

Additives for Plastics

7.1 INTRODUCTION

The bulk properties of a polymer can often be altered considerably by the incorporation of additives. Probably the most well-known examples of this occur in rubber technology where variations in the choice of additives can produce such widely differing products as tyres, battery boxes, latex foam upholstery, elastic bands and erasers. It is also possible to achieve variations as extensive as this amongst plastics materials, in particular with PVC from which rigid rainwater piping, baby pants, conveyor belting, footballs and domestic insulating flex may all be prepared.

In some cases an additive may be encountered in a variety of polymers for a wide range of end uses, for example certain antioxidants. In other instances the additive may be very specific to a certain polymer for a particular end use.

Physically, additives may be divided into four groups, solids, rubbers, liquids and gases, the last of these being employed for making cellular polymers. In terms of function there are rather larger numbers of groups, of which the following are the most important:

- (1) Fillers.
- (2) Plasticisers and softeners.
- (3) Lubricants and flow promoters.
- (4) Anti-aging additives.
- (5) Flame retarders.
- (6) Colorants.
- (7) Blowing agents.
- (8) Cross-linking agents.
- (9) Ultraviolet-degradable additives.

In general, additives should have the following features unless by virtue of their function such requirements are excluded:

- (1) They should be efficient in their function.
- (2) They should be stable under processing conditions.

- (3) They should be stable under service conditions.
- (4) They should not bleed or bloom.
- (5) They should be non-toxic and not impart taste or odour.
- (6) They should be cheap.
- (7) They should not adversely affect the properties of the polymer.

Most of the above requirements are self-explanatory but the phenomena of bleeding and blooming require some discussion. *Bleeding* of an additive into an adjacent material occurs when the additive has a degree of solubility in the polymer into which it is incorporated and also in the adjacent material, which could be liquid or solid. Such bleeding could colour or otherwise contaminate the adjacent material. When conditions causing bleeding are fulfilled the rates of bleeding will be covered by the laws of diffusion. It will therefore depend on the size of the 'holes' in the polymer, and on the size of the diffusing molecules and on the concentration of these molecules in the original polymer. It is not surprising to find that bleeding is much more extensive from polymers which are above their T_g (and melting point T_m if crystalline) than from polymers below this temperature. It is also quite common practice to replace small molecules, with a propensity to bleed, with larger molecules of similar structure in order to reduce the effect.

Blooming is a separate phenomenon but is again associated with solubility. It occurs when an additive has totally dissolved in the polymer at the processing temperature but is only partially soluble at ambient temperature. As a result some of the additive is thrown out of solution on cooling and some of this may collect on the surface of the polymer mass. If the additive is only partially soluble at the processing temperature the residual material may form nuclei around which the additive molecules, which are thrown out of solution, can congregate so that much less of the additive will bloom on to the surface. It is also possible that another additive might form suitable nuclei in each of the two above instances. Blooming will not occur either if the additive is totally insoluble at processing temperature or if it is totally soluble at room temperature. It should be pointed out that solubility should be considered with respect to the polymer compound as a whole, including, for example, plasticisers and lubricants and not just to the polymer itself.

Table 7.1 summarises the blooming expectancies of additives in polymer compounds but it should be stressed that there may be exceptions to these very general rules.

Table 7.1 Blooming in polymer compounds

Example	Concentration of additive	Solubility at ambient temperature	Solubility at processing temperature	Expected effect
1	x	0	0	No blooming
2	x	$<x$	$<x$	No blooming
3	x	$<x$	$>x$	Blooming unless nucleated <i>in situ</i> by another additive
4	x	$>x$	$>x$	No blooming

7.2 FILLERS

The term filler is usually applied to solid additives incorporated into the polymer to modify its physical (usually mechanical) properties. Air and other gases which could be considered as fillers in cellular polymers are dealt with separately. A number of types of filler are generally recognised in polymer technology and these are summarised in *Figure 7.1*.

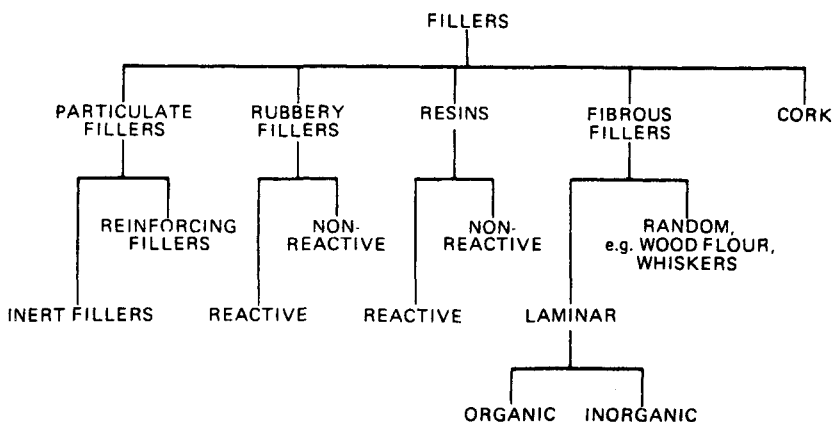


Figure 7.1. Classification of fillers in polymer compounds

Particulate fillers are divided into two types, 'inert' fillers and reinforcing fillers. The term *inert filler* is something of a misnomer as many properties may be affected by incorporation of such a filler. For example, in a plasticised PVC compound the addition of an inert filler will reduce die swell on extrusion, increase modulus and hardness, may provide a white base for colouring, improve electrical insulation properties and reduce tackiness. Inert fillers will also usually substantially reduce the cost of the compound. Amongst the fillers used are calcium carbonates, china clay, talc, and barium sulphate. For normal uses such fillers should be quite insoluble in any liquids with which the polymer compound is liable to come into contact.

