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FUNGICIDAL AND ANTIFOULING PROPERTIES OF HALOMERCURYACETALDEHYDES

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Abstract. A study has been made of the fungicidal and antifouling properties of halomercuryacetaldehydes. The fungicidal action was tested against the organism *Aspergillus niger* (vanteigh) and the results were compared with phenylmercury halides and acetates. Iodomercuryacetaldehyde was found to be the most effective, while the bromo and chloromercuryacetaldehydes were rather weaker fungicides. Antifouling tests were carried out by impregnating the candidate antifoulants on porous panels and immersing them under the sea. The preliminary investigations revealed that these compounds might be antifoulants.

Growth of organisms on surfaces causes much damage to the paint films both in the air and under the sea.

In the air, fungi growing in damp places may cause extensive damage of painted surfaces in tropical, subtropical and even in temperate climates. In 1952 it was reported[1] that 68% of painted surfaces were discoloured in U.S.A. by mildew infections, which occur in an atmosphere of continuously high humidity. The critical humidity being about 75% relative humidity.[2] Mildew occur frequently in damp places such as lavatories, basements, baths, swimming halls, kitchens, fermentation cellars, dairies and bakeries. The moulds and fungi establish themselves on the layers of dust which collect on the walls and ceilings and once a paint film is attacked it becomes discoloured and porous and is finally destroyed.

Under the sea, the growth of animals and plants on the surfaces of submerged objects rapidly causes severe corrosion and fouling of ships/hulls resulting in high fuel consumption, reduction of speed and which make the costly removal of the offending animals and plants essential.

The growth of the organism could be controlled by incorporating certain compounds of metals such as copper, silver and mercury into the paint films, which slowly leach out and act as poison. Horsefall[3] has reviewed the use of chemicals to control the fungicidal growth. Among the most studied metals are copper, silver and mercury. The rate of uptake of these metals are of the order of silver > mercury > copper.[4] However, silver being an expensive metal the most modern fungicides of today are either of copper or mercury. It has been found that inorganic mercurials are less effective than organic.[4] The effective organic mercurials are taken up by the organism and penetrate cells more readily.[5,6] Among mercury fungicides phenylmercury halides and acetates have given very promising results[7] to control the growth of fungi on painted surfaces and are very good antifoulants used in the paints to control the marine fouling. But the cost of these materials have limited their use.

In the present studies halomercuryacetaldehydes have been prepared and their effectiveness as fungicides and antifoulants have been compared with phenylmercury halides and acetates.

Experimental

Preparation of Compounds. The halomercuryacetaldehydes were prepared by the method of Nesmeyanov and Lutsenko.[8] Mercuric acetate (320 g) was dissolved in 1.5 litres distilled water and filtered. To the filtrate was added vinyl acetate (80 g). They were shaken and filtered to remove complex formed. To this filtrate KCl (75 g), KBr, (119 g), and KI (116 g,) were added separately to obtain chloro, bromo- and iodomercuryacetaldehyde respectively. The yields were 100% w.r. to mercury. The physical properties of the compounds are given below.

Compounds	Water solubility at room temp(%)	M.P.(°C)
$ClHgCH_2CHO$	0.004	132
$BrHgCH_2CHO$	0.003	118
$IHgCH_2CHO$	0.0035	126

Fungitoxicity experiments were carried out on the organism *Aspergillus niger* (vanteigh).[9,10] The tests were carried out by two different methods: (A) agar diffusion method against *Aspergillus niger* and (B) fungitoxicity on painted surfaces.

Method A

Agar Diffusion Method Against Aspergillus niger (*vanteigh*). Phenylmercury acetates and phenylmercury chlorides were compared with chloro-bromo and iodomercuryacetaldehydes at 0.01, 0.02, 0.03, 0.04, 0.05% concentrations.[11] The compounds were dispersed in Sabouraud's dextrose agar, spore suspension was prepared in sterile distilled water and 0.1 ml of this suspension was inoculated in sterilised 9 cm dia dishes, then Sabouraud's agar was poured in these dishes. The observations were noted till the growth of control plates reached a maximum of 9 cm. The plates were kept at room temperature. The percentage inhibition of the growth of *Aspergillus niger* are given in Table 1.

