



## CHAPTER I

### INTRODUCTION

#### 1.1 A fungicidal in paint

Paint is one type of surface coating which have both decorative and protective properties (1). Paint consists of two main ingredients; pigment and vanish. Pigment is any fine solid particles. It decorates and to some extent it protects, but it rubs off. So most paint contain the other part called vashish. The varnish consists of the binder, volatile solvent, and various additives. The binder is the film former and is usually a polymer or reactive components that form a polymer on curing. Therefore the binder or film former binds together the pigment particles and hold them on to the surface. If the pigment is left out, the film former covers and protects the surface, decorated it by giving it gloss (2). It is difficult to attach coating that are not fluid to any flat or gently curving surface. The fluidity of paint permits penetration into the most intricate crevices. It is achieved by dissolving the binder in the liquid portion which is usually a mixture of solvent. Furthermore, there are other additives which are added into paint in a small quantity to carry out special job(2).

Exterior coatings supplied by the paint industry must provide a pleasing appearance, as well as protection, to enjoy continued acceptance by the homeowner. Defacement of painted

surface by the growth of a wide variety of microorganism, however, continues to be a major problem for paint industry (3). Thus it become more of appearance factor since considerable microorganism can be growing on the surface without serious deterioration of the paint film. The almost universal approach to microorganism thus far has been the addition of toxic materials to prevent the growth of microorganism on paint surface. Such materials are referred as preservative and fungicide. The current approach to solve this problem is to blend a mercurial fungicide into the paint formulation. The most serious one is that the fungicide tends to be leached or vaporized from the paint film over long time periods. After the concentration of fungicide drops below critical levels, microorganism may start growing on the coating surface (4).

Several factors must be considered in selecting a fungicide to be added in paints. The four most important factors, other than cost; are toxicity, solubility, volatility, and UV stability. Toxicity to fungi must be high, but toxicity to humans should be low. The solubility of any candidate fungicide must be carefully considered for several reasons. The fungicide must not be water soluble since it would be leached from in the coatings during rain. Even a slight water solubilty eliminates many fungicides for selection in paints. Also, the fungicide needs to be soluble in the paint or to be dispersed without setting or agglomerating. Fungicides with appreciable vapor pressure cannot be considered for paint use since they would vaporize from the paint after application to a surface. Ultraviolet

photodecomposition may degrade certain fungicides and such fungicides must be avoided (4-6). None of the commercially available fungicides meet all of these requirements.

Mercury-containing mildewcide have come into disfavor due to the high toxicity to human(4). Since mercury salts have been widely used for fungal control in paints more acceptable replacements have been increasingly sought in recent years. The Paint Research Institute at the University of Alabama was undertaken to look for organic biocides which could replace mercury salts(4). Since organic fungicide may leach or vaporize from thin, high surface area paint films, the anchoring fungicides on the polymer binder of the paint was developed (4-8)

Some of the advantages of polymer-anchoring a fungicide to the binder, as compared with simply mixing it into the paint, are illustrated in Figure 1.1 (6). Since the polymer-attached fungicide would be dispersed molecularly along the polymer chain, it would not agglomerate into discrete particle as the film dried. Solubility, volatility and migration problems would be eliminated, humans would not be exposed to toxic vapor because the fungicide would be part of the polymer (4,6).

