

CHAPTER II

THEORETICAL AND LITERATURE REVIEWS

The determination of flame retardant property of many polymers can be achieved by different techniques. Some techniques involve the absorption of heat evolved during combustion and release water. Some are based on scavenging of radicals or suppress the oxygen flow and build up char layered during combustion process.

2.1 Combustion Theory

In the case of fire, three ingredients are needed for fire dynamics as shown in Fig. 2.1 [1].

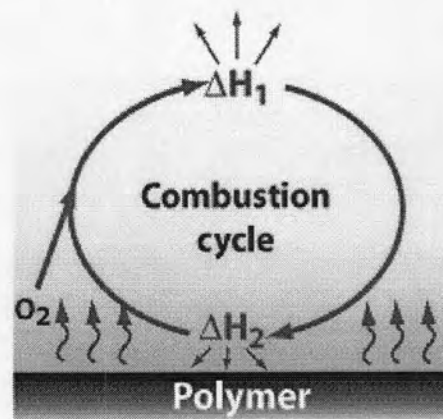


Figure 2.1 Fire cycle.

- Fuel- volatile combustibles from carbon rich source.
- Heat- supplied by the destruction of fuel.
- Oxidizing agent- oxygen provided by air.

To inhibit the fire by removal one of three components from the cycle, several techniques are available to break down this combustion circle.

2.2 Flame Retardant Process

Flame retardant filler can suppress the combustion process by chemical or physical in either the gas or condensed phase.

2.2.1 Condensed phase

In condensed phase two types of reactions can take place.

2.2.1.1 Breakdown of the polymer can be accelerated by flame retardants. It leads to pronounced flow of the polymer which decreases the impact of the flame which breaks away.

2.2.1.2 Flame retardants can cause a layer of carbon (charring) on the surface of polymer as shown in Fig. 2.2. This occurs, for example, through the dehydrating action of the flame retardant generating double bonds in the polymer. These processes form a carbonaceous layer via cyclizing and cross-linking processes cycle.

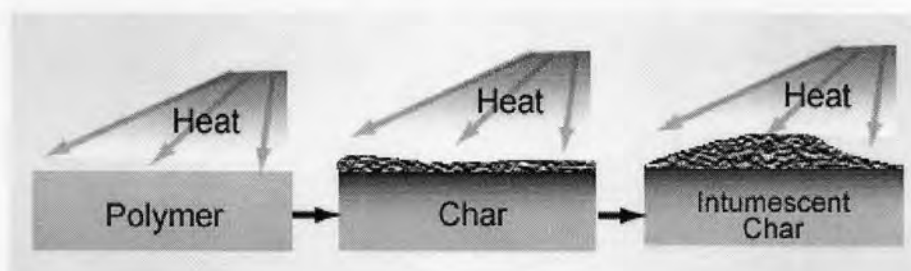
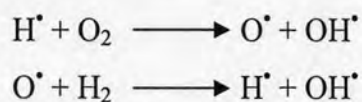


Figure 2.2 Char and intumescence formation.

2.2.2 Gas phase

The gas phase reaction in the flame consists of a radical chain reaction which starts with the radicals or molecular fragments released by pyrolysis of the polymer, and continues rapidly due to the very “hot” (extremely reactive) radicals OH^\bullet and H^\bullet , which are generated in great amounts by the so-called branching reaction with oxygen.



Some flame retardants such as the phosphorus based can produce the volatile phosphorus species: P_2 , PO , PO_2 and HPO_2 during the thermal decomposition. These species will interrupt the branching reaction to reduce the concentration of hydrogen atom in gas phase.

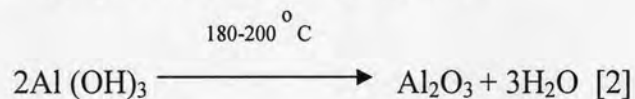
2.3 Mechanism of Flame Retardant [2]

2.3.1 Dilution of combustion mass

The pyrolysis of the substrate or decomposition of filler on solid phase will generate the inert gas which enters to the gas phase and forms a protective layer at the interface, so lowering the concentration of oxygen and reducing the extent of smouldering and glowing processes. It means a decreasing exothermic energy.

