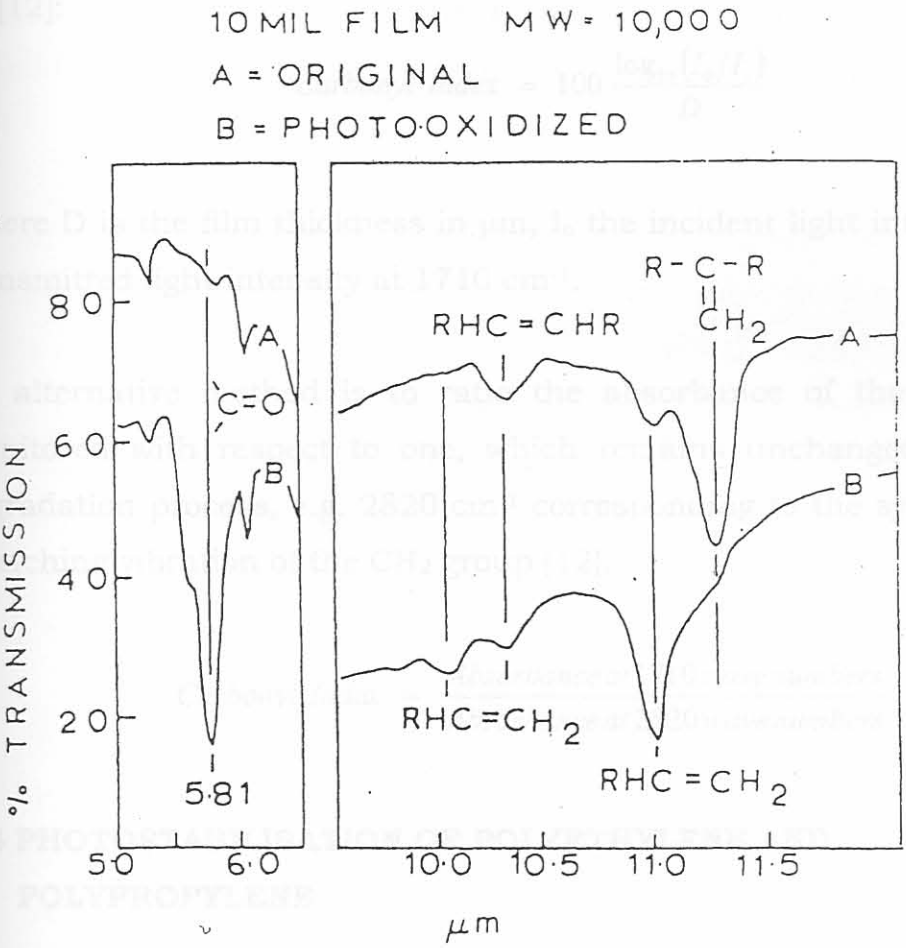


Figure 2.3. Infra-red spectrum of polyethylene (low density) before irradiation and after photo-oxidation. (After Rugg et al., 1977).

2.3.7 QUANTIFYING DEGRADATION: THE CARBONYL INDEX

Carbonyl groups are formed during the oxidation of polymers. These include ketones, aldehydes, acids, esters systems and cyclic esters (e.g. lactones) [8-12]. Therefore, the pure polyolefin contains no carbonyl groups. The concentration of carbonyl groups in the material will give an indication of the degree of degradation that has occurred. This is measured by IR spectroscopy.

In most oxidised polymers, carbonyl absorption lies in the range 1780 – 1640 cm^{-1} [8 – 12]. It is conventional to use the Carbonyl Index as a measure of the degree of oxidation that has taken place. It can be defined as [12]:

$$\textit{Carbonyl Index} = 100\,\frac{\log_{10}(I_0/I_t)}{D}$$

Where D is the film thickness in μm, I_o the incident light intensity, I_t the transmitted light intensity at 1710 cm^{-1}.

An alternative method is to ratio the absorbance of the band to be monitored with respect to one, which remains unchanged during the degradation process, e.g. 2820 cm^{-1} corresponding to the symmetric C-H stretching vibration of the CH_2 group [12].

$$\textit{Carbonyl Index} = \frac{\textit{Absorbance at } 1710 \textit{ wave numbers}}{\textit{Absorbance at } 2820 \textit{ wave numbers}}$$

2.4 PHOTOSTABILISATION OF POLYETHYLENE AND POLYPROPYLENE

2.4.1 MECHANISM OF PHOTOSTABILISATION

Oxidation of polyolefins, in the absence of any additives, results in rapid chain scission, crosslinking and formation of oxygen – containing functional groups in the polymer [10, 12].

The photostabilisation of light – sensitive polymers involves the retardation or elimination of the various photophysical and photochemical processes that occur during photo-oxidation and may be achieved in many ways, depending on the type of stabiliser and the type of mechanism that is operative in the polymer [1-7].

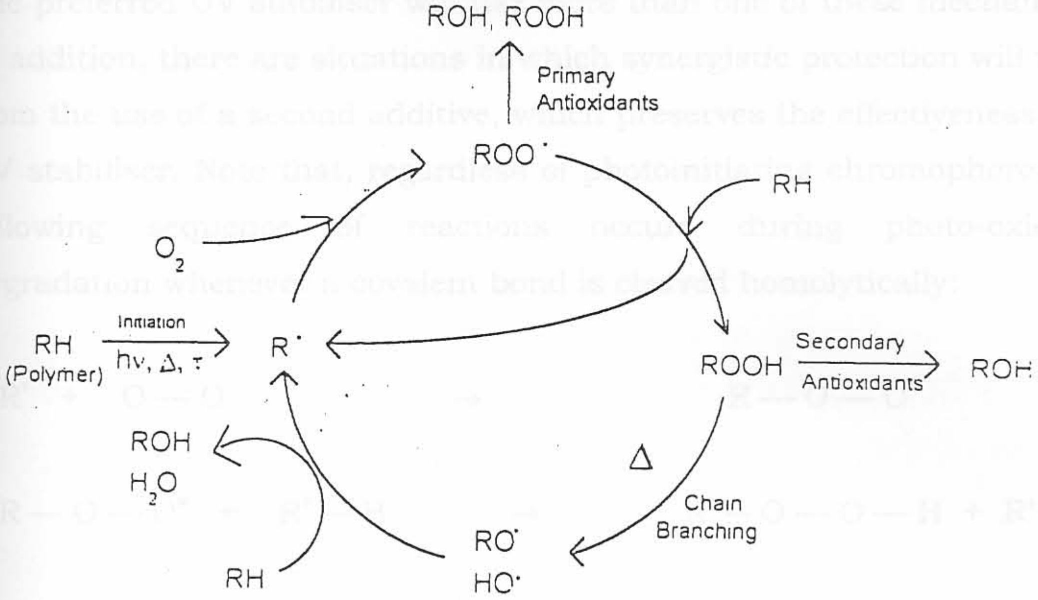
The compounds, which are used to retard or arrest these processes, have traditionally been referred to as 'stabilisers' in plastic technology and 'antioxidants' in rubber technology [35-38]. The commercially available UV stabilisers range from extremely good to poor in protecting polyolefins against sunlight and have largely been developed by empirical routes [38].

