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HALOMERCURY ACETALDEHYDE AS ANTI-FUNGAL AGENT FOR POLY (VINYL ACETATE) EMULSIONS

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Organomercury compounds prepared from vinyl acetate monomer itself i.e. chloro, bromo and iodo mercury acetaldehydes were found most suitable as antifungal agents for poly (vinyl acetate) emulsions containing more than 50 % solids.

The antifungal tests were carried out on common out door and indoor fungi such as; *Aspergillus niger, Aspergillus flavus* and *Pencillium* spp. The results were compared with the known standard compounds currently in use such as pentachlorophenol and phenyl mercury acetate. Their activities can be rated as iodo > bromo > chloro mercury acetaldehyde.

Key words: Fungicide, PVA emulsion, Halomercury acetaldehyde.

INTRODUCTION

The principal constituent of plastic emulsion paint is poly (vinyl acetate) emulsion which is blended with the pigment paste in any standard mixer to form an even composition. These water based coatings have become very popular in the recent past for both the exterior and interior finishes.

Though these emulsions are sterilised during manufacture but the ingredients such as natural and synthetic colloids which include starches and cellulose derivatives are prone to be attached by fungi. The main point of attack of mould is on the surface of the paint specially when it is exposed to humid air. These moulds are often *Penicillium* sp. Moulds tend to attack readily in damp and warm places. They hardly grow on dry films free from moisture. Kitchens and food factories usually provide suitable atmosphere for mould's growth. The moulds which attack indoor are usually *Aspergillus niger,* and *Aspergillus flavus.*

In order to inhibit micro biological growth, it is necessary to add a suitable agent to control microbial growth as a protection against both can spoilage and attack on the paint film under suitable conditions.

It is evident that the amount of fungicide which will inhibit the growth of the unwanted organism should be kept to a minimum to avoid affecting the properties of the paint adversely.

Scource of fungicides have been developed and are available in various trade names for use in plastic emulsion paints. Pentachlorophenol and its sodium salts, mercurials such as phenyl mercury acetate, organo-tin compounds, zinc dimethyl di-thio carbamate, tetramethyl thiurium disulfide and even zinc oxide have been used as fungicides. There have been many problems reported in the literature [1], such as tetra ethyl thi-urium disulfide inhibits the drying of the paint films while at least 20 % of the pigment weight of zinc oxide is required to be effective as fungicide.

In this paper organo mercuric compounds prepared from vinyl acetate monomer itself, have been described as an effective fungicide for poly (vinyl acetate) emulsions as compared with commercial compounds.

MATERIAL AND METHODS

Preparation of halomercury acetaldehydes. The halomercury acetaldehyde (Cl $HgCH_2$ CHO, BrHg CH_2 CHO I $HgCH_2$ CHO) were prepared in the laboratory by Nesmeyanov and lustenko's [2,3] method. Mercuric acetate was dissolved in distilled water uniformly, in molar ratios, and filtered. Filtrate was then treated with one mole of vinyl acetate. They were throughly shaken and filtered to remove any complex formed. KCl, KBr and KI were added to this filtrate separately in molar ratios to obtain chloro, bromo and iodo mercury acetaldehyde respectively. The yields obtained were 100 % with respect of mercury. The physical properties of the mentioned compounds are as under:

Table 1.

	Halomercury acetaldehydes	Water Solubility at room temp. (%)	M.P °C
1.	Chloromercury acetaldehyde	0.003	132
2.	Bromo mercury acetaldehyde	0.0035	118
3.	Iodo mercury acetaldehyde	0.004	126

Preparation of poly (vinyl acetate) emulsion. The standard procedure was adopted for the preparation of poly (vinyl acetate) emulsions having 54 % solids. Hydroxyethyl cellulose (Natrosol – Hercules Chemical Co. USA) and fully saponified poly (vinyl alcohol) G 117 Kurharay Chemicals Osaka, Japan was used as protective colliod. Ammonium persulphate as initiator. The monomer vinyl acetate was added slowly. The reaction was complete after about 5 hrs. The halomercury acetaldehydes, pentachloropherol, and phenyl mercury acetate were added in the end in the given quantities.

Fungicidal tests

Isolation of fungi. The test fungi – *Aspergillus niger, Aspergillus flavus* and *penicillium* spp. were isolated from air and *citrus* fruits in petri dishes containing sabourands dextrose agar medium. The cultures were maintained in this medium throughout these fungicidal tests.