2.3.2 Endothermic decomposition

Metal hydroxide such as ATH is the representative of this class which releases the molecule of water to cool the polymer substrate to a temperature which is below the one required for sustaining the combustion process (physical action in the condense phase). The release of water dilutes the amount of fuel and avoids the critical fuel/oxygen-ratio (physical action in the gas phase).



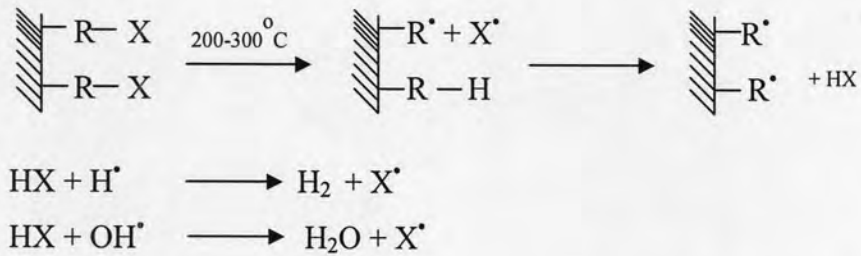
2.3.3 Char formation

If the polymer substrates have the chemicals favoring char formation such as organic structures rich in C=C double bonds or hydroxyl ether and ester group, in case of fire a charred layer may occur to cover the substrate like a glaze and retarding the combustion process in two ways:

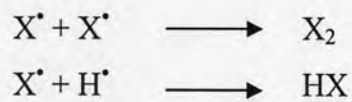
- a) Hinder the heat transfer into the substrate thus the sustention combustion is retarded.
- b) No combustible product from condense phase into gas phase, thus limiting the supply of combustible materials in the fire.

2.3.4 Radical scavenging

The most radical scavengers are halogen radicals (X^\cdot) which are released from the flame retardant contained in condense phase then react with the "hot" radicals H^\cdot and OH^\cdot in the gas phase.



The “cool” halogen radicals formed the stable products in the gas phase until recombine with one another, thus the chain reaction will be terminated.



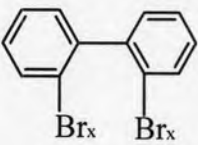
2.4 Groups of flame retardants

2.4.1 Halogen-based flame retardants

Consumption of the halogen-containing retardants makes up approximately one third of the total use of flame retardants. The reaction is based on the scavenging of radicals formed during combustion. Among halogens, fluorine cannot be used for flame retardant because of its very high electro negativity and thus the difficulty in breaking its bond. Iodine is a very large atom and can easily be separated from the compound it is bonded to even at low temperature. So chlorine and bromine are the best radical scavengers. Due to chlorine compounds being not easily degraded in nature, therefore in the last decade the interest has shifted from chlorine to bromine flame retarders [3].

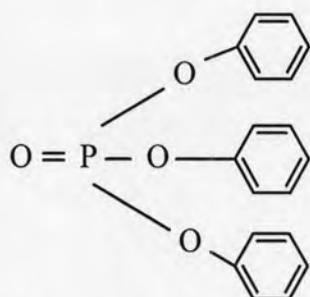
In fire, halogenated compounds generate corrosive and physiologically hazardous acidic gases. The corroding action on metallic parts and electrical wiring may present serious problems. Certain halogenated flame retardants are tabulated in Table 2.1.

Table 2.1 Samples of halogenated flame retardants. [2]

Item	Structure	Used for
Chlorinated paraffins	$\begin{array}{c} \text{Cl} \\ \\ \text{H}-(\text{CH})_n-\text{H} \end{array}$	Plasticizer for PVC
Chlorinated alkyl phosphates	$\begin{array}{c} \text{CH}_2-\text{Cl} \\ / \\ \text{O}=\text{P}-\text{O}-\text{CH} \\ \backslash \\ \text{CH}_2-\text{Cl} \end{array}$	Rigid and flexible PU
Poly bromodiphenyls		Thermoplastic