In many cases antioxidant and light stabiliser degradation products can reduce the final stability of the polymer. The development of UV stabilisers and their mode of action have received widespread interest in the field of research over the years. Four different classes of stabilising systems have been developed and it is now believed that the mechanisms operating during stabilisation are more complex and more diverse. However, all stabilisers are believed to owe their mode of action to some or all of the following mechanisms [10, 12]:

(i)- ultraviolet screening;
(ii)- ultraviolet absorption;
(iii)- excited state deactivation; and
(iv)- free radical scavenging and/or hydroperoxide decomposition.

Of these, it is generally believed that (iii) and (iv) are the most effective mechanisms.

The mechanisms involved in photostabilisation are directly dependent on those involved in photo-oxidation and these, in turn, depend on the polymer structure and other variables, such as manufacturing operations, processing conditions, and so forth [8]. Most or, indeed, all stabilisers are believed to be multifunctional in their mode of operation in inhibiting photo-oxidation of a polymer. Many factors have to be taken into consideration such as light and heat stability of the stabiliser at its compatibility with the polymer [12]. A schematic representation of stabilisation is shown in Scheme 2.4.



Scheme 2.4. Inhibition of the oxidation mechanism by Antioxidants

We can describe the photo-oxidation of hydrocarbon polymers with the following sequence: absorption of photons by chromophores, resulting in electronic excitation of the chromophores. The breaking of some bonds by a fraction of the excitation energy to produce free radicals; subsequent reaction(s) of the radicals, frequently with atmospheric oxygen, in chain processes. A large number of secondary reactions may occur.

The Scheme 2.4 indicates the potentially useful functions of additives that impart UV stabilisation:

- absorbers to reduce the number of photons absorbed by chromophores,
- compounds which can deactivate excited species, such as R^{*} and O_2, normally in some collisional process,
- compounds which can catalyse the decomposition of peroxides before these groups absorb photons,
- compounds, which can react with free radicals and thus interrupt degradation chain processes.

The preferred UV stabiliser will use more than one of these mechanisms. In addition, there are situations in which synergistic protection will result from the use of a second additive, which preserves the effectiveness of an UV stabiliser. Note that, regardless of photoinitiating chromophores, the following sequence of reactions occurs during photo-oxidative degradation whenever a covalent bond is cleaved homolytically:

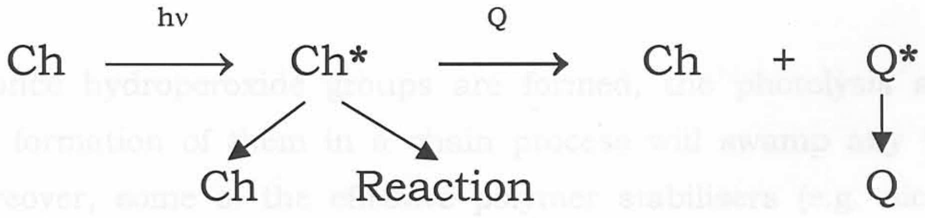
$$R^{\bullet} + O—O \rightarrow R—O—O^{\bullet}$$

$$R—O—O^{\bullet} + R'—H \rightarrow R—O—O—H + R'^{\bullet}$$

Since polymeric hydroperoxides absorb in the near ultraviolet, this group will usually be a significant chromophore. Thus, photodegradation should be reduced if stabilising additives can interrupt radical chain reactions. Finally, although initiating chromophores vary from one polymer to the next, Scheme 2.4 indicates that UV stabilisation can be approached in the same general way for all hydrocarbon polymers.

2.4.2 PHOTOSTABILISATION BY EXCITED-STATE QUENCHING

Following absorption of a photon, a chromophore (Ch) may revert to the ground state by some photophysical processes; it may react; or it can be made to transfer its excess electronic energy to a quenching additive (Q):



If the rate of energy transfer to quencher can compete with reaction by Ch* and if Q* can dissipate the excess energy harmlessly, then the system is stabilised. Energy transfer can occur efficiently only if the energy level of the quencher is below that of the chromophore [8].

One of the more common chromophores in macromolecular systems is the carbonyl group. Not only is it present in the repeat units of many systems (polyesters, polyamides, polyalkyl or aryl vinyl ketones, ethylene, etc), it is also present as a low-level impurity in many "non-absorbing" polymers, frequently as a consequence of thermal oxidation. Absorbers in " non- absorbing" polymers such as PP, PE, PS, PVC, etc. are [9, 10]:

- Peroxides and hydroperoxides
- Carbonyls
- C = C
- Catalyst residues
- O_2 – Hydrocarbon change transfer complexes

Polymeric carbonyl groups absorb UV radiation and an electronically excited C = O will cause bond-breaking breaking reactions when it undergoes a Norrish – type process [8-10]. In principle, a quenching additive should impart photostability to a wide variety of polymer types. During the light deterioration of polymeric materials, singlet molecular oxygen can be formed by the interaction of atmospheric oxygen with electronically excited chromophores. If this occurs, the singlet oxygen $^1O_2$ will interact with the carbon – carbon unsaturated present in many polymers to form hydroperoxide groups by the "ene" mechanism [12].