The method. The diffusion plate method has been used to test chemicals against fungi. Spore suspensions were made from actively growing cultures of the test fungi in sabourand glucose broth. (Liquid medium), After shaking well, 0.2 ml from this broth was transferred to sterile petridishes-plates sabourand's glucose agar when cooled down to temperature around 35°-40° was poured (about 25 ml) into it and the petri-dishes were rotated slightly to spread evenly in the medium. After solidification a well was made through borer (6 mm in diameter) in the center of the dish. 0.5 g of poly (vinyl acetate) emulsion was placed into the well. The petri dishes were incubated at 28-30° for 2-3 days. Control plates without the test compound were also placed.

The zones of inhibition were observed after 3,5,7 and 15 days. There were very slight differences in zone of inhibition after 7 days of incubation.

RESULTS AND DISCUSSIONS

The results of the action of halomercury acetaldehydes against the common indoor and outdoor fungi are given in Tables 2,3 and 4. The sparingly water soluble halomercury-acetaldehydes were added to the poly (vinyl acetate) emulsions during polymerisation. A fixed quantity of 0.1 g/100 PVA emulsion was used as fungidies so that the results could be compared with other known fungicides. The results of the action of Cl, Br, Iodo mercury acetate dehydes were compared with phenyl mercury acetate and commonly used Commercial fungicide pentachloropherol (commercial names, margal, afrotin, dowcide etc). The test fungi were *Aspergillus niger, Aspergillus flavus* and *Penicillium* spp.

Table 2. Halomercury acetaldehyde as antifungal agents for poly vinyl acetate (PVA) emulsion on *Aspergillus niger.*

S. No.	Active ingradient in PVA emulsion	Inhibition zone (cm) at different interval of time			
		3 days	5 days	7 days	15 days
PV_{12}	Nil	None	None	None	None
PV_{14}	Cl $HgCH_2$ CHO	2.1	2.1	2.0	2.0
PV_{15}	Br $HgCH_2$ CHO	1.8	1.8	1.6	1.6
PV_{16}	I $HgCH_2$ CHO	2.0	2.0	2.0	1.9
PV_{17}	Margal	1.0	1.0	1.0	1.0
PV_{28}	Phenyl mercury acetate	2.5	2.5	2.5	2.4
PV_{30}	Phenyl mercury acetate	2.1	2.1	2.0	2.0

Table 3. Halomercury acetaldehyde as antifungal agent for poly acetate (PVA) emulsion on *Aspergillus flavus.*

S. No	Active ingradient in PVA emulsion	Inhibition zone (cm) at different interval of time			
		3 days	5 days	7 days	15 days
PV_{12}	Nil	None	None	None	None
PV_{14}	ClHg CH_2 CHO	2.5	2.5	2.3	2.1
PV_{15}	Br $HgCH_2$ CHO	2.0	2.0	2.0	1.9
PV_{16}	I $HgCH_2$ CHO	2.5	2.5	2.3	2.3
PV_{17}	Margal	1.6	1.6	1.5	1.5
PV_{28}	Phenyl mercury acetate	2.9	2.9	2.8	2.8
PV_{30}	Phenyl mercury acetate	2.5	2.4	2.3	2.3

Table 4. Halomercury acetaldehyde as antifungal agent for poly vinyl acetate (PVA) emulsion on *Pencillium* sp.

S. No.	Active ingradient in PVA emulsion	Inhibition zone (cm) at different interval of time			
		3 days	5 days	7 days	15 days
PV_{12}	Nil	None	None	None	None
PV_{14}	Cl $HgCH_2$ CHO	2.0	1.8	1.6	1.5
PV_{15}	Br $HgCH_2$ CHO	1.9	None	None	None
PV_{16}	I $HgCH_2$ CHO	2.2	2.0	2.0	2.0
PV_{17}	Margal	1.1	1.0	0.5	None
PV_{28}	Phenyl mercury acetate	3.5	3.3	3.2	3.2

The mode of action of halomercury acetaldehydes against the test fungi is quite similar to margal and phenyl mercury acetate. The results of % inhibition v/s time (days) have been plotted and is given in Fig. 1,2 and 3. These