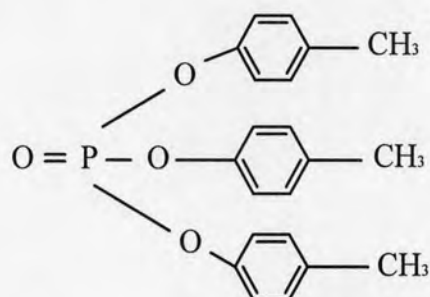
2.4.2 Phosphorus-containing flame retardants

Most phosphorus-containing flame retardants are used as plasticizer such as phosphoric acid ester, triethylphosphate and diphenylcresylphosphate. They can be classified into four groups, namely, inorganic phosphate such as red phosphorus and ammonium polyphosphate, organic phosphorus such as amine phosphate and trialkyl phosphate, halogenated alkyl phosphate and phosphonates and reactive organic phosphorus compounds such as phosphorus-containing diol and polyols. [4] Some examples of phosphorus-based flame retardants were shown below.



TPP, triphenylphosphate

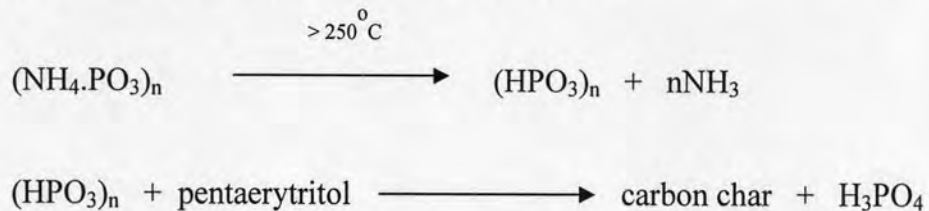
Used in ABS



TCP, Tricresylphosphate

Used in PVC as plasticizer

Ammonium polyphosphate (APP) and other phosphorus-based act as flame retardant by various physical modes such as the formation of polymeric acid as a surface coating, the heat sink action of the vaporizing phosphorus compound, dilution of the combustible pyrolysates by a less combustible vapor and reduction of melt viscosity to favor a melt drip mode of flame retardant.



When plastic or other materials containing APP are exposed to an accidental fire or heat, the flame retardant starts to decompose, commonly into polymeric phosphoric acid and ammonia. The polyphosphoric acid reacts with hydroxyl or other groups of a synergist to a non stable phosphate ester. In the next step the dehydration of the phosphate ester follows. A carbon foam is built up on the surface against the heat source (charring) as shown in Fig. 2.3. The carbon barrier acts as an insulation layer, preventing further decomposition of the material.

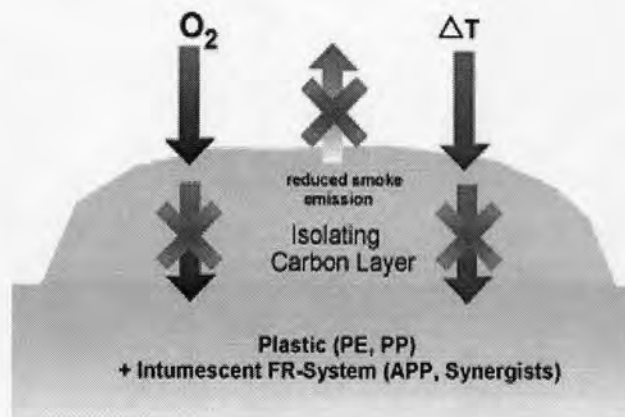


Figure 2.3 Chemical effect in condense phase “Intumescence”.

2.4.3 Inorganic flame retardants

The use of hydrated fillers such as ATH, magnesium hydroxide, antimony oxide, zinc borate increases every year. The main reason is the reduction of the final cost, improvement in processability and achievement of specific properties. [6]

The disadvantage of these flame retardants is that high filler loads are necessary for the good flame retardant property, whereas their great advantage is that ATH produces no toxic gas or corrosive gases, so it can be considered as physiologically harmless.