It is important to stress that with each chemical type of filler a number of grades are usually available. Such grades may differ in the following ways:

- (1) Average particle size and size distribution.
- (2) Particle shape and porosity.
- (3) Chemical nature of the surface.
- (4) Impurities such as grit and metal ions.

When employed in elastomeric systems it is commonly observed that the finer the *particle size* the higher the values of such properties as tensile strength, modulus and hardness. Coarser particles will tend to give compounds less strong than compounds with the filler absent, but if the particle size is sufficiently fine there is an enhancement in the above-mentioned properties (at least up to an optimum loading of filler) and the phenomenon is known as reinforcement. The *particle shape* also has an influence; for example, the somewhat plate-like china

clay particles tend to be oriented during processing to give products that are anisotropic. Other particles tend to have an uneven surface and are difficult to wet with polymer whilst others are porous and may absorb other additives and render them ineffective.

The *chemical nature* of the surface can have a vital effect. Mineral fillers often have polar groups, for example hydroxyl groups, on the surface which render them attractive to water but not to organic polymer. To improve the wetting of polymers to fillers and hence obtain better products mineral fillers are often treated. For example, calcium carbonate may be treated with stearic acid, the acid group attaching itself to the filler particles whilst the aliphatic chain is compatible with the polymer. Some clays are amine-treated whilst others are coated with a glycol or similar product. Besides improved wetting such treatment can have a second function. Surface hydroxyl groups tend to H-bond to other additives such as antioxidants and some cross-linking components, making them ineffective. Preferential absorption by a less expensive additive such as a glycol can give much improved results. The most recent developments are *coupling agents* such as certain silanes which in effect form a polymer shell around the surface of the particle and improve the wetting to the main polymer. These are discussed further in the next section.

Impurities in mineral fillers can have serious effects. Coarse particles (grit) will lead to points of weakness in soft polymers which will therefore fail under stresses below that which might be expected. Traces of copper, manganese and iron can affect the oxidative stability whilst lead may react with sulphur-containing additives or sulphurous fumes in the atmosphere to give a discoloured product.

Reinforcing particulate fillers are effective primarily with elastomers although they can cause an increase in tensile strength with plasticised PVC. Pure gum styrene-butadiene rubber (SBR) vulcanisates have tensile strengths of about 3 MPa. By mixing in 50 phr of a reinforcing carbon black the tensile strength can be increased to over 20 MPa. In a crystalline rubber such as natural rubber such large increases in tensile strength are not observed but as with SBR an increase in modulus, tear resistance and abrasion resistance can be seen. It is often found that a property such as tensile strength usually goes through a maximum value with change in carbon black loading. At first the increase in polymer-black interfacial area is the dominating effect but if the black concentration becomes too high the diminishing volume of rubber in the composite is insufficient to hold the filler particles together. In general reinforcement appears to depend on three factors:

- (1) An extensity factor—the total amount of surface area of filler per unit volume in contact with the elastomer.
- (2) An intensity factor—the specific activity of the filler-polymer interface causing chemical and/or physical bonding.
- (3) Geometrical factors such as structure (aggregation) and porosity of the particles.

For equivalent particle size the carbon blacks are the most powerful reinforcing fillers. However, fine particle size silicas can be very useful in non-black compounds whilst other fillers such as aluminium hydroxide, zinc oxide and calcium silicate have some reinforcing effect.

Rubbery materials are often incorporated into rigid amorphous thermoplastics to improve their toughness but it is a moot point whether or not they should be

referred to as *rubbery fillers*. Attempts were made in Chapter 3 to explain the mechanism by which such materials functioned. Well-known examples are SBR and polybutadiene in polystyrene, butadiene–acrylonitrile rubbers in PVC and ethylene–propylene rubbers in polypropylene. These materials will be discussed further in the appropriate chapters.

Whilst the plastics technologist may incorporate rubber into his resins or plastics materials the rubber technologist often incorporates *synthetic resins* or *plastics* into his rubbers. Butadiene–styrene resins containing at least 50% styrene may be blended with rubber to produce compounds for shoe soles and for making car wash brushes. Phenolic resins which have a low viscosity at processing temperatures may enhance the flow and hence processability of rubber compounds but during the vulcanisation of the rubber will simultaneously cross-link, leading to a comparatively rigid product.