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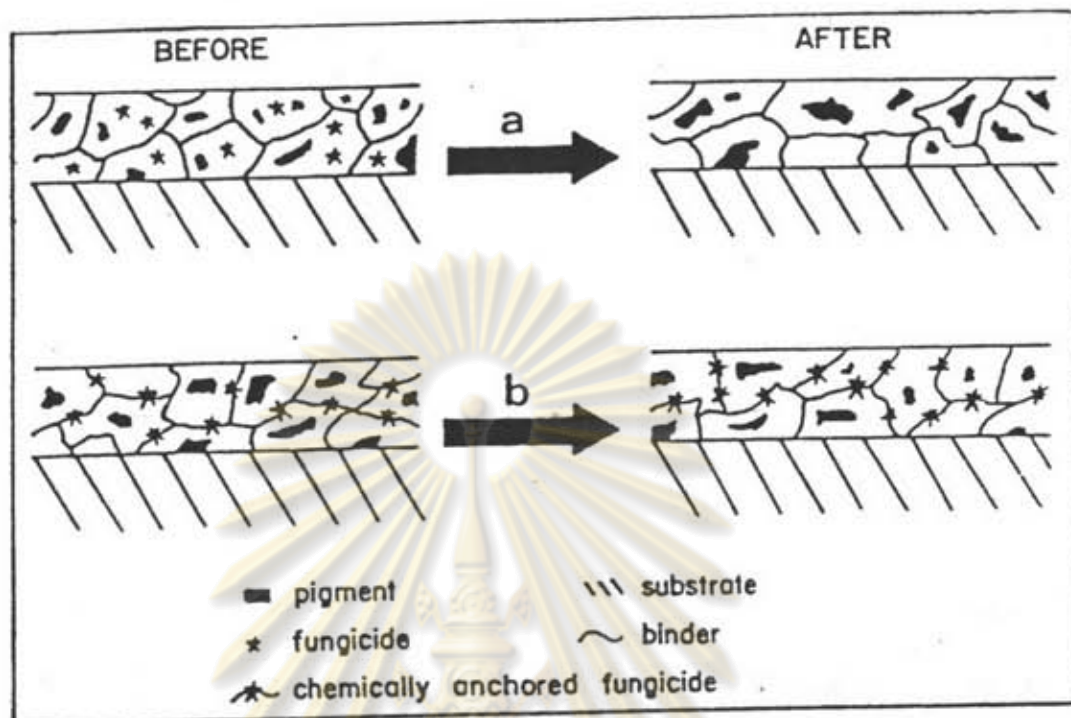


Figure 1.1 The paint film before and after exterior exposure

a) simply blending a fungicide

b) anchoring a fungicide to the binder

A fungicidal compound can be attached to the polymer through a functional group which later can be hydrolyzed to free the fungicide (4). Though the hydrolytic process could, potentially, occur under the environmental conditions, it might be found that fungicide release would accelerate only under condition of microbiological attack on the paint film. In the latter concept, exocellular enzymes from the microorganism would, themselves, release the fungicide ( Figure 1.2 ). This mode of hydrolysis would supply the fungicide only when it is needed (6).

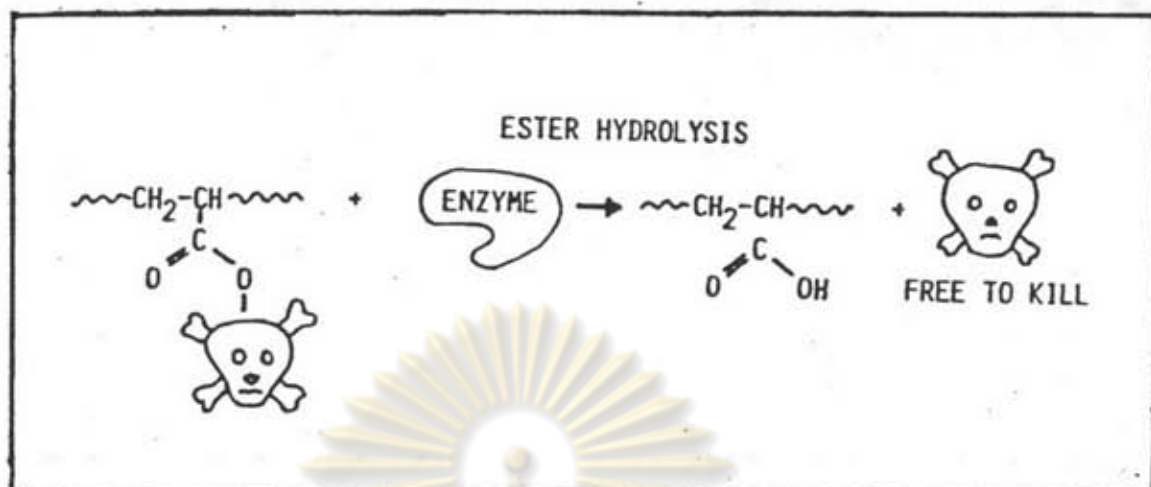


Figure 1.2 A polymer releasing fungicide on attack by fungi.