ATH is widely used to provide the best balance of flame retardant properties versus cost of inorganic filler flame retardant. Metal hydroxides contribute to several flame retardant actions. They first decompose endothermally and release water. The endothermally decomposition acts as heat pump that leads to cool the substrate and to decrease the pyrolysis of the polymer (physical action in the condensed phase). The release of water dilutes the amount of fuel and avoids the critical fuel/oxygen-ratio (physical action in the gas phase) and refractory oxide Al_2O_3 that act like a protective layer on the substrate surface.

ATH is an excellent flame retardant for materials processed at temperature below its decomposition point (190-230°C). It is used as flame retardant in elastomers, thermosetting resin and thermoplastics. Certain examples of inorganic flame retardants are presented in Table 2.2.

Table 2.2 Examples of inorganic flame retardant [2]

Item	Structure	Decomposition temperature
Aluminium trihydroxide	$\text{Al}(\text{OH})_3$	180-200°C
Magnesium hydroxide	$\text{Mg}(\text{OH})_2$	approx. 340°C
Boric acid	H_3BO_3	2 steps: 130-200°C 260-270°C

2.5 Flammability testing

There are different techniques to evaluate the effect of fire on the paints. Depending on the country and type of use, for example, in Germany the fire protection regulations for building purpose are divided into five categories following DIN-4102.

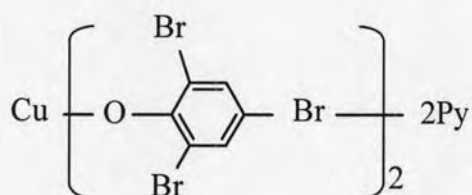
Paint or coating is the material in terms of building construction. The most widely used and adapted testing methods is Oxygen Index (OI) test.

OI shows the resistance of the material to the ignition. The higher OI means that the material burns less easily and that the retardant increases the material's resistance to ignition.

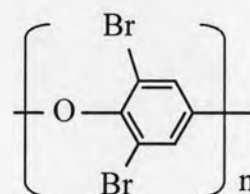
2.6 Flame retardant history

Flame retardant paint is one of efficient ways to protect the material against a fire and become an important topic in the construction world. During fire, any materials distort due to the collapse of building and as a consequence to human life and economic losses.

Several researchers have addressed several methods to improve the flame retardant property of thermoplastics. For instance, in 1999 Gunduz *et al.*, [3] studied the flame retardant property of long oil alkyd resin and styrenated alkyd resin by incorporation of *bis*-pyridine *bis*-tribromophenoxy copper (II) complex and polydibromo-phenylene oxide (PDBPO) as shown in below figures.



CC, Bis(2,4,6-tribromophenoxy)
copper(II) complex



PDBPO
Polydibromophenylene oxide

Oxygen index (OI) is used for determining the flame retardant property of long oil alkyd and styrenated alkyd resins. The increased amount of PDBPO increases OI values of both resins. An example of oxygen value curve is depicted in Fig. 2.4.

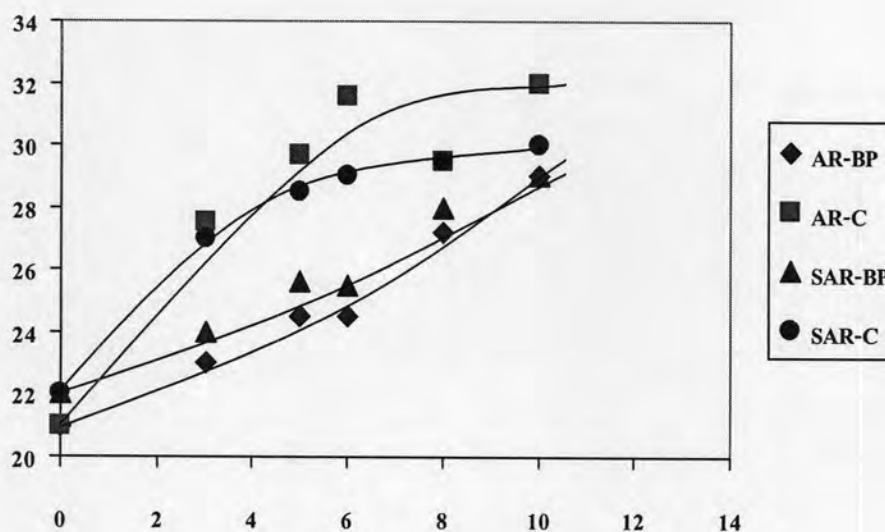


Figure 2.4 Oxygen index curve.