Note that once hydroperoxide groups are formed, the photolysis and subsequent formation of them in a chain process will swamp any $^1O_2$ effects. Moreover, some of the effective polymer stabilisers (e.g. nickel chelates, amines) will, among other things, quench singlet oxygen.

There is good evidence that hydroperoxides, formed in polymers through inadvertent thermal oxidation during processing, are significant

chromophores in the photodegradation of polyolefins [39], polyvinyl chloride [1], polystyrene [40], and possibly polyamide [41].
Further more, formation and photolysis of hydroperoxides are important in the photodegradation of at least one strongly absorbing polymer, poly(ethylene terephtalene) [42].

It is obvious from Scheme 2.4 that hydroperoxides will be significant in the photo-oxidation of any hydrocarbon polymer, owing to the sequence:

$$R^{\bullet} + O{-}O \rightarrow R{-}O{-}O^{\bullet} \xrightarrow{R'H} R^{\bullet} + R{-}O{-}O{-}H$$

$$\xrightarrow{h\nu} R{-}O^{\bullet} + H{-}O^{\bullet}$$

Effective photostabilisation must cope with this chain reaction in one of the following ways. One can not quench an electronically excited hydroperoxide (after it has absorbed a photon) because the first excited state is dissociative. There are additives, however, which can catalyse the decomposition of hydroperoxides and thus reduce the rate of photoinitiation, at least for “non-absorbing” polymers.

A truly universal feature of the deterioration of all hydrocarbon polymers is the homolytic cleavage of covalent bonds (Scheme 2.4). Inevitably there will be a profusion of radicals (including alkyl, peroxyl, alkoxyl, hydroxyl) regardless of the photoinitiating species; and one or more of these reactive radicals will be involved in a kinetic chain – carrying sequence that perpetuates photodegradation. Free radical scavenging is important in the UV stabilisation of polymer [40] and it can lower the rate of photo-oxidation by irradiating hydroperoxidised polymer film into which scavenging additives have been diffused [22].

Efforts have been made to identify the mechanism(s) by which hindered amines derived from piperidine provide such effective UV stabilisation for a number of polymers [43, 44]. It is generally agreed that the starting structure of the additive is altered during UV exposure [45]:

$$=\mathrm{N}-\mathrm{H} \xrightarrow[\mathrm{O_2}]{\text{Radicals}} =\mathrm{N}-\mathrm{O}^{\bullet} \xrightarrow{\mathrm{R}^{\bullet}} =\mathrm{N}-\mathrm{O}-\mathrm{R}$$

A low level ($\cong 10^{-4}$ M) of nitroxide (nitroxyl) radical persists until brittle failure of the irradiated polymer film occurs.

The $=\mathrm{N}-\mathrm{O}-\mathrm{R}$ entity reacts with peroxyl radicals to interrupt the degradative chain – reaction sequence and to regenerate nitroxide radicals:

$$=\mathrm{N}-\mathrm{O}-\mathrm{R} + \mathrm{R}-\mathrm{O}-\mathrm{O}^{\bullet} \rightarrow =\mathrm{N}-\mathrm{O}^{\bullet} + \mathrm{R}-\mathrm{O}-\mathrm{O}-\mathrm{R}$$

It may be that this reaction is quite efficient because of the relatively long half -life of peroxy radicals.

2.5 FUNCTIONAL ADDITIVES FOR POLYMERS

2.5.1 INTRODUCTION

Functional additives are chemical agents that are added at relatively low dosage levels to a system in order to achieve a desired effect. As polymers find new applications, they face increasingly stringent requirements regarding their service life, durability, and many other properties. A variety of approaches are taken to meet these requirements. One approach is to modify the chemistry of the macromolecules from which polymers are made (e.g., by using new monomers or copolymerisation). Current developments in the area of polymer blends also offer a great deal of scope for innovation. Another important way of improving the properties of plastics is to employ additives. These agents have made a decisive contribution to the widespread use of polymers and promise to be useful tools for solving future problems.

Polymer additives can be classified into three main groups [4, 18, 19, 36, 37, 38, 45]:

(i)- **Additives that stabilise polymers against degradation and aging processing during use**. Degradation usually involves chain cleavage of the macromolecules and can proceed through the addition of energy (e.g., shear forces, heat, UV light) or chemical attack (e.g., oxidation, hydrolysis). These additives are called antioxidants, light stabilisers, or heat stabilisers.

(ii)- **Additives that facilitate or control processing** (e.g., lubricants, mold-release agents, or blowing agents).

(iii)- **Additives that impart new, desirable qualities to polymers**, such as resistance to burning, transparency or color, improved mechanical or electrical properties, dimensional stability, and degradability. Such additives include flame retardant, fillers, dyes, pigments, antistatic agents, nucleating agents, optical brighteners, impact modifiers, and plasticisers. The concentration of additives varies greatly, ranging from a few parts per million for some stabilisers to more than 50 % for certain flame retardants or fillers.

Although additives can be added to the monomer prior to polymerisation, they are usually introduced immediately after polymerisation, blended, and extruded to form granular (pelletised) products and compounds. Polymers generally contain many additives. Preblended additive systems and combination masterbatches are commercially available; they contain optimal proportions of additives that are mutually compatible or have a synergistic action.

2.5.2 PHYSICAL PROPERTIES OF ADDITIVES

Polymer additives are primarily responsible for enhancing the properties and performance of commodity polymers. Loss and migration of additives are a major concern because of adverse effects on polymer performance and durability [37].

The secondary bonding forces present in polymers, e.g. Van der Waals and dipole – dipole forces, are identical to those present in small molecules. In polymers, however, all the types of electrostatic forces can be present and acting between different parts of the same molecule. The strength of these bonds increases with increasing polarity. Van der Waals forces are the weakest type of intermolecular bonds found in polymers. Linear, non-polar polymers, such as polyethylene, that have only Van der Waals attractions between the chains, must have relatively high molecular weights. It should not be too surprising that many commercial polymers contain polar functional groups that provide stronger dipole-dipole interactions between the chains. Ester groups are common pendant substituents. Polar ester linkages are also incorporated in many polymer chains [25, 37, 54].