Fibrous fillers have been long used in plastics materials. Wood flour, cotton flock, macerated fabric, macerated paper and short lengths of synthetic organic fibres such as nylon can improve the impact strength and often the rigidity and toughness of moulding compositions. Inorganic fibres such as asbestos and glass fibre are also used in moulding compositions, both thermoplastic and thermosetting, where heat resistance and strength respectively are required. More recently, chopped carbon fibre and whiskers (single crystals of high length–diameter ratio of very high strength) have been used for highly specialised purposes.

Fibrous fillers are often embedded in a laminar form. The fibres used have higher moduli than the resins in which they are embedded so that when the *composite* of resin plus fibre is strained in the plane of the fibrous layer the bulk of the stress is taken up by the fibre. This results in an enhancement of both strength and modulus when compared with the unfilled resin.

As a general rule woven fabrics give higher figures for strength and moduli than papers and mats, an exception occurring with asbestos mats. Of the woven fabrics in common use, those from glass fibres suitably treated to ensure good wetting give the highest strength. Exceptionally high tensile strengths can sometimes be obtained using carbon fibres but the resulting laminates have a low interlaminar strength. Attempts to improve on this by stitching between layers with carbon fibre have been described. Fibrous fillers are dealt with in further detail in the chapters on phenolics, aminoplastics and polyesters.

7.2.1 Coupling Agents

A filler cannot be used to best advantage in a polymer unless there is good adhesion between them. In particular the filler particle–polymer interface will not be stress-bearing and therefore provides a point of mechanical weakness.

One way of improving the adhesion between polymer and filler is to improve the level of wetting of the filler by the polymer. One approach, which has been used for many years, is to coat the filler with an additive that may be considered to have two active parts. One part is compatible with the filler, the other with the polymer. Probably the best known example is the coating of calcium carbonate with stearic acid. Such coated or ‘activated’ whittings have been used particularly with hydrocarbon rubbers. It is generally believed that the polar end attaches itself to the filler particle whilst the aliphatic hydrocarbon end is compatible with the rubbery matrix. In a similar manner clays have been treated with amines.

A much more positive attempt to increase the adhesion between polymer and filler was to link them by covalent bonds using *coupling agents*. The earliest of these were the methacrylato-chrome chloride coupling agents introduced in the mid-1940s. These materials were used primarily in conjunction with glass fibres and marketed as Volan or, later, Volan A treatments for use in polyester-glass reinforced plastics. They were believed to react as shown in *Figure 7.2*. Chemical bonding to the surface of the glass fibre occurs through Cr—O—Si links. Bonding to the unsaturated polyester resins occurs via a polymerisation reaction involving double bonds in the polyester, in styrene monomer present as diluent and in the methacrylato groups present in the coupling agent. Reaction is also sometimes possible with saturated polymers via the hydroxyl, CrCl, CrOH and carboxyl groups that are present.

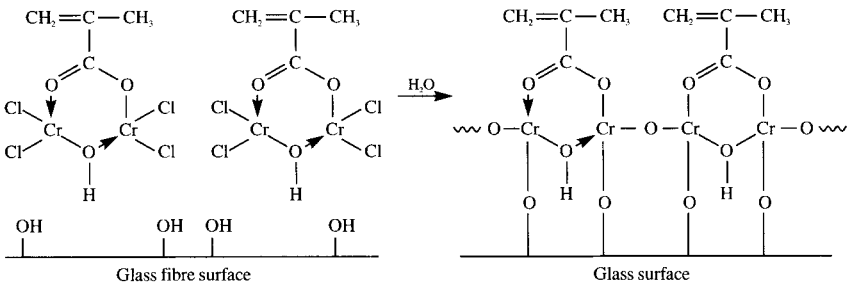


Figure 7.2

The appearance of the methacrylato-chrome chloride treatments was soon followed by glass fibre treatments involving silanes. One of the first such materials was vinyltrichlorosilane. As can be seen in *Figure 7.3* these are joined to the glass via Si—O—Si (siloxane) linkages. As with the chrome complexes the coupling agent may then be linked to an unsaturated polyester resin via the unsaturated vinyl group.

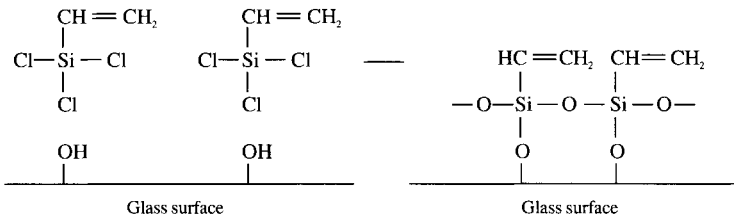
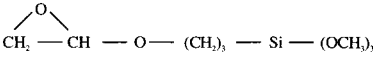
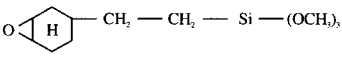
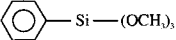


Figure 7.3

For the first few years after their introduction the main use for coupling agents, and one of continuing great importance, was for coupling glass fibre to polyester laminating resins. In due course coupling agents were developed to increase the adhesion of other polymers to glass fibres and, later, to other fillers, particularly particulate fillers and even to other types of additives. For example silane coupling agents with epoxy or amino functional groups were used to couple glass

fibre to epoxide resins and, in some cases phenolics. Coupling agents with mercaptan groups were used in conjunction with diene rubbers. A number of silanes, including some of the above, were also introduced for use with thermoplastics. In many cases the materials were non-reactive but the presence of saturated alkyl, haloalkyl, aryl or haloaryl groups, for example, improved the level of wetting, and hence the adhesion, between polymer and glass fibre. It is a debatable point as to whether such materials should be referred to as coupling agents in these circumstances since covalent bonding to the polymer does not occur. Nevertheless examples of this type are included in *Table 7.2*, which lists some examples of coupling agents.

