CHAPTER 9

Stabilisers: General Aspects

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9.1 INTRODUCTION

PVC polymers and copolymers are susceptible to degradation by heat (the thermal degradation is sometimes referred to as 'thermolysis') and by light (photolysis, also called photodegradation, and—in some contexts—photochemical degradation): in both cases degradation is rapid and more severe in the presence of oxygen. In the practical context photochemical effects are of special concern in outdoor exposure of PVC materials, where they may be accompanied by those of other factors instrumental in weathering (see Chapter 12, Section 12.6) so that the overall deterioration can be faster and more drastic than that caused by exposure to light alone.

Heat stabilisers are incorporated in all PVC compositions to protect the polymer against thermal degradation at the high temperatures of processing (higher for uPVC, and generally ranging—depending on composition and process—from about 170°C to about 220°C) and also subsequently in service. UV-absorbing and antioxidant additives are included where appropriate as stabilisers against photochemical degradation. Many heat stabilisers have some antioxidant action. An antioxidant is also often incorporated as a component in composite commercial heat stabiliser systems.

Formulation components other than the base polymer may also suffer degradation: e.g. chlorinated polyethylene (by dehydrochlorination and oxidation on excessive heating!), rubbery impact modifiers (by disruption and oxidation—e.g. on weathering—of the double bonds their molecules contain), and chlorinated paraffin
extenders (which can undergo dehydrochlorination with further breakdown and formation of unsaturated compounds on strong heating\(^2\)). Like the PVC polymer, some of these additives can benefit from the presence of stabilisers in the composition.

### 9.2 DEGRADATION OF PVC POLYMER

The degradation of polyvinyl chloride (and some copolymers), and the ways in which various stabilisers counteract and modify the process, have been widely studied for many years. The subject is complex and much still remains to be elucidated and verified, *inter alia*, in regard to the chemical and morphological effects of photochemical attack (and weathering generally), and to the mode of action of stabilisers, especially in systems involving some synergistic effects. However, at least the basic features of degradation and stabilisation are now fairly well understood, and there is reasonable general agreement as to the principal underlying mechanisms. The extensive literature of the subject includes useful reviews by Voigt,\(^3\) Silberman,\(^4\) Thinius,\(^5\) Onozuka and Asahina,\(^6\) the staff of Ciba-Geigy,\(^7\) Braun\(^8\) and Nass.\(^9\)

#### 9.2.1 Thermal Degradation

The main outward manifestations of thermal degradation of PVC (at temperatures sensibly below those of pyrolytic decomposition and combustion, against which no stabilisation is possible) are the evolution of hydrogen chloride, development of colour (progressing with the extent of breakdown from light yellow, through reddish brown, to almost black in severe cases) and deterioration of physical, chemical and electrical properties.

It is widely accepted that dehydrochlorination involves progressive 'unzipping' of neighbouring chlorine and hydrogen atoms along the polymer chain (although the actual mechanism of this process is still in some doubt\(^*\)): a double bond is formed between the carbons to which the two atoms were originally attached—this constitutes an allyl chloride structure with (i.e. is in the 3,4 position in relation to) the next Cl down the chain, which is thereby strongly activated (cf. Chapter 1,

\(^*\) An ionic mechanism is favoured by some investigators,\(^7,8\) and a free-radical one by others.\(^10,11\)