An efficient additive should be soluble in the polymer to be stabilised. The efficient stabiliser should be able to diffuse easily throughout the polymer matrix. However, the diffusion rate should be optimal i.e. providing a sufficient mobility of the stabiliser while keeping the physical losses low [54]. Solubility of the stabiliser in the polymer will determine how many additives can exist in the matrix at equilibrium. The solubility depends on both the interactions between the small molecule and the polymer and on the physical states of the polymer and additive. Linear polymers are only soluble in solvents that have the solubility parameters very close to their own (like dissolves like) [25].

The criteria for effective additives depend not only on intrinsic additive activity, but also on the parameters that affect permanence, the most important of which are solubility and the ability of the additive to stay in the polymer (low volatility). In general, additives are less soluble in macromolecules than in lower molecular weight analogues. At concentrations greater than their equilibrium concentration additives may diffuse to the surface of the polymer, where they may deposit on the surface (blooming) and be subsequently lost [37].

2.5.3 ULTRAVIOLET STABLE ANTIOXIDANTS

Antioxidants prevent or retard the auto-oxidation of polymers and minimise associated damage (e.g., discoloration, reduction in gloss, cracking, and embrittlement); i.e., they stabilise the physical properties of polymers. Oxidation reactions generally proceed via different mechanisms that depend on the structure of the polymer. Catalyst residues and contaminants often catalyse them. They are also accelerated by the addition of thermal or mechanical energy during polymer production and processing.

Three forms of stabilisation are used: prestabilisation, stabilisation during processing and long-term stabilisation. Most antioxidants are themselves oxidised and consumed in performing their function, so that the oxidation behaviour of the additive in a given polymer is crucial for its effectiveness. A number of other requirements apply to antioxidants [12]:

I- They must be thermally stable and non-volatile at processing temperatures.
II- They must be soluble in polymers and no chalking should occur at service temperatures.
III- They must not have an intrinsic colour, and their oxidation products must have minimal colour.
IV- Any acidic hydrolysis products must not corrode machinery.

V- They must resist extraction.
VI- They must be odourless and tasteless.
VII- They must not create toxicity problems.

Antioxidants act by interrupting the degradation process (See Scheme 2.4). They trap the free radicals (primary antioxidants) formed in the polymer, reduce hydroperoxides to alcohols (secondary antioxidants) and deactivate trace metals by complexation (metal deactivators). A commonly encountered classification is:

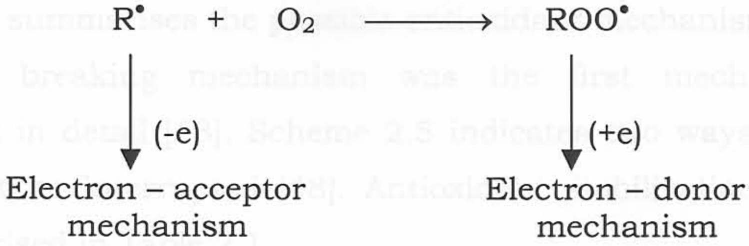
- **Primary antioxidants (HA) typically are hydrogen donors**. They function by a chain breaking mechanism by terminating the propagation reaction. However, they also permit the chain initiating hydroperoxide to be regenerated. They are generally consumed in the stabilisation process.

- **Secondary antioxidant (D) decompose hydroperoxides to non-radical products**. As these are the root cause of oxidative degradation, they represent an ideal case. They often operate by a catalytic mechanism.

In summary, the two basic mechanisms can be represented as following:

Primary: $ROO^{\bullet} + AH \rightarrow ROOH + A^{\bullet}$
Secondary: $ROOH + D \rightarrow$ non radical products

Ultraviolet stable antioxidants operate by inhibiting the propagation processes in the oxidative chain. Scott [47] has classified antioxidants into two types, namely kinetic chain breaking (radical scavengers) and initiation preventive (hydroperoxide decomposers). The first type embraces the aromatic amines and the phenols, and the second includes the transition metal complexes.



Scheme 2.5. Chain – breaking mechanism

Table 2.1. Antioxidant stabilisation mechanisms.

STABILISER TYPE	MECHANISM	EXAMPLES
Radical scavengers	Convert active free radicals into non – reactive ones	Sterically hindered phenolics aromatic amines
Peroxide decomposers	Remove hydroperoxides as potential sources of oxidation initiators	Divalent Sulphur compounds (Sulphides/thioethers) Trivalent phosphorus compounds (phosphites, phophonites)
HALS	Trap alkyl and peroxy radicals	Hindered amines
Synergism	Combination of primary and secondary antioxidants often provide improved stabilisation	- Phenols plus Sulphides - Phenols plus Phosphites
Antagonism	Under certain circumstances, combination of antioxidants may also result in decreased stabilisation.	-HALS and Thioethers

Scheme 2.4 summarises the possible antioxidant mechanism routes. The chain breaking mechanism was the first mechanism to be investigated in detail [48]. Scheme 2.5 indicates two ways in which the chain might be interrupted [48]. Antioxidant stabilisation mechanisms are summarised in Table 2.1.

2.5.4 LIGHT STABILISERS

Synthetic and natural polymers vary in their sensitivity to environmental influences. Ultraviolet radiation in sunlight plays a critical role because it has sufficient energy to break chemical bonds. The cleavage sites react with atmospheric oxygen and accelerate degradation (free – radical chain reactions). Many polymers therefore suffer yellowing, surface cracking, embrittlement, reduction of gloss, or chalking after a short time in outdoor service, and ultimately disintegrate. Light stabilisers are used to maximise protection against photodegradation [19, 49].

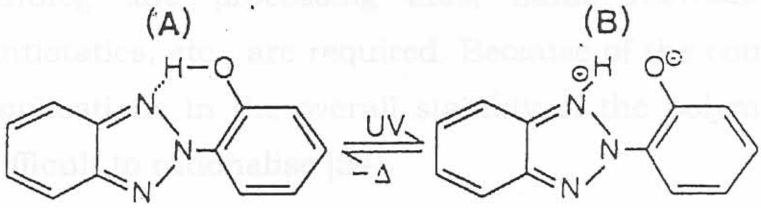
Ultraviolet radiation is subdivided into UV – A (λ = 320 – 400 nm), UV – B (λ = 280 – 320 nm), and UV – C (λ < 280 nm). Only UV – A and UV – B reaches the Earth's surface in sunlight, and UV – B is largely responsible for the degradation of polymers. Polymers are generally fairly stable in the long – wavelength UV – A (350 – 400 nm). Most polymers are sensitive to wavelengths of 290 – 320 nm.

