

## CHAPTER I

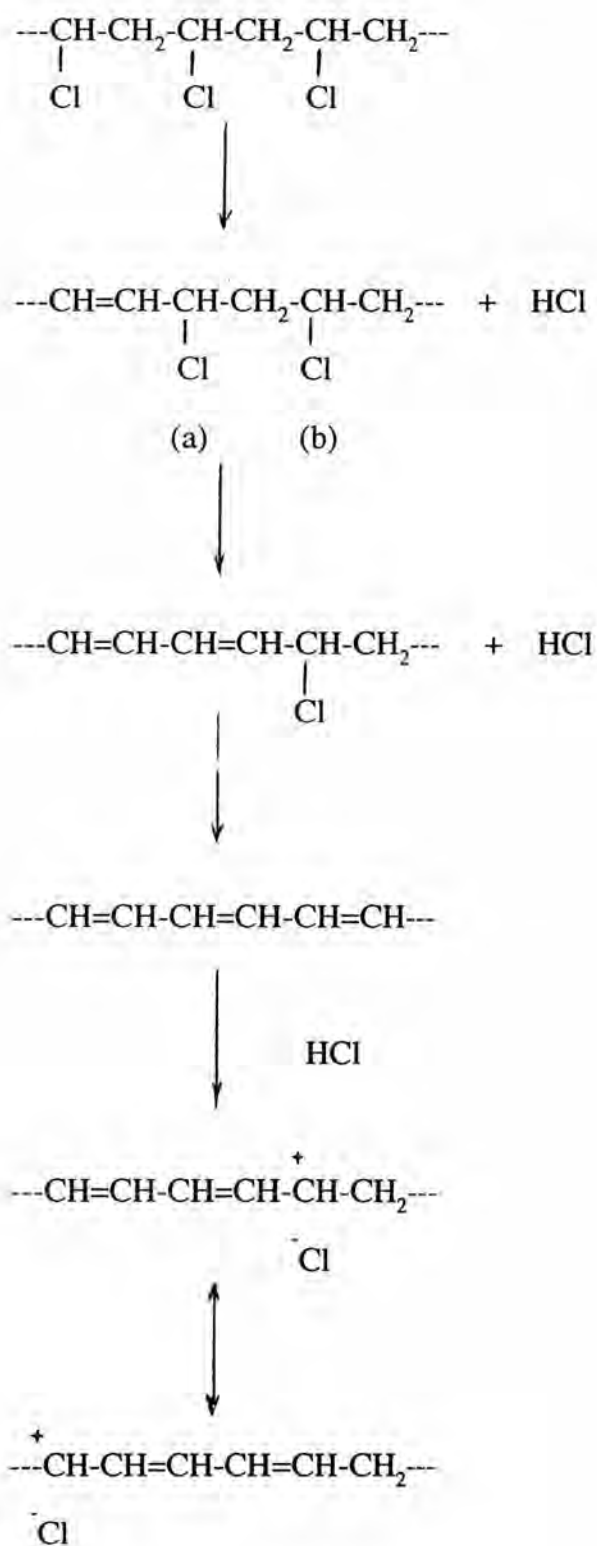
### INTRODUCTION

PVC is a thermoplastic polymer with low heat stability. At the elevated temperatures required for processing it is degraded and consequently tends to change its color from colorless to brown. This problem can be alleviated or solved by adding stabilizers. For rigid PVC profiles, lead containing stabilizers are popular because of their high efficiency. However, in many countries the use of lead compounds tends to decrease because of their harmful effect, as lead compounds can accumulate in the human body. In the long term this accumulation leads to damage to the brain.

In order to avoid the use of lead containing compounds as stabilizers for rigid PVC profiles, Ca/Zn stabilizers were investigated. Ca/Zn stabilizers for PVC are approved by the United States Food and Drug Administration (FDA) for food packaging, toys and blood transfusion tubings. The efficiencies of Ca/Zn stabilizers are lower than those of lead stabilizers but can be improved by addition of co-stabilizers. In this work, the suitability of some co-stabilizers was investigated.