In 2000 Pinto *et al.*, [6] expressed the effect of ATH on flame retardant property, mica to improve processability and mechanical properties in thermoplastic polyurethane (TPU) elastomers. ATH has a few mechanisms which contribute to the reduction in thermal decomposition such as heat absorption and release large volume of water during the reaction that promotes the heat absorption, water vapor produced which promotes the gas phase dilution and refractory oxide Al_2O_3 that act like a protection layer on the substrate surface. The results of OI and UL-94 were used to evaluate the flame retardant property and found that, the composites with 70 and 80 phr of ATH present fire retardancy and the use of mica did not deteriorate the flame retardant behavior. On the other hand, the composites which were incorporated with ATH and mica showed the higher mechanical properties.

In 2003 Barfar *et al.*, [7] reported the effect of zinc borate, $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$ on flammability of cross-linked PVC. Flammability can be estimated by limit oxygen index (LOI), where a sample is placed vertically in a flaming atmosphere of oxygen and nitrogen and ignited at the top. The highest LOI achieved was 31% for PVC formulations containing 2:8 ratio of $\text{Al}(\text{OH})_3$:zinc borate.

In 2004 Duquesne *et al.*, [8] investigated the role of the binder in an intumescent paint (Intumescent products are those which could expand to several times their original size when activated by high temperature). When the intumescent coating degrades, the foam char layer has formed to protect the substrate from fire. In order to achieve the barrier effect to heat and fire, a slow diffusion of gases in the structure during intumescence allows the formation of an expanded structure. This was not achieved if the viscosity of the material is too high or too low. The combination of a cross-linked copolymer with a Newtonian copolymer presenting a good reactivity with the intumescence additive allows adaptation of the viscosity in order to optimize the char formation and structure and to create an efficient protective layer. This paper has been shown that the use of substituted styrene favors the reactivity of the binder resin with the intumescence additives.

2.7 Effect of biocides on paints

In today's world, reports of outbreaks of disease in hospitals or problems caused by food poisoning are quite frequent occurrences. Organic coatings are susceptible to microbial attack, and the properties of the coating and its composition, the nutrients on the surface and the nature of substrates represent the main parameters that determine types of biofilm formation by microorganisms as shown in Fig. 2.5 [9].

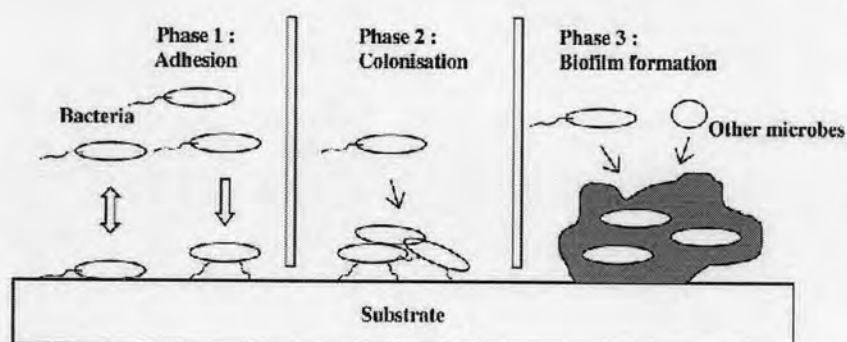


Figure 2.5 Schematic of biofilm formation by microorganism.

Biocides are an important element designed to keep bacteria from spoiling paint during storage, or to keep fungi from growing on the applied paint. Microbial growth can lead to both aesthetic and physical degradation of the coating or painted surface. In addition to the obvious aesthetic effects of mold, mildew and algae growth, physical deterioration by their enzymes can lead.