Two methods are used to protect polymers against photodegradation: (1) incorporation of light stabilisers in the bulk polymer, and (2) coating with a light - stable or light – stabilised material that is largely opaque to the dangerous UV range.

Light stabilisers must have light absorption; must resist extraction with water, hydrolysis, and thermal volatilisation; and they must be stable toward UV radiation. Ideally, a light stabiliser should not be consumed while carrying out its function; it should operate in a closed cycle so that it still exists in active form even after a long period of weathering or use [50]. Other requirements include solubility in the polymer, stability under processing conditions, compatibility with other additives, and colourlessness.

Light stabilisers can more than double the service life of a polymer. Modern systems extend service life by a factor of 10 – 20 in many polymers, thus permitting their outdoor use [27, 45].

The first thrust of light stabiliser development was the inhibition of the photoinitiation processes. Thus additives were incorporated into the polymers that absorb UV light energy or quench the photo – excited states of the chromophores. The excited state quenchers return excited states of the chromophores on the polymer chains to their ground state by means of an energy transfer process. The UV absorber instead competes with the chromophores for the damaging UV radiation. In the ideal case the UV radiation is preferentially absorbed by UV absorber and then dissipated harmlessly as heat. UV absorbers do not themselves rapidly degrade because through a process known as tautomerism, they convert UV energy into harmless heat energy (Scheme 2.6).



Scheme 2.6. Tautomerism of a typical UV absorber [49]

Both tautomeric forms A and B have the same atoms and the same molecular weight; they only differ in the way the electronic bonding is arranged. Moreover, they are in equilibrium. The absorption of UV energy by molecule A results in the formation of the molecule B, which through the dissipation of heat energy, reverts to the original form, molecule A. This process can be repeated many times.

For UV absorbers to effectively screen a polymer, an exact matching of the absorption maximum of the UV absorber with those wavelengths at which the polymer concerned is most photosensitive is a prime consideration. But other requirements such as heat stability, volatility, effect of colour and synergistic effects with other additives must also be taken into account.

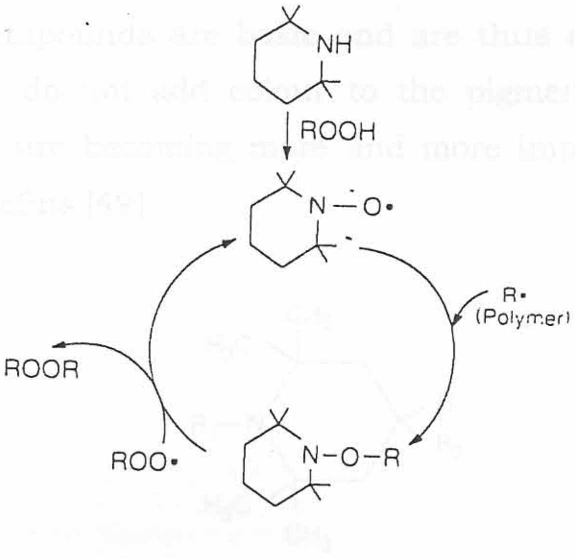
Hindered Amine Light Stabilisers (HALS) represents an important class of inhibitors of the photo-oxidation of polymers that are especially efficient in polyolefins [43, 51-54]. During the last 20 – 25 years many authors have published papers on their mechanism of action, the interaction with other stabilisers (phenolic antioxidants, phosphites, thioethers, etc.) and their mechanism of action is not yet fully elucidated [12]. In most of the applications HALS are used jointly with other stabilisers in order to achieve the best stability performances of the final manufactures through all the manufacturing steps. Processing stabilisers such as phenolic antioxidants and phosphites are necessary, together with long-term antioxidants such as thioethers. In some other case additives like, for example, antifog and processing aids, flame retardant, dyes and pigments, antistatics, etc., are required. Because of the complexity of the system, complications in the overall stability of the polymer often arise which are difficult to rationalise [54].

The high efficiency of HALS in some polymers is commonly ascribed to a fortunate combination of several factors [18, 49, 51, 52]:

(i)- first, as polar additives they tend to concentrate in oxidised regions of hydrocarbon polymers where initiation of the photo-oxidation is most likely to occur as a consequence of the photolysis of hydroperoxides and/or ketones;

(ii)- secondly, HALS are oxidised there to stable nitroxy radicals acting as scavengers of alkyl radicals. Formation of N – alkyloxy compounds thus competes with propagation of the oxidative process;
(iii)- last but a key aspect is that the nitroxy radicals can be regenerated from the N – alkyloxy compounds as these react with peroxy radicals. The high efficiency of nitroxy radicals, even at very low steady state concentration, is thus also associated with a new catalytic type of termination involving alkyl and peroxy radicals.

UV stabilisers have been developed which function by radical scavenging and hydroperoxide decomposition mechanisms. In this case the UV stabiliser undergoes chemical reactions with the products of photo – induced polymer degradation. In some cases the UV stabiliser is gradually consumed during this process, in other cases it has been postulated that UV stabiliser forms an active group which interacts with polymer radicals in a cyclic manner decomposing the polymer radical while at the same time regenerating itself. This mechanism has been put forward to explain the effectiveness of Hindered Amine – type (HALS) Stabilisers (Scheme 2.7).



Scheme 2.7. The regenerative mechanism of Hindered Amine – type stabilisers (HALS) [49]

HALS are able to affect in many ways the chemical and physical factors controlling the polymer stability. In 1986 Allen [55] summarised the possible modes of action of HALS as following:

I- Chain breaking donor/acceptor redox mechanism through the nitroxyl/substituted hydroxylamine intermediates.

II- Decomposition of hydroperoxides by the amine during processing.