Over the past few years several fungicide have been converted to monomers containing ester, amide, or ether function which bind the fungicide and the polymerization of these monomers was studied (4-11). The fungicides examined included pentachlorophenol; 8-hydroxyquinoline; 3,4',5-tribromosalicylanilide; o-benzyl-p-chlorophenol; salicylanilide; 2-(4'-thiazoyl benzimidazole; and 2-mercaptopyridine-N-oxide (5-10). The incorporation of fungicides into the polymer would have to be kept at low mole percent, 0.1 to 0.5 (11,12) to avoid changing substantially the polymer's properties (4).

The chemical anchoring of fungicides to polymer represents an approach to the problem of preparing coating with long-lasting fungicidal activity (4). In this research presents the details of synthesis of fungicidal films of methyl methacrylate by chemically attached and polymer blends.

## 1.2 Phase-transfer catalysis in the chemical modification of polymer

For most reaction which proceed by a bimolecular mechanism, the transformation occurs only when the reactants are in the same phase and proximate to one another. These are capacity of successful heterogeneous reactions, but these generally depend on some slightly solubility of one reactant in the other or of both in a mutual cosolvent.

In the past, phase transfer catalysis(PTC) became a recognized technique from the work of Makosza and coworkers in 1968(13-18). The term "phase transfer catalysis" was coined by Starks and first used in patent in 1968 (16). The phase transfer technique approach as a new method for occurring problems of mutual solubility as well as offering the potential for activation of anion(13-17). PTC permits or accelerates reactions between ionic compound and organic, water-insoluble substrates in solvent of low polarity. The catalysts most commonly used are quaternary ammonium or phosphonium salts (18).

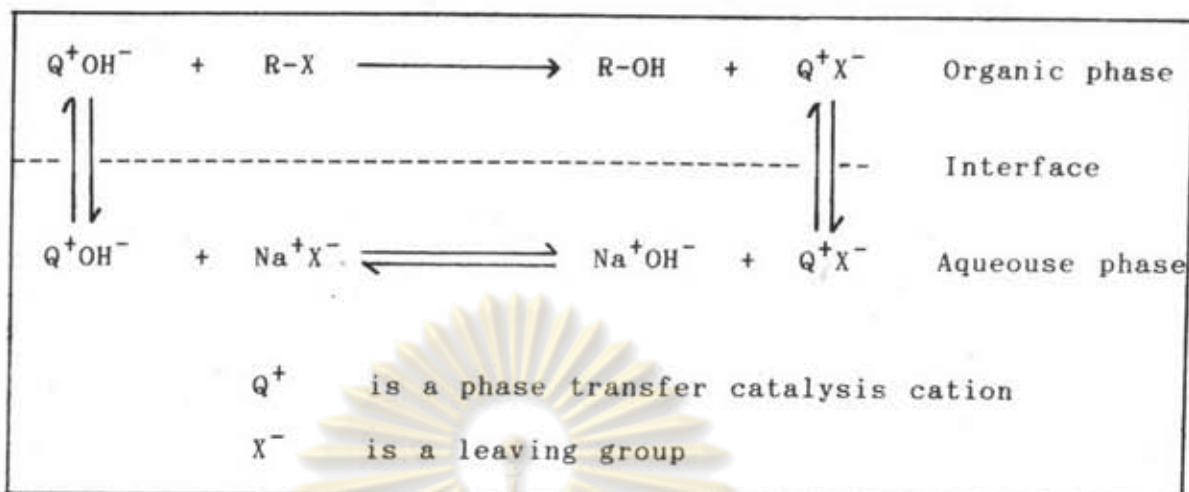
Herriott and Picker have also reported a careful study of catalyst efficiencies (19). They are as follows, i) the larger quaternary ions are more effective than small ones, ii) the catalytic efficiency increases the length of as the longest chain increases, iii) the more symmetrical ions are more effective than those with only one long chain (20). A certain minimum carbon number is required for the catalyst to be soluble and effective in the organic medium. The better catalysts seem to be those

which have the minimal lipophilicity and also have bulky groups surrounding the quaternary positively charged heteroatom (20).