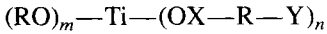
Table 7.2 Examples of silane coupling agents

<i>Name</i>	<i>Composition</i>	<i>Used with</i>
1. Trichlorovinylsilane	$\text{CH}_2 = \text{CH} - \text{SiCl}_3$	Polyester
2. Triethoxyvinylsilane	$\text{CH}_2 = \text{CH} - \text{Si} - (\text{OC}_2\text{H}_5)_3$	Polyester
3. γ -Glycidoxypropyl-trimethoxysilane		Polyester Epoxide M/F P/F
4. γ -Aminopropyltrimethoxysilane	$\text{H}_2\text{N} - (\text{CH}_2)_3 - \text{Si} - (\text{OC}_2\text{H}_5)_3$	Epoxide M/F P/F
5. [β -(3,4-Epoxy-cyclohexyl)-ethyl]trimethoxysilane		Polyester Epoxide Polycarbonate
6. γ -Mercaptopropyl-trimethoxysilane	$\text{HS} - (\text{CH}_2)_3 - \text{Si} - (\text{OCH}_3)_3$	Diene rubbers
7. Trichloromethoxysilane	$\text{CH}_3 - \text{Si} - \text{Cl}_3$	
8. Trimethoxyphenylsilane		

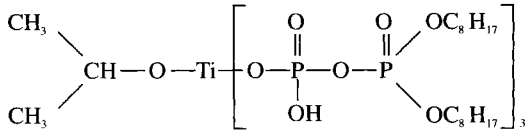
It is perhaps worthwhile observing at this point that it is quite feasible to couple a chemical onto the surface of a material such as glass to *reduce* wetting and hence the level of adhesion by a polymer by incorporating some group incompatible with or even repellent to the polymer.

In the 1960s and 1970s development with coupling agents was extended to use with particulate fillers, in particular silicas, silicates and clays for use in rubber compounds. One useful feature was that the coupling agent could be added during the rubber compounding stage when rubber, filler and other additives were being mixed together. Later, attention turned to fillers in PVC, hydrated alumina fire retarders in unsaturated polyester resins and to fillers such as

calcium carbonate in polypropylene. More recently there has been interest in *titanium coupling agents*. The most important of these have the general form



typified by isopropyl tri(dioctyl pyrophosphate) titanate:



Use of as little as 0.1% of materials of this type on the total formulation can, it is claimed, significantly reduce the viscosity of filled PVC plastisols (see Chapter 12). It is also claimed that when used in polypropylene or high molecular weight polyethylene a '70% loading of titanium-treated calcium carbonate filler gives a product with an impact strength some 7.5 times greater than obtained with untreated polymer'. In addition to improving impact strength the flow properties of the melts of filled polymers are also claimed to be improved. Thus it is reported that a 90% loading of a titanium-treated ferric oxide in polypropylene had similar flow properties to an unfilled polymer.

Another interesting innovation is that developed by the Malaysian Rubber Producers Research Association. In this case the coupling agent is first joined to a natural rubber molecule involving an 'ene' molecular reaction. The complex group added contains a silane portion which subsequently couples to filler particles when these are mixed into the rubber.

7.3 PLASTICISERS AND SOFTENERS

It has been common practice to blend plasticisers with certain polymers since the early days of the plastics industry when Alexander Parkes introduced Parkesine. When they were first used their function was primarily to act as spacers between the polymer molecules. Less energy was therefore required for molecular bond rotation and polymers became capable of flow at temperatures below their decomposition temperature. It was subsequently found that plasticisers could serve two additional purposes, to lower the melt viscosity and to change physical properties of the product such as to increase softness and flexibility and decrease the cold flex temperature (a measure of the temperature below which the polymer compound loses its flexibility).

Today plasticisers are used in a variety of polymers such as polyvinyl acetate, acrylic polymers, cellulose acetate and, most important of all, poly(vinyl chloride).

It was pointed out in Chapter 5 that plasticisers were essentially non-volatile solvents. Consequently they were required to have solubility parameters close to that of the polymer and a molecular weight of at least 300. If the polymer or the plasticisers had a tendency to crystallise then there would need to be some sort of specific interaction between the polymer and the plasticiser. *Tables 5.4 and 5.6* gave some figures for the solubility parameters of polymers and plasticisers.

Of particular interest is the fact that two plasticisers of similar molecular weight and solubility parameter can, when blended with polymers, lead to compounds of greatly differing properties. Many explanations have been offered of which the most widely quoted are the polar theory and the hydrogen bonding theory.