This deterioration can include an increase in porosity of the surface coating; loss of adhesion to the substrate, whether wood or masonry; and moisture penetration at can lead to fungal decay of the paint.

Type of biocides for water based or latex paints are typically more prone to contamination and need an antimicrobial or biocide to act as an in-can preservative. In-can microbial growth or degradation most frequently occurs from contaminants, bacteria and yeasts in the raw materials. The same organic paint components act as the microbial food source, causing possible discoloration, gas generation, foul odors, coagulation, rheological, rheology changes and corrosion.

Typical in can preservative chemistries include: isothiazolones and formaldehyde donors. These preservatives are bactericides and their killing action must be quick. Typical in can preservative dosages are 0.1% or higher if excessive bacteria levels are present.

Dry film preservatives that protect the surface coating from mold, mildew and algae growth are typically fungicides. The dominant fungal species can vary with environment, climate and condition of the paint film. Optimum fungal growth conditions include a humid environment, a neutral to acidic environment with an organic food source.

Typical fungicides used in the paint industry for dry film preservation include: chlorothalonil, iodopropynylbutyl carbamate (IPBC), octyl isothiazalone and zinc pyrithione. [10]

2.8 Classification of biocides

The benefits and features of biocides can be divided in two classes.

2.8.1 In-can preservative

The health, safety, air quality, and odor concerns associated with the solvents in oil-based paints have moved people towards water-based latex paints. Environmentally-compatible, water-based coatings are susceptible to bio-deterioration. Bacteria, fungi and yeast can develop inside the can and damage the quality of the paint.

All water-based paints require customized In-can preservation to prevent contamination of the paint and allow a longer storage capability. Many active agents are available on the market but to choose the right In-can biocide the formulation has to find the perfect mix to achieve the required level of performance and protection.

These substances include, for example, aldehydes and aldehyde-releasing compounds, substances with activated halogen compounds, isothiazolinones and organometallic compounds. [2]

2.8.2 Film preservative

In Europe, facades are made of mineral materials such as stucco and gypsum, as well as wood materials which favor the growth of micro-organisms. Once a painted surface is colonized by micro-organisms, the integrity of the paint is compromised, and it may result on undesirable color changes and loss of adhesion. Then substrates are vulnerable and breakdowns may result. There are also dirt-pick up and stain problems that are not caused by micro-organisms. The substances for example, benzimidazoles, zinc pyrithione, diuron, *etc* [2].

2.9 Literature review on antifungal agents

In 2005 Jeongyun *et al.*, [11], studied the antifungal effects of cement mortar with an organic antifungal agent on *Aspergillus niger*. Two types of organic antifungal agents: isothiazoline/cabamate and nitrofurantoin were directly added into the cement mortar.

Aspergillus niger was used in this study to investigate the antifungal effect which was corresponding to an antifungal zone and found that the antifungal zone of cement mortar was observed when isothiazoline/ carbamate at 0.3%, 2% and 5% were used (Fig. 2.6). On the contrary, the antifungal effect in the case of nitrofurantoin did not appear as shown in Fig. 2.7 (no antifungal zone).

