotin	–	5; 3; 3	5; 5; 4	3; 5; 4	37
3 original	6.6	1; 1; 0	2; 1; 1	2; 2; 3	13
3 organotin	–	3; 2; 2	4; 2; 3	4; 3; 3	26
4 original	5.7	0; 0; 1	2; 2; 2	2; 2; 1	12
4 organotin	–	3; 1; 1	4; 3; 4	2; 3; 3	24
5 original	4.8	0; 0; 1	0; 1; 1	0; 1; 2	6
5 organotin	–	2; 1; 2	2; 3; 3	2; 3; 3	21
Totals		59	84	81	224

Table 5. Formulation of Pigmented Resins

Component	Percent by Weight
Resin	28
Rutile	28
Powdered silica	18
Solvent	26

Table 6. Growth Resistance of Blends of Unpigmented Organotin Resins With the Corresponding Original Resins

Resin Number	Percent by Weight		Growth Resistance Ratings of –		
	Original	Organotin	*A. pullulans*	*A. Oryzae*	*A. niger*
1	100	0	2; 2	3; 2	3; 2
	25	75	2; 4	3; 4	3; 4
	17	83	4; 4	4; 5	3; 5
	13	87	5; 4	5; 5	5; 5
	0	100	5; 4	5; 4	5; 5
2	100	0	1; 3	1; 2	2; 3
	25	75	3; 4	4; 4	2; 4
	17	83	3; 3	3; 4	3; 3
	13	87	3; 4	4; 5	3; 3
	0	100	4; 3	4; 4	3; 4

Table 7. Growth Resistance of Blends of Pigmented Organotin Resins With Organotin Linseed Oil Ester

Resin Number	Percent Organotin Linseed Oil Ester	Growth Resistance Rating of *A. pullulans*
1	10	5; 5
	20	5; 5
	30	5; 5
3	10	3; 4
	20	5; 5
	30	5; 5

LABORATORY LEACHING EXPERIMENT

An experiment was conducted to determine the effect of leaching paint films with rainwater on the resistance of resins to fungal growth. Four resins were used in this experiment. One was the original Resin 1 with 1% TBTO added to it, and the others were organotin Resins 1, 2, and 3. They were pigmented as indicated in Table 5. The resin selections were made to compare the lasting effect of TBTO added to a resin that has a slight natural resistance to growth to organotin resins of relatively high, medium, and low tin contents. The pigmented resins were cast at a dry film thickness of 0.003 inch (0.008 cm) onto sheets of mylar plastic. After complete curing, the resin films were subjected to continuous leaching with water in a wind-driven rain machine of the type described in TT-C-555 [17]. Samples were taken of each film after 0, 24, 48, and 72 hours of leaching and tested for resistance to growth of *A. pullulans* by the method described in the previous section.

The results of the leaching experiment are summarized in Table 8. It can be seen from this table that, after 72 hours, the average rating of original Resin 1 with the added TBTO dropped to that of the original resin alone (see Table 4), while organotin Resins 1 and 2 (which contained 9.2 and 4.8% tin,* respectively) had no loss and Resin 3 (which contained only 1.4% tin* and, thus, was much less resistant to growth) showed only a very slight loss in growth resistance.

Table 8. Resistance of Leached Resins[a] to Growth of *A. pullulans*

Pigmented Resin Tested	Leaching Time (hr)	Growth Resistance Rating
Resin 1, Original plus 1% TBTO	0	3;[b] 5; 3[b]
	24	5; 3;[b] 3[b]
	48	3;[b] 3;[b] 3[b]
	72	2; 2; 3[b]
Resin 1, Organotin	0	5; 5; 5
	24	5; 5; 5
	48	5; 5; 5
	72	5; 5; 5
Resin 2, Organotin	0	5; 5; 3[b]
	24	5; 5; 5
	48	5; 5; 3[b]
	72	5; 5; 3[b]
Resin 3, Organotin	0	3;[b] 3;[b] 5
	24	3;[b] 3;[b] 4[b]
	48	3;[b] 3;[b] 3[b]
	72	3;[b] 3;[b] 3[b]

[a] Pigmented as shown in Table 5.
[b] Zone of inhibition around part of paint resin.

* In the unpigmented resin.

CONCLUSIONS

1. The organotin resins showed more resistance to fungal growth than the unreacted resins.

2. Resistance to fungal growth generally increased with increasing tin content of the resin.

3. Of the three organisms tested, *A. pullulans* grew the most abundantly and *A. oryzae* the least abundantly.

4. When TBTO was simply added to a resin at a concentration generally used in a paint, the resistance to fungal growth was lost more readily by leaching than when the TBTO was reacted with the resin.

FUTURE WORK

Paints have been prepared from alkyd organotin resins in 5-gallon batches. Wooden specimens painted with them are currently undergoing tropical exposure to determine how they perform in the field.

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