The polar theory suggests that plasticisers do not simply act as spacers but form links, albeit possibly momentary, with the polymer molecules. Dipole interaction is said to occur between a polar group on the polymer molecule, for example a chlorine atom forming part of a carbon–chlorine dipole, and a polar group on the plasticiser, for example an ester group. Where there are links from the plasticiser to two or more molecules a form of polar cross-linking occurs. Some molecules not only contain polar groups but may also contain polarisable groups such as benzene rings which reinforce the polar linkage. A range of plasticisers therefore exist which have varying degrees of polarity and polarisability. It is suggested that it is this difference that accounts for the different effects of the highly polar and highly polarisable tritolyl phosphate and the less polar dioctyl sebacate when used as plasticisers in PVC. The stronger linking of the phosphate tends to affect the spacing effect of a plasticiser so that the resultant compounds have a greater modulus and hardness and higher cold flex temperature than would be expected through a spacing effect alone. With a sebacate the spacing effect is much less offset by any polar linking.

Doubts have been cast as to whether differences in polarity could account for such extensive differences in properties and the hydrogen bonding theory is preferred by many. This suggests that links between plasticiser and polymer are through hydrogen bonds. In the case of PVC the hydrogen on the same carbon as the chlorine atom is activated so that the polymer molecule acts as a proton donor. Certain chemical groups in plasticiser molecules are proton acceptors. In general, phosphates are strong acceptors as also are esters and ethers. Aromatic esters are more powerful acceptors than aliphatic ethers. The intermediate position of general purpose phthalates compared to phosphates and sebacates can be seen in this context.

In the rubber industry hydrocarbon oils are often used to reduce the softness and facilitate the processing of hydrocarbon rubbers. These appear to have a small interaction with the polymer but spacing effects predominate. Such materials are generally referred to as *softeners*. The rubber industry, like the plastics industry, commonly uses the term plasticisers to describe the phthalates, phosphates and sebacates which are more commonly used with the more polar rubbers.

It has already been mentioned in Chapter 5 that plasticisers are often replaced in part by *extenders*, materials which in themselves are not plasticisers but which can be tolerated up to a given concentration in a polymer–plasticiser system. Refinery oils and chlorinated waxes are widely used in PVC for this purpose with the prime aim of reducing cost although the chlorinated waxes may also be of use as flame retardants (q.v.).

7.4 LUBRICANTS AND FLOW PROMOTERS

The term lubricant or lubricating agent is often encountered to describe certain additives incorporated into plastics materials. There are, however, various types

of lubricants with varying functions and it is important to distinguish between them. The three main types are:

- (1) Materials which reduce the friction of mouldings and other finished products when these are rubbed against adjacent materials which may or may not be of the same composition. The most well-known examples here are graphite and molybdenum disulphide used in quantities of the order of 1–2% in nylons and other thermoplastics used in gear and bearing applications.
- (2) Materials which during processing exude from the polymer composition to the interface between the molten polymer and the metal surfaces of the processing equipment with which they are in contact. The resultant thin film layer then helps to prevent the plastics composition from sticking to the machinery and thus in the normal way facilitates processing. Such materials, known commonly as *external* lubricants, have a low compatibility with the polymer and in addition often possess polar groups to enhance their affinity to metals. The choice of lubricant will depend not only on the type of polymer but also on processing temperatures involved. With PVC typical external lubricants are stearic acid and its calcium, lead, cadmium and barium salts, myristic acid, hydrocarbons such as paraffin wax and low molecular weight polythene and certain esters such as ethyl palmitate.

Because by their very nature these materials exude from the polymer mass during processing, problems can occur in their use, particularly if employed to excess (1% is a common maximum figure for PVC external lubricants although in some cases it may be less). For example, the exudation may contain traces of other additives such as colorants which contaminate, colour or stain the processing equipment and hence contaminate subsequent batches of material being processed. This is most common under conditions of high shear and/or pressure such as occurs in high-speed calendering and in the head of an extruder. The presence of such lubricants may also affect clarity and haze of sheet and the ability to print on to or heat seal such sheet. A further possible problem occurs when gelling PVC but this phenomenon will be considered in Chapter 12.

The choice of lubricant for a particular composition and process can be quite critical but beyond stating that such materials will normally be fluid at processing temperature and should have a solubility parameter at least $3 \text{ MPa}^{1/2}$ different from the polymer, little further fundamental guidance can be given and selection is normally made by an empirical trial and error basis.

- (3) The third group of lubricants comprise low molecular weight materials which promote the flow of the polymer in the melt but which unlike plasticisers have little effect on the solid state properties—the term *internal lubricant* has been applied here. Some external lubricants appear also to function as internal lubricants but for this function incompatibility is not a requirement and may be a disadvantage. Amongst internal lubricants used for PVC are amine waxes, montan wax ester derivatives, glyceryl esters such as glyceryl monostearate and long chain esters such as cetyl palmitate. As with external lubricants the choice and amount of lubricant can be highly critical and tests on laboratory scale equipment may well not reflect behaviour on full scale plant.