Method B

Fungicidal Action of Painted Surfaces. Filter papers of 2.5 cm dia were coated with paint containing the three halomercuryacetaldehyde, phenylmercury acetate and phenylmercury iodide in the fixed concentration

TABLE 1. PERCENTAGE INHIBITION OF *Aspergillus niger*.

Compounds	Toxicant (Concn %)					
	Nil	0·01	0·02	0·03	0·04	0·05
$ClHgCH_2CHO$	—	9	61	61	86	100
$BrHgCH_2CHO$	—	9	16	28	100	100
$IHgCH_2CHO$	—	100	100	100	100	100
PhHgCl	—	80	100	100	100	100
PhHg acetate	—	85	100	100	100	100
Inoculated control	0	—	—	—	—	—
Uninoculated control	100	—	—	—	—	—

TABLE 2. PERCENTAGE INHIBITION OF *Aspergillus niger* ON PAINTED SURFACES.

Compounds	Inhibition (%)			
	After 48 hr	After 1 week	After 2 week	After 4 week
$ClHgCH_2CHO$	100	75	40	35
$BrHgCH_2CHO$	100	70	35	30
$IHgCH_2CHO$	100	100	100	100
PhHg acetate	100	100	100	90
PhHg iodide	100	100	100	100
Control	20	0	0	0
Check	0	0	0	0

TABLE 3. ATTACK OF THE SEA ANIMALS ON PAINTS AFTER 2 MONTHS.

Panels treated with	Barnacle	Algae	Hyroids	Corals	Arthro-podes
$ClHgCH_2CHO$	—	++	—	—	—
$BrHgCH_2CHO$	—	—	++	++	++
$IHgCH_2CHO$	—	++	—	++	—
PhHg acetate	—	—	++	++	+++
PhHg chloride	—	—	++	++	—

of 0.5%. These filter papers were placed in 9 cm dia petri dishes alongwith check (painted filter paper without any toxic material) and control specimen (filter paper only). The sterilised petri dishes were inoculated with 0.1 ml spore suspension and then poured with the medium. The poured plates were kept at 10°C for 30 min to solidify, then painted filter papers were placed in the centre of the dish. Iodomercuryacetaldehyde, phenylmercury iodide and acetate prevented the growth of *Aspergillus niger* (vanteigh) for 4 weeks, the other substances were less effective. The percentage inhibition of the *Aspergillus niger* (vanteigh) on painted surfaces are given in Table 2.

Antifouling Properties. The antifouling properties were tested by the method of Freiberger and Cologer.[12] The antifoulant chemicals alongwith phenylmercury acetate and phenylmercury chloride were impregnated in the porous concrete panels by dispersing or dissolving in acetone. The panels were dried under vacuum for 2 hr, then immersed under the sea by the pontoon of the Pakistan Naval Dockyard Laboratory. Every week the panels were examined for development of fouling. Table 3 shows the growth of animals and plants on the panels after 2 months. No growth was observed for any impregnated panel in 1 month, but after 2 months similar growth was found in all the panels. An untreated panel exhibited growth of fouling animals and plants after 1 week only.

Discussion

The antifouling and fungicidal properties of halomercuryacetaldehydes have been compared with phenylmercury iodide, acetates and chlorides. Fungitoxicity experiments (Table 1) have shown that iodomercuryacetaldehyde is an effective fungicide at 0.01% concentration compared to the same concentration of phenylmercury chloride and acetate. Similar results were obtained when the fungitoxicity experiments were carried out on painted surfaces (Table 2). Iodomercuryacetaldehyde inhibited the growth of *Aspergillus niger* (vanteigh) for 4 weeks. The chloro- and bromomercuryacetaldehydes are rather weak fungicides and require higher concentrations for the inhibition of the growth of the organism. Their effectiveness could be of the order of Iodo > bromo > chloro- mercuryacetaldehydes.

Preliminary investigations about the antifouling properties of halomercuryacetaldehydes, as compared to phenylmercury iodide and acetate, have shown that the pattern of inhibition (Table 3) of growth of animals and plants is similar, but a detailed investigation by formulating them into paints have to be made before any positive conclusions are drawn. One of the advantages of the compounds understudy is that they will be much cheaper and very easy to manufacture.

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