## 1.1 Degradation of PVC

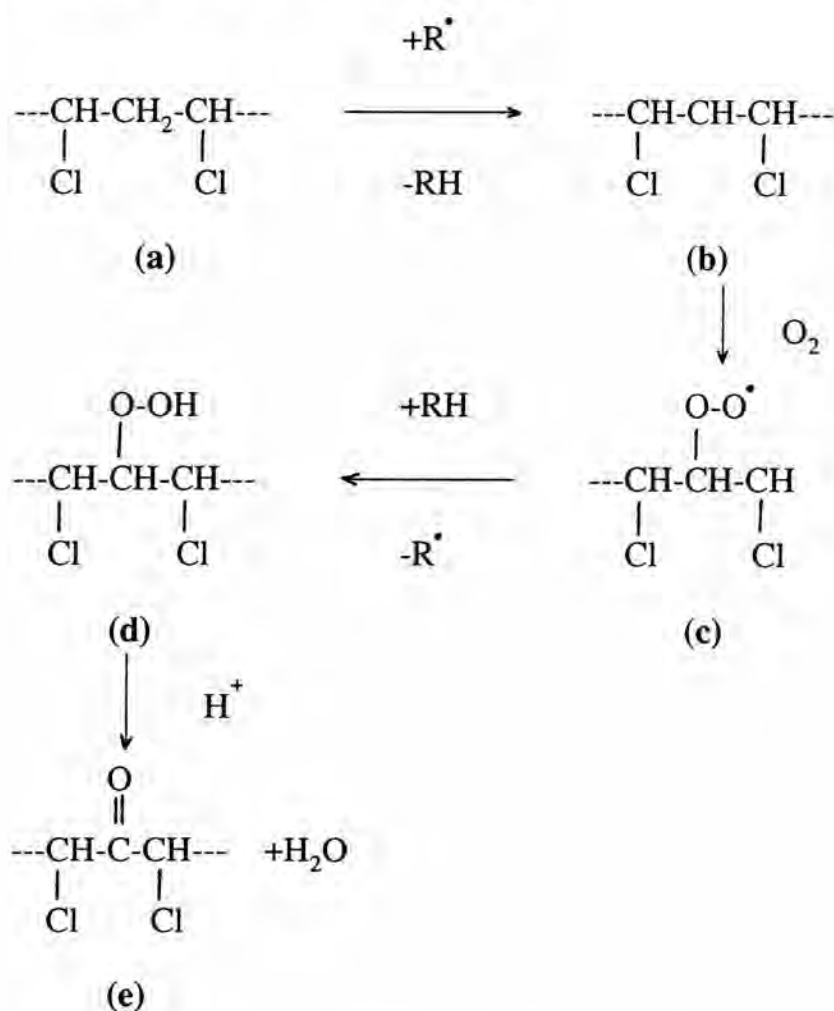
PVC is degraded by dehydrochlorination (release of hydrogen chloride), the predominant reaction during processing, leading to increasing discoloration. The initiation mechanism of dehydrochlorination is still uncertain, but it results in the formation of allylic chlorine-carbon bonds in the PVC chain. The energy of the allylic chlorine-carbon bond (position a in Eq. 1.1) is about 250 kJ/mol while the regular chlorine-carbon (position b in Eq. 1.1) bond energy<sup>(1)</sup> is about 300 kJ/mol. For this reason allylic chloride bonds in a PVC chain are likely to give rise to conjugated double bonds. The reaction progresses “zipper-like” and leads to the formation of long polyene sequences which, if contain more than a few double bonds, are colored<sup>(1)</sup>. The electron-rich character of polyenes is responsible for potential carbenium salt formation,<sup>(2)</sup> which further enhances the discoloration.



Eq 1.1 : Degradation of PVC by dehydrochlorination

## 1.2 Autooxidation and degradation of PVC

The release of hydrogen chloride on dehydrochlorination in the presence of nitrogen is decreased when compared to that in the presence of oxygen<sup>(3)</sup>, as attack by oxygen results in the formation of new initiation sites (Eq. 1.2). Attack on methylene groups leads to the formation of hydroperoxides (d in Eq. 1.2) in a radical chain reaction. The decomposition of hydroperoxides by an ionic reaction mechanism leads to labile carbon-chlorine bonds (e in Eq. 1.2).



Eq. 1.2 : Formation of new initiation site by autooxidation

### 1.3 Mode of action of heat stabilizers

In order to alleviate the degradation of PVC, heat stabilizers must be capable of preventing the dehydrochlorination reaction or at least be able to retard this reaction. Additionally, they should shorten polyene sequences and destroy carbenium salts. It can be concluded that the function of heat stabilizers are :

1. Displacement of labile chlorine atoms from the PVC chain in order to eliminate defect sites.
2. Absorption of hydrogen chloride (destruction of carbenium salts and autocatalytic effect).
3. Prevention of autooxidation (to prevent formation of new initiation sites).
4. Addition to polyene sequences in order to preclude the formation of conjugated double bonds.

## **1.4 Lead stabilizers vs. calcium/zinc stabilizers**

### **Lead stabilizers**

The main technical advantages of lead stabilizers are good heat-stabilizing power and particular suitability for use in electrical insulation (because they are non-conductors and the inert nature of the chloride formed by reaction with HCl). However, they are not suitable for clear composition, where freedom from sulphur staining is necessary, or where toxicity presents a hazard, as, for example, in food-contact application and products for medical use or children's toys. Lead stabilizers are comparatively cheap. Although they are heaviest (costing is often on a volume basis) and are generally used at a relatively high loadings, they can frequently prove most cost-effective. Subject to their above-mentioned limitations they are, therefore, always worth considering first. Typical application areas include pipes, pipe fittings, interior and exterior profiles, cable coverings, conveyor belting and electrical insulation tape<sup>(3)</sup>.

### **Calcium/zinc stabilizers**

They are the most widely used non-toxic stabilizers for PVC. They are permitted in most countries for use in rigid and plasticized compositions for the production of food-packaging materials and containers, medical goods and toys.

Calcium/zinc combinations are not among the most powerful stabilizers. Wherever practicable they are used in conjunction with epoxy co-stabilizers to improve the stabilizing effects against both heat and light, and with organic phosphite synergists. Other synergists available for use to improve the stabilizing action and efficiency of calcium/zinc system include stearylbenzoylmethane and some proprietary polyol compounds<sup>(3)</sup>.