It has been seen that internal lubricants are essentially low molecular weight flow promoters which, unlike plasticisers, have little effect on the

finished polymer. This realisation has led to the search for other materials, quite different from traditional lubricant-like chemicals, which might function in a similar way with perhaps additional desirable features being conferred on the polymer. This has led to a number of *polymeric flow promoters* being introduced, particularly for PVC. These materials generally have similar solubility parameters to the base polymer but are much lower in viscosity at processing temperature although not necessarily much softer at room temperature. In some cases, however, the additives are somewhat rubbery whilst in other instances, and as with the use of phenolic resin in natural and synthetic rubbers, cross-linking of the flow promoter during moulding can result in an increase in hardness. Polymeric flow promoters have been developed to the greatest extent for unplasticised and often transparent PVC compounds and include certain ethylene–vinyl acetate copolymers, styrene–acrylonitrile copolymers, styrene–methyl methacrylate copolymers and chlorinated polyethylenes. It is interesting that other polymers in these and related classes which are somewhat less compatible with PVC are often used as *impact modifiers*, i.e. to enhance impact strength, for PVC compositions.

7.5 ANTI-AGING ADDITIVES

The properties of most plastics materials change with the passage of time and usually in an adverse manner. These property changes are a result of structural modifications of which there are four main types:

- (1) Chain scission—resulting in a loss in strength and toughness.
- (2) Cross-linking which may lead to hardening, brittleness and changes in solubility.
- (3) Development of chromophoric groups leading to colour formation.
- (4) Development of polar groups such as carbonyl groups in polyolefins causing a deterioration in electrical insulation properties and also changes in chemical activity.

Such structural changes are a consequence of chemical reactions of which the most common are oxidation, ozone attack, dehydrochlorination and ultraviolet attack. (Reactions due to high-energy radiation or to high temperature are not considered here as causing natural aging.) Over the years many materials have been introduced as antioxidants, antiozonants, dehydrochlorination stabilisers and ultraviolet absorbers—originally on an empirical basis but today more and more as the result of fundamental studies. Each of these additive types will be considered in turn.

7.5.1 Antioxidants

The oxidation of hydrocarbons, including hydrocarbon polymers, takes the form of a free-radical chain reaction. As a result of mechanical shearing, exposure of ultraviolet radiation, attack by metal ions such as those of copper and manganese as well as other possible mechanisms, a hydrocarbon molecule breaks down into two radicals



Such hydrocarbon radicals ($R\cdot$) rapidly combine with oxygen to form a peroxide radical



Such a radical will then react with a hydrocarbon by the following propagation reaction



Whilst the $R\cdot$ radical again reacts as in equation (7.2) the hydroperoxide may decompose by the following mechanisms



or react as follows

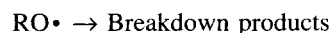


Reactions (7.2), (7.3) and (7.4) form a series of chain reactions, with reaction (7.3) the rate-determining stage. The chain reaction terminates by the reactions



It will be seen that reactions (7.5b) and (7.5c) if they occur more than once per hydrocarbon molecule (radical) will lead to chain extension and, if on average more than twice, to cross-linking.

It is also possible that reactions may occur which cause decomposition of the peroxide radicals by reactions of schematic form

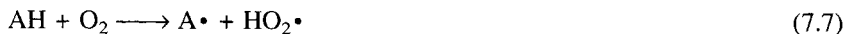


Whether decomposition or cross-linking occurs is therefore a function of both the polymer type and the environmental conditions. If an antioxidant is to function it must interrupt the above reaction sequence. It is usual to recognise two types of antioxidant:

- (1) Preventive antioxidants which prevent the formation of radicals by reactions (7.1) and (7.3).
- (2) Chain-breaking antioxidants which interrupt the propagation cycle by reacting with the radicals $R\cdot$ and $RO_2\cdot$, introducing new termination reactions.

In addition, other additives may exist which react with $R\cdot$ and $RO_2\cdot$, introducing new propagation reactions which lead to a slower chain reaction. Such materials would be referred to as *oxidation retarders*.

In the past the greatest attention has been paid to the chain-breaking antioxidants and oxidation retarders of general structure AH, which may function in the following ways.



Reaction (7.7) is largely pro-oxidant; reactions (7.8a) and (7.8b) are propagation reactions and reactions (7.9a) and (7.9b) termination reactions. For chain breaking, reactions (7.8a), (7.9a) and (7.9b) should be preferred. In cases where reaction (7.8a) is preferred to reaction (7.3) and when (7.8b) is rate determining it is possible for the material to be an effective oxidation retarder.

It will be noticed that with chain-breaking antioxidants the additive will be consumed whilst if we assume that the AO_2H molecule will regenerate $\text{A}\cdot$ radicals the oxidation retarder is not effectively consumed. The difference between the two is illustrated schematically in *Figure 7.4*.