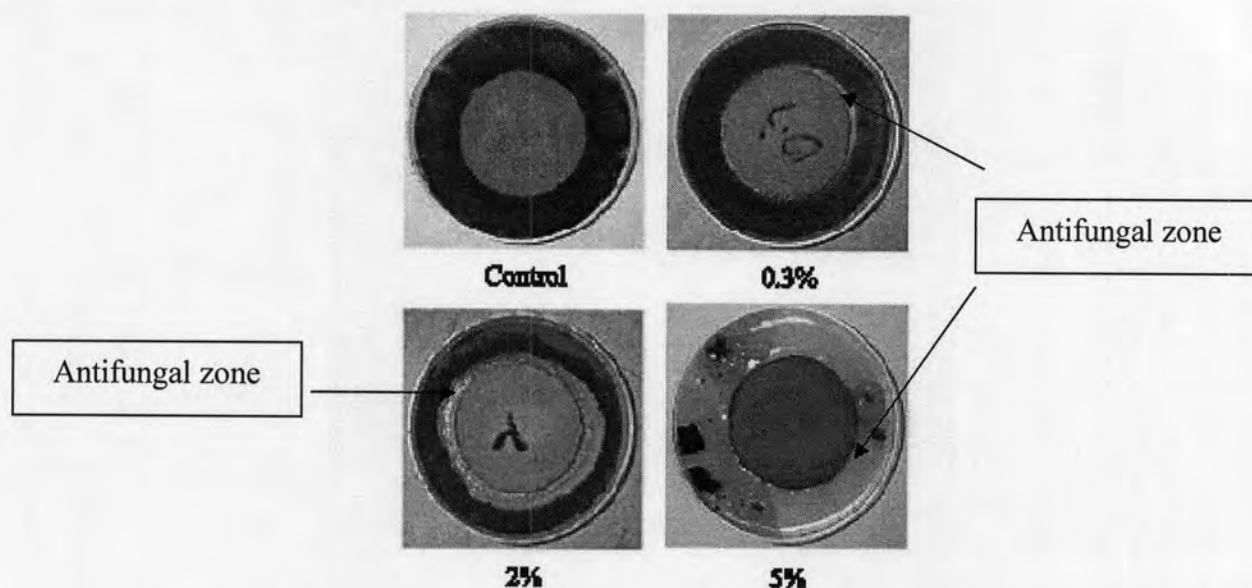


Figure 2.6 Antifungal effect of isothiazoline/ carbamate.

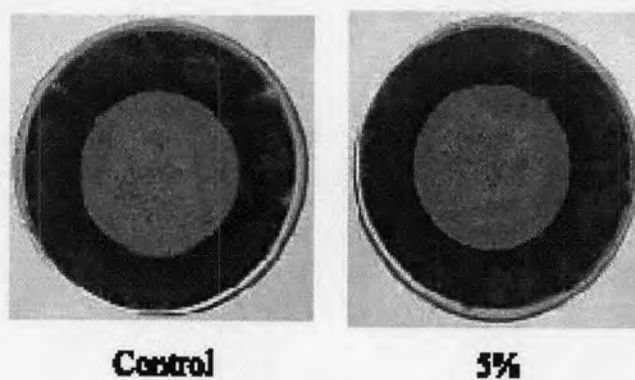


Figure 2.7 Antifungal effect of nitrofurantoin.

In 2005, Zimmermann *et al.*, [12] combined IPBC with 2-methylisothiazolin-3-one (MIT). The mixed antifungal exhibited the synergistic effect that is greater than that possessed by each of those compounds alone. The antifungal activity according to

this invention can be used in very different areas. It is suitable for use in paint, plasters, adhesives, product containing starch and asphalt emulsions.

In 2004, Bedi *et al.*, [13] synthesized the amidine derived 1,3-diazabuta-1,3-dienes compound and tested antimicrobial activity with Gram positive; *Bacillus subtilis* MTCC 121, *Bacillus cereus* MTCC 1272 and Gram Negative microorganisms; *Escherichia coli* MTCC 42 and *Pseudomonas aeruginosa* MTCC 1034. while antifungal screening of the synthesized compounds was determined against *Candida albicans* MTCC 183 and *Aspergillus niger* MTCC 404.

In 2005, Gaglani *et al.*, [14] addressed the ratio between IPBC and its derivatives of thirum and zirum against *Aspergillus niger* in emulsion paint. The optimum ratio that gave the best antifungal result were 75:25 and 25:75 for IPBC:thirum (fungal growth value = 1.7), while 50:50 and 75:25 for IPBC:zirum (fungal growth value = 3.5 and 3.7, respectively). Fungal growth results were recorded as fungus units determined by comparison to standard chart with a range of 1-15 fungus units. A fungal growth values of 15 indicated that the painted squares were totally covered with fungus. Values 5 through 15 showed the gradations of growth from very little fungus growing on the surface to the total coverage of 15. A rating of 4 showed growth on the edges of the test square only, 3 showed the growth up to the edges and 1 indicated no growth touching the test square.