III- Inhibition of photo - reaction of α, β - unsaturated carbonyl groups in polyolefins.

IV- Reduction in quantum yield of hydroperoxides photolysis.

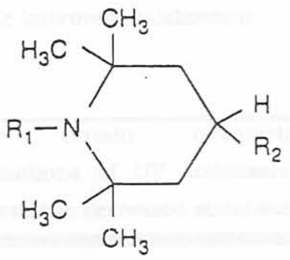
V- Singlet – oxygen quenching (only in polydienes).

VI- Complexation with hydroperoxides/oxygen.

VII- Complexation with transition metal ions.

Each one the above listed actions has been demonstrated to be part of the reaction mechanism of HALS and may contribute, in a complementary fashion, to the overall stabilisation process although the relative relevance can be strongly different for different substrates.

The Hindered Amine Light Stabilisers, which have the characteristic tetramethyl piperidine structure (Scheme 2.8) are the newest type of UV stabiliser and have been proved effective in many applications[56, 57, 58]. HALS compounds are basic and are thus acid sensitive. However, because they do not add colour to the pigment system and are very effective they are becoming more and more important especially in the area of polyolefins [49].



Scheme 2.8. Characteristic structure of HALS compounds [49]

On the other hand, even though HALS compounds undoubtedly represent a major advance in UV stabiliser technology their basicity and reactivity with some additives will limit their usefulness in some applications.

Furthermore synergistic and antagonistic effects with other stabilisers may result in different reaction pathways being activated with suppression of some chemical species or generation of others and drastic changes in the overall results. UV stabilisation mechanism is summarised in Table 2.2.

Table 2.2. UV stabilisation mechanisms

STABILISER TYPE	MECHANISM	EXAMPLES
Ultraviolet Screener	Prevents UV light from reaching the polymer substrate	Reflective or opaque pigments or coatings, carbon black, Zinc Oxide, Titanium dioxide
Ultraviolet Absorber	Filters UV light by absorbing it and dissipating it as heat. Not effective in thin films and fibers	2-hydroxy-benzophenones and 2-hydroxyphenyl-benzotriazoles
Energy Quencher	Deactivate excited states by absorbing energy from excited polymer region and dissipating it as heat	Nickel complexes
Hydroperoxide decomposer	Decomposes hydroperoxides, which can lead to chain splitting and free radical formation, into less harmful species	Transition metal complexes particularly those containing sulphur e.g. metal dithiocarbamates
Radical Scavenger	Scavenges free radicals in a regenerating cycle	Aromatic amines and phenols, hindered amines (HALS) and benzoate esters
Synergism	Combinations of UV stabilisers often provide improved stabilisation	-Nickel quencher plus Absorber -HALS plus benzoate esters -Dithiocarbamates with 2-hydroxyphenones
Antagonism	Under certain circumstances, combinations of UV stabilisers may also result in decreased stabilisation	HALS plus nickel quencher

2.5.5 SYNERGISM AND ANTAGONISM

Synergism occurs when the stabilising effect of a combination of additives in the polymer is greater than the sum of their separate effects [18, 57, 59, 60]. The opposite behaviour is termed antagonism [8-10]. Figure 2.4 shows a typical diagrammatic representation of the synergism and antagonism effects [12].

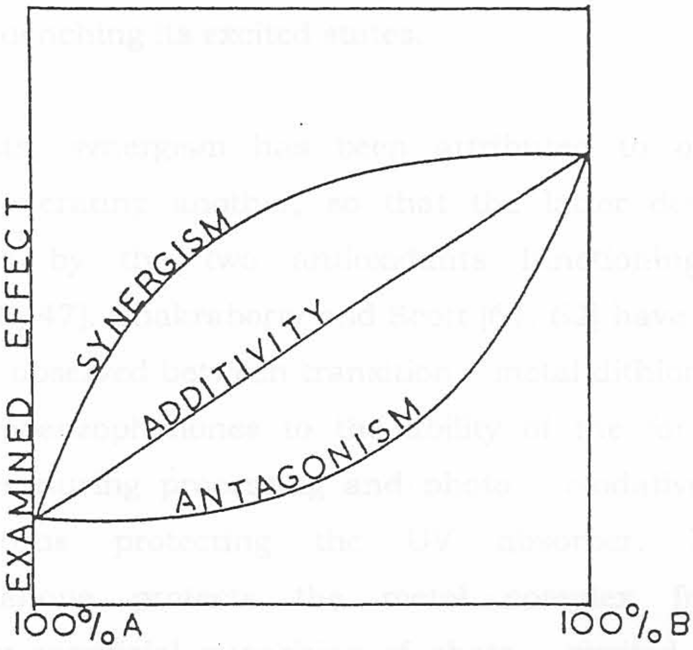


Figure 2.4. Synergism and antagonism effects (After Allen NS and Mc Kellar JF, 1979).

In commercial systems, it may be that, although synergism occurs, one additive may be sufficiently less expensive than the other(s) for more to be used to achieve the required stability and still give the lowest overall cost. Many light stabilisers and antioxidants give synergism. There are two complementary effects here [12]:

1- absorber prevents the antioxidant from photolysis;
2- antioxidant inhibits/destroys POOH which can (via PO· and OH·) attack the absorber.

There are many examples of synergism between ultraviolet stabilisers and antioxidants. This is presumably due to the stabiliser protecting the antioxidant during irradiation so that it may scavenge free radicals or decompose hydroperoxides while the stabiliser also performs its normal function. The light stabiliser may protect the antioxidant by either screening or quenching its excited states.

In antioxidants, synergism has been attributed to one antioxidant effectively regenerating another, so that the latter does not become consumed, or by the two antioxidants functioning by different mechanisms [8, 47]. Chakraborty and Scott [61, 62] have thus attributed the synergism observed between transition – metal dithiocarbamates and the 2 – hydrobenzophenones to the ability of the former to destroy hydroperoxides during processing and photo – oxidative conditions in polyolefins, thus protecting the UV absorber. In turn, the hydrobenzophenone protects the metal complex from photolytic destruction by sacrificial quenching of photo – excited species formed from the metal complex during photo-oxidation.