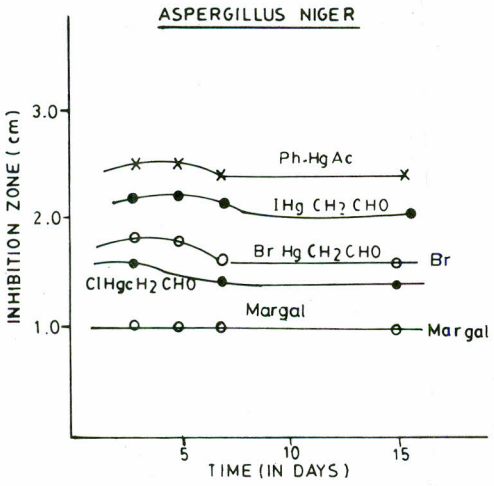


Fig. 1.

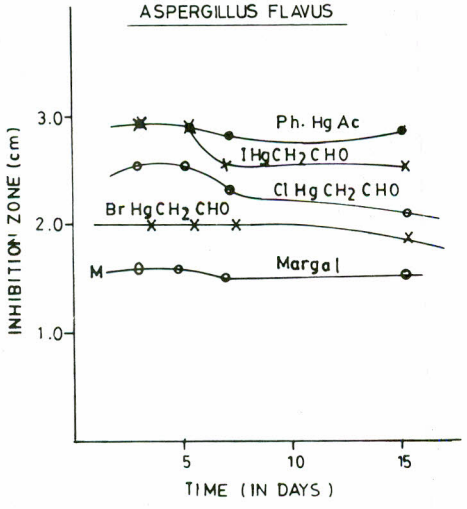


Fig. 2.

results show that the halomercury acetaldehydes are better fungicides than margal but lesser effective than phenyl mercury acetate. This may be due to the fact that phenyl mercury acetate is more soluble than halomercury acetaldehydes.

The results show that among the halomercury-acetaldehydes iodo derivative is more effective than either bromo or chloro derivative. The order of activity can be rated as iodo > bromo > chloro. There is a slight variation in the mode of activity of these compounds towards fungi. If we look into the liner structure of halomercury acetaldehydes.

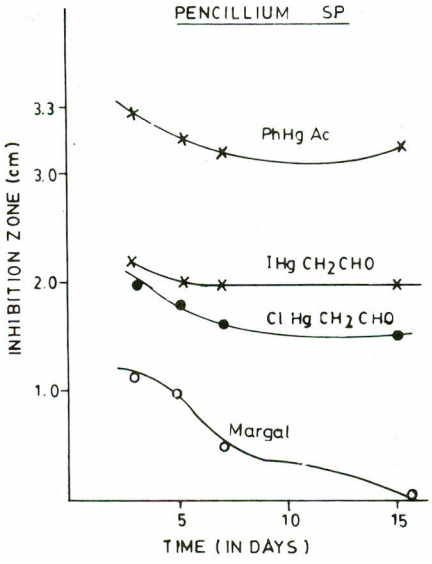
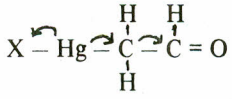


Fig. 3.



where X is halogen. The halogens on one side of the Hg-halogen bond and carbonyl group on the other side of Hg-C bonds, both the electromeric and inductive effect tend to combine and stablise the molecule. It will be expected the mode of action of these compounds should be similar. However there is a slight difference in the solubilities of the halomercuryacetaldehydes. (Table 1) which may be responsible for this mode of action against fungi. The iodo is slightly more soluble than bromo or chloro derivatives. It has been reported [1,7] that the organic radical attached to mercury that controls the fungicidal activity rather than the anion. However the variation in the values [6] of electronegatives of halogens (Cl=3.3, Br= 2.8, I= 2.5) can not be ignored.

Another important factor that has to be considered is the minimum quantity that has to be used to make it as an effective fungicide. Jackobowski [4] carried out experiments on emulsion paints based on poly (vinyl acetate) and concluded that organic mercurials (phenyl mercury acetate) were effective in the concentration of 0.009 percent of mercury metal while pentachlorophenol failed upto 0.5 %. Haloacetamides have been reported [5] as a useful fungicides in PVA emulsions but the quantities required were 0.5-2.0 %. Halomercury acetaldehydes have been found to be effective as fungicides in the concentration of 0.1 % and the results are quite similar to phenyl mercury acetate.

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