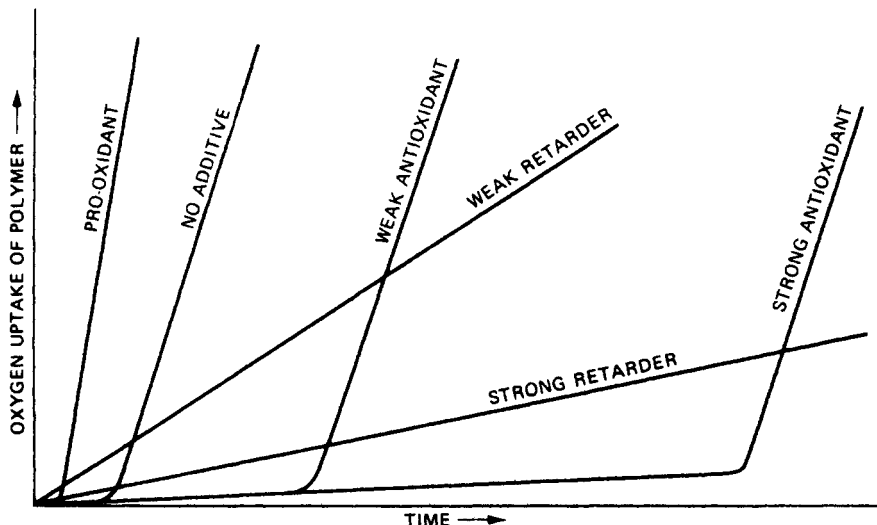


Figure 7.4. Schematic relationship showing effect of pro-oxidants, antioxidants and oxidation retarders on the oxygen uptake of a polymer

The shape of the 'curves' is of some interest. An induction period is noted during which no oxygen uptake, i.e. oxidation, is observed. At the end of this induction period, when in effect antioxidant moieties have been consumed, oxygen uptake is rapid unless some retardation mechanism is at work.

Table 7.3 Main types of chain-breaking antioxidants

<i>Class</i>	<i>Example</i>	<i>Staining</i>	<i>Comments</i>
<i>Amines</i>			
Ketone–amines	Acetone–diphenylamine and acetone–aniline (I)	Yes	Main use in rubber compounds for good heat aging.
Aldehyde–amines	Aldol–naphthylamines	Yes	Not often used. Possibilities of carcinogenic hazard with some types.
Phenyl naphthylamines	<i>N</i> -Phenyl- β -naphthylamine (II)	Yes	Once widely used in rubber industry because of good all-round effect in diene rubbers. Now almost obsolete.
Substituted diphenylamines	4,4'-Dioctyldiphenylamine (III)	Yes	Moderate antioxidants. Some use in polychloroprene rubbers.
Paraphenylene-diamine derivatives	<i>N,N'</i> -Diphenyl- <i>p</i> -phenylenediamine (IV) <i>N,N'</i> -Di- β -naphthyl- <i>p</i> -phenylenediamine (V)	Yes Yes	Powerful antioxidants. Have been used in a variety of plastics materials. Tendency to bloom, bleed and stain mitigates against more extensive use. Compound (V) now withdrawn by some suppliers.
<i>Phenols</i>			
Substituted phenols	4-Methyl-2, 6-di- <i>t</i> -butylphenol (VI)	No	Often used in non-toxic formulations. Very low level of staining. Widely used to protect polymers during synthesis and fabrication. Volatility restricts high-temperature and long-term use.
Phenylalkanes	Bis-[2-hydroxy-5-methyl-3-(1-methylcyclohexyl)phenyl]methane (VII)	Very slight	Most powerful phenolic antioxidants. Widely used in polyolefins and some usage in PVC.
	1,1,3-Tris-(4-hydroxy-2-methyl-5- <i>t</i> -butylphenyl)butane (VIII)	Very slight	
Phenyl sulphides	4,4'-Thiobis-(6- <i>t</i> -butyl- <i>m</i> -cresol) (IX)	Very slight	Not so powerful as phenylalkanes as a class but synergistic with carbon black.
Phosphites	Tris-(<i>p</i> -nonylphenyl) phosphite (X)	No	Widely used in conjunction with conventional stabilisers (q.v.) in PVC. Some types appear to be useful heat and light stabilisers in polyolefins. Function primarily as peroxide decomposers rather than chain-breaking antioxidants.

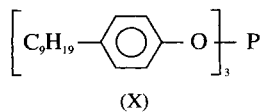
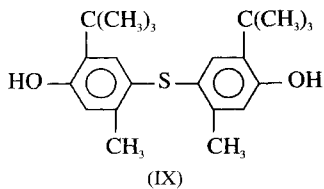
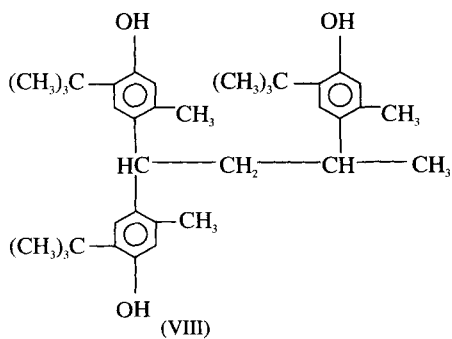
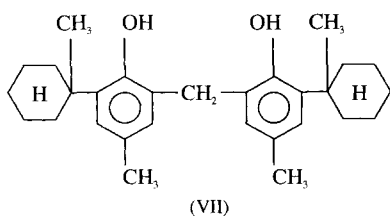
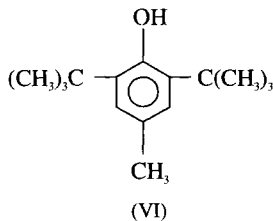
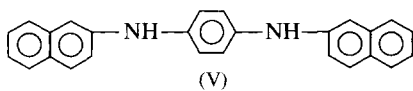
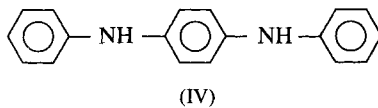
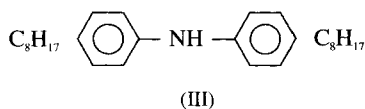
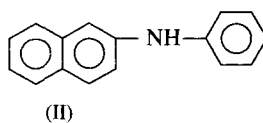
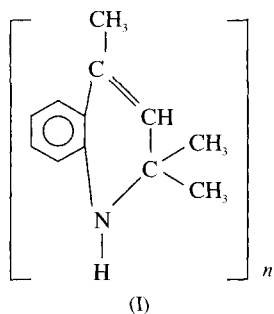