Synergism is more easily understood when it occurs with two additives which operate by different mechanisms. Thus, powerful antioxidant effects have been observed with chain – breaking antioxidants and peroxide decomposers [63]. In addition to synergism combination of antioxidants, antagonism effects have also been observed [64, 65]. The hindered piperidines show a complex behaviour in combination with other additives [8, 63]. A recent wide ranging survey of phenolic antioxidants and hindered piperidine compounds and their interactions during thermal and photochemical oxidation in both polypropylene and high-density polyethylene has been carried out. During thermal oxidation (oven ageing) the interactions are seen to be synergistic in most cases, whereas on photo-oxidation the majority of the effects are seen to be antagonistic. For high-density polyethylene the effects were also highly synergistic during oven ageing whereas during photo-oxidation the effects were found to be variable, both synergism and antagonism being operative. In many cases the stability of the phenolic antioxidant itself was the determining factor in controlling performance. Synergism thermally and photochemically is probably associated with the fact that the generated nitroxyl and hydroxylamine products from the parent amine are scavenging macroalkyl and macroperoxy radicals and protecting the phenolic antioxidant [12].

2.5.6 FACTORS CONTROLLING THE CHOICE OF STABILISER

If any significant protection is to be derived from an ultraviolet stabiliser then the following factors must be considered [8-12]:

(1)- the stabiliser must be compatible with the polymer: many stabilisers may exude from the polymer during fabrication, storage or irradiation. One effective method of overcoming this problem is to substitute a long aliphatic hydrocarbon chain (alkyl chain) in the stabiliser molecule.
Other ways include – grafting onto polymer chains,
- polymeric stabilisers,
- copolymerisable stabilisers.

(2)- The stabiliser must, of course, be stable to light: despite the high inherent ultraviolet stability of many light stabilisers, their concentrations nevertheless do fall steady during irradiation. Many stabilisers are photolysed early in the degradation process and the products are often better light stabilisers [12].

(3)- The stabiliser must be stable to high temperature processing conditions for sufficiently long periods of time.

(4)- The stabiliser must not react chemically with the polymer.

Other important factors, which have to be considered when choosing a stabiliser, are:
(5)- Low toxicity
(6)- Colour. A coloured stabiliser may often be undesirable.
(7)- cost. Lowest consistent with stabiliser performance.

2.6 PHOTODEGRADABLE POLYMERS

2.6.1 INTRODUCTION

In the early 1960s and 1970s it was realised that sensitised photodegradation could be an effective method of combating environmental pollution by plastic litter [24]. There was awareness that discarded plastics materials posed a potential threat to the environment not only on the land but also the sea. Since then, numerous patents have been filed claiming the use of systems that will accelerate the photodegradation of various plastics and this has led to the new concept of photodegradable plastics [7, 11, 45].

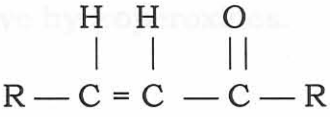
Photodegradable plastics are used for applications where materials are used out-of–doors for a limited time only and it is not economically desirable to collect the residual materials after use. Examples are agricultural cordage and films, packaging films and drinking cups. Although recycling has been considered, it needs to be more effectively implemented. For most thermoplastics recycling results in the formation of inferior products that often end up as fuel. In this respect many of the bulk thermoplastics that end up as waste products are made photo – and/or biodegradable [45].

Many unstabilised plastics such as polypropylene are themselves light sensitive, if ultraviolet deterioration by sunlight exposure is desirable then it is important to be able to control and, indeed, monitor this effect. At present there are two ways of achieving this aim: one is the use of specially prepared photosensitive plastics, and the other, appropriate selection of photoactive additives which are incorporated in the commercial plastic during processing. Presently, many plastic articles such as plastic carrier bags are made to be photodegradable by law, e.g. Italy [12].

2.6.2 PHOTOSENSITIVE PLASTICS

One effective method of preparing photosensitive plastics is to copolymerise the monomer with variable amounts of carbon monoxide or a vinyl ketone monomer. The plastics will degrade when exposed to outdoor sunlight of wavelengths > 300 nm but will remain intact if kept indoors which transmits light above 330 nm. This is because the ketonic groups introduced into the plastics do not absorb light of wavelengths greater than about 330nm. On exposure out-of-doors, where the light also contains radiation in the region 290 – 330 nm, the same ketonic groups are photoactive and can initiate degradation of the polymer by Norrish type – II process [8, 12]. Control of photodegradation is achieved by varying the concentration of carbon monoxide gas or ketone monomer during polymerisation.

Sensitised photodegradation is believed to occur predominantly by the Norrish type – I and II processes involving the 'in-chain' ketone groups [10]. The general structure of a vinyl ketone monomer is:



$$\mathrm{R-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-R}$$

2.6.3 PHOTOACTIVE ADDITIVES

A wide range of derivatives of aromatic aldehydes, ketones and quinones effectively sensitise the photodegradation of polymer [8] and carbonyl compounds were amongst the first such types of structures.

These compounds sensitise through a primary photochemical process of hydrogen atom abstraction from the polymer involving the photo-excited triplet-state of the carbonyl group. A macroradical is formed that initiates the oxidative chain process. The sensitising efficiency of these molecules may be controlled through altering either their concentration or more effectively the nature of the substituents. Variables in the concentrations of these molecules will produce polymers with different life expectancies [8-12].

Apart from the carbonyl – based prodegradants, certain types of transition metal complexes and salts have also been found to be effective as photosensitisers in polymers [8, 11, 12, 64, 65, 66].