In general, there are two immiscible phase. One of aqueous phase contains a reservoir of the salt expected to function either as base or nucleophile. The second phase is organic and contains the substrate which is expected to react with the salt (20). Because the salt containing phase is insoluble in the substrate containing phase, there will be no reaction observed in the absence of interfacial phenomena (17). A phase transfer catalyst is added to the mixture. This is ordinarily a quaternary ammonium or phosphonium halide or bisulfate which contains a lipophilic cation. The lipophilic cation soluble in both aqueous and organic phase and when in contact with the aqueous reservoir of salt, exchanges anions with the excess of anion in the salt solution.

Once the strong base (50% NaOH) is in solution in organic media, the substitution or deprotonation can take place with product formation (13,18). The assumed mechanism of PTC in the case of nucleophilic displacement in particular (13,16) shown in Scheme 1.1.

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Scheme 1.1 Phase transfer catalysis in nucleophilic substitution reaction

The catalyst cation ( $Q^+$ ) migrates with anion  $OH^-$  from the aqueous phase into the organic phase, where the weakly solvated ion pair formed undergoes very fast further reaction after which  $Q^+$  returns to the aqueous phase with the anion  $X^-$  (20).

This phase-transfer catalysis often has considerable advantages over conventional methods, namely: expensive anhydrous or aprotic solvents no longer required; lower reaction temperatures; shorter reaction time, aqueous alkali metal hydroxides can be employed instead of alkoxides, sodamide, sodium hydride or metallic sodium and many cases easier work-up (18-21). Further special advantages are also found e.g. occurrence of reaction that does not otherwise proceed, modification of the selectivity, modification of the product ratio (e.g. O vs. C alkylation) and increased yields through the suppression of side reaction (18).



Phase transfer catalysis has been used widely in organic synthesis since it was reported by Stark (16-17). Surprisingly, this method has received very little attention in the field of the chemical modification of polymers (22). However, it has been reported that PTC technique has been used satisfactorily in polyether synthesis (23-25) at mild condition which normally must be prepared at high temperatures and in polar solvent (23). Polystyrene (26) and other polymers (27-29) were also prepared by using PTC technique.

Furthermore, Percec and coworkers (24-25) have proposed phase transfer catalyzed Williamson polyetherification as a new and convenient method for the preparation of alternation block copolymers (24). N'Guyen et.al. have shown that PTC can be successfully employed for the reaction of amine with chloromethylated polymers and copolymers (22).

In order to apply PTC technique to chemical modification of polymer matrix in this study, it is the aim to saponification of poly (methyl methacrylate).

### 1.3 Polymer blends

Polymer can be blended to form a wide variety of random or structured system with desirable combination of properties (30-32). Thus the study of polymer blends has received considerable attention. This is due to the variety of bulk properties that may potentially be obtained at a lower cost than the production of a new homopolymer or copolymer (31). Accordingly, polymer blends has attracted the increasing

attention of polymer industrial communities (30-35).

Polymer blends is a physical mixture of two or more different polymers which do not usually lead to chemical bonding between the components (34-36). It can be prepared by the following methods :

- i) mechanical mixing on rubber mills or extruders,
- ii) polymerization of on monomer in the presence of another polymer solution,
- iii) evaporation or precipitation from mixture of polymer solution,
- iv) coagulation of a mixture of polymer lattice (31,36).

Broadly classified, the two types of polymer blends are homogeneous (i.e., miscible or compatible) blends and heterogeneous (i.e., immiscible or incompatible) blends. At a given temperature, homogeneous blends give rise to a single phase in which individual components are mutually soluble in one another. In most cases, compatible blends have mechanical properties superior to those of incompatible blends. Therefore, in the past, much effort has been spent on developing experimental techniques (e.g., electron microscopy, small angle X-ray diffraction, light scattering, and dynamic mechanical analysis) to determine the compatibility of a pair of polymers(35-40). Therefore, continuing development efforts are needed (35).

#### 1.4 Objective

In this research work; the polymeric binders, poly(methyl

methacrylate) containing various organic fungicides, were synthesized by using chemical modification of polymer matrix. Additionally, the other approach to prepare the polymer bound fungicide by using polymer blends technic has also been performed in order to accommodate the paint production in industry. The fungicides chosen for this study were pentachlorophenol; 2,4,5 - trichlorophenol; 2,4,6-trichlorophenol; and 4-chloro-3-methylphenol.



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