Figure 7.5. Chemical formulae of typical antioxidants referred to in Table 7.3

Table 7.4 Reactions responsible for initiation of autoxidation. (After Scott¹)

Reactant	Radical products				
	Heat	Light	Metal ions		Ozone
			M ⁺	M ⁺⁺	
1. Saturated hydrocarbon RH	$R\cdot + H\cdot$	$R\cdot + H\cdot$	-	$R\cdot$	$RO\cdot + \cdot OOH$
2. Unsaturated hydrocarbon $RCH=CHCH_2R'$	$RCH=CH\dot{C}HR' + H\cdot$	$R\dot{C}H-\dot{C}HCH_2R'$ or $RCH=CH\dot{C}HR' + H\cdot$	-	$R\dot{C}H\dot{C}HCH_2R'$	$RCH=CH\overset{R'}{\underset{ }{C}}HO\cdot + \cdot OOH$
3. Chlorinated hydrocarbon RCl	$R\cdot + Cl\cdot$	$R\cdot + Cl\cdot$	-	-	-
4. Carbonyl compound RCOR'	$RCO + R'\cdot$	$R \begin{array}{l} \diagup \\ \diagdown \end{array} \dot{C}-\dot{O}$ or $R\dot{C}O + R'\cdot$	-	-	-
5. Hydroperoxide ROOH	$RO\cdot + \cdot OH$ $ROO\cdot + \cdot OH + H_2O$	$RO\cdot + \cdot OH$	$RO\cdot$	$RO_2\cdot$	-

In the absence of added radical generators the relatively unstable hydroperoxides, which are themselves generated by the oxidation process, are the major source of chain initiating radicals.

Two main classes of *chain-breaking antioxidant* have been developed over the years, amines and phenols. The latter are usually preferred in polymers because of their lower preponderance to staining, discoloration, blooming and bleeding. Amines are still used, however, particularly in rubber tyres where such disadvantages are outweighed by the favourable cost and high effectiveness of some of these materials. The main types of chain-breaking antioxidants are indicated in *Table 7.3* and *Figure 7.5*. Such materials are used in quantities of the order of 0.02–1%. In excess they may show pro-oxidant tendencies, that is they will facilitate oxidation.

Free-radical initiation of the chain reaction of oxidation can arise from the action of heat, light, metal ions and, sometimes, ozone on a variety of chemical moieties such as those indicated in *Table 7.4*.

Any agent which functions to prevent the formation of radicals by these processes may be considered as a *preventive antioxidant*. In practice three classes are generally recognised:

- (1) Peroxide decomposers.
- (2) Metal deactivators.
- (3) Ultraviolet light absorbers.

Materials that promote the decomposition of organic hydroperoxide to form stable products rather than chain-initiating free radicals are known as peroxide decomposers. Amongst the materials that function in this way may be included a number of mercaptans, sulphonic acids, zinc dialkylthiophosphate and zinc dimethyldithiocarbamate. There is also evidence that some of the phenol and aryl amine chain-breaking antioxidants may function in addition by this mechanism. In saturated hydrocarbon polymers diaryl thiodipropionate has achieved a pre-eminent position as a peroxide decomposer.

Phosphites are also believed to function, at least in part, in this way. Proposed mechanisms for the thio and phosphite compositions are shown in *Figure 7.6*.

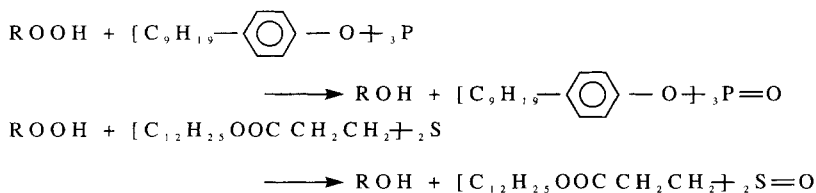
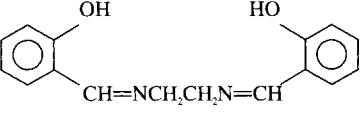
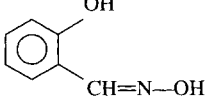