It is interesting to note that only the transition metal salts are photosensitisers. Among different transition–metal complexes, iron complexes are particularly favoured because of their low cost and low toxic [12]. Ferric stearate is believed to sensitise by first absorbing light [11], then undergoing electron transfer to give a carboxylic acid free radical. This species then dissociates to give an alkyl radical, which initiates polymer degradation, and carbon dioxide, the former being attached by oxygen to give hydroperoxides.

$$Fe^{3+}(O^{-}{}_2CR)_3 \xrightarrow{h\nu} Fe^{2+}(O^{-}{}_2CR)_2 + {}^{\bullet}O_2CR \rightarrow CO_2 + R^{\bullet}$$

With regard to the factors controlling the rate of photo-oxidation of polymers, the behavior of transition – metal acetylacetonates and dithiocarbamates have been of considerable interest. The photosensitising efficiency of transition – metal acetylacetonates in polyethylene, for instance, decreases in the order Co(III) > Fe(III) > Zn(II) > Ni(II) [12]. The Cobalt(III) complex is very powerful photosensitiser whereas the Nickel(II) complex is a mild photostabiliser. In contrast to the acetylacetonates, the transition – metal dithiocarbamates exhibit a completely different pattern of behaviour. In polyethylene for example, while the Nickel, Zinc and Cobalt complexes are more stable towards ultraviolet light and indeed act as mild light stabilisers, the Iron and Copper complexes are much less stable and act as effective sensitisers [8-12].

One major difference between the two types of complexes is that the acetylacetonates are all much less oxidatively stable and are destroyed rapidly during the processing procedure. Further, the acetylacetonates exhibit no antioxidant activity and this can lead to thermal breakdown of the polymer.

2.7 WEATHERING OF POLYMERS

2.7.1 INTRODUCTION

The increased outdoor use of polymers has created a need for a better understanding of effect of the environment on polymeric materials. The environmental factors have significant detrimental effects on appearance and properties. The severity of damage depends largely on factors such as the nature of the environment, geographic location, type of polymeric material, and duration of exposure [63, 67, 68, 69]. The effect can be anywhere from a mere loss of colour or a slight crazing and cracking to a complete breakdown of the polymer structure. Any attempt to design polymer parts without a clear understanding of the degradation mechanisms induced by the environment would result in a premature failure of the product. The major environmental factors that seriously affect polymers are:

1- Solar radiations – UV, IR, X – rays.
2- Microorganisms, bacteria, fungus, mould.
3- High humidity.
4- Ozone, oxygen.
5- Water: vapour, liquid, or solid.
6- Thermal energy.
7- Pollution: industrial chemicals.

The combined effect of the factors mentioned above may be much more severe than the effect of any single factor, and degradation processes are accelerated many times. Many test results do not include these synergistic effects that almost always exist in real – life situation.

2.7.2 AGEING AND WEATHERING OF POLYMERS

No material is immutably stable. The outdoor weathering of polymers is dependent on many atmospheric factors include light intensity, ambient temperature, humidity and wetness, all of which are in turn subject to seasonal, yearly and location variations [22].

The processes of metallic corrosion have their counterparts in the science of polymers. Even the mildest of human environments may be extremely aggressive to a synthetic material. To compensate for this, the resistance to what are ordinarily regarded as highly corrosive, substances may be excellent. Each application and each material must be considered carefully and objectively. Almost all polymers age at a significant rate unless steps are taken to stabilise them. In some cases the rate of deterioration of commercial formulations may set surprisingly short limits on the excepted lifetime.

Loss of appearance frequently occurs long before the component becomes functionally unserviceable. Quite reasonably the designer and the consumer seek reliable information on durability from materials suppliers. Polymer scientists and technologists have studied intensively the problems of predicting weathering performance [67-72].

The natural environment is enormously varied. Weathering is the result of exposure of polymers to conditions under which thermal oxidation and photo-oxidation may proceed simultaneously; and in addition the effects of water, abrasion and atmospheric pollution need to be evaluated. Microclimates may vary even over small distances, and features of the component such as its surface – to – volume ratio and the aspect of its surfaces may strongly influence weathering.

It is of course impossible to obtain information on long – term weathering performance quickly. Many possible methods of accelerated testing have been advocated. Testing machines range from crude devices (in which, for example, test samples are simply exposed to high intensity visible/ultraviolet radiation) to elaborate environment simulators. Inevitably, however, the process of photodegradation are somewhat distorted by the intensification of the environmental conditions, the greater the acceleration the less the reliability [15, 22]. Despite this, accelerated test methods are widely employed and for limited extrapolations may be useful.

The degradation rate of polymers depends markedly on the intensity and energy distribution of the solar spectrum in the ultraviolet region, both of which vary with the season [22].

2.7.3 ACCELERATED WEATHERING TESTS

Most data on the ageing of polymers are acquired through accelerated tests and actual outdoor exposure. The latter being a time – consuming method, accelerated tests are often used to expedite screening the samples with various combinations of additive levels and ratios. A variety of light sources are used to simulate the natural sunlight. The artificial light sources include carbon arc lamps, xenon arc lamps, fluorescent sun lamps, and mercury lamps. These light sources, except fluorescent, generate a much higher intensity light than natural sunlight. Quite often, a condensation apparatus is used to simulate the deterioration caused by sunlight and water as rain or dew [21, 22, 71, 72].

There are three major accelerated weathering tests:

1- Exposure to carbon arc lamps.
2- Exposure to xenon arc lamps.
3- Exposure to fluorescent UV lamps.

2.7.4 PHOTODEGRADATION TESTS

When new materials are developed it is often important to determine how durable they will be when exposed to the weather. Will they chalk, haze, craze or peel? Or will they retain a reasonable percentage of original appearance and physical properties. Today, it is not important to wait a year or two for outdoor exposure tests to show whether the latest "improved" formulation is really an improvement. In these times, there is the need of weatherability data in a matter of weeks, not years [10].

Three crucial concepts provide the key to successful accelerated weathering in the laboratory [73]:

1- It is not necessary to simulate the full spectrum of sunlight in order to simulate the UV effects of sunlight. In fact, the best approach is to reproduce just the lowest part of the UV region, i.e. the UV – B range.
2- The most stringent way to simulate the effect of humidity is to use hot condensation. Not water immersion, high humidity, spray or fog but condensation, and condensation at elevated temperature at that.

3- The effects of UV and condensation are further enhanced by elevating the test temperature.

The Q.U.V accelerated weathering tester has been designed to meet the requirements of the above concepts.

2.7.5 ASSESSMENT OF WEATHERING

Prediction of the weathering performance or service life of a polymer formulation may also be very dependent on the technique used to measure the rate of degradation [9, 10]. Therefore, the criterion used to assess weathering performance will depend heavily on the end – use of the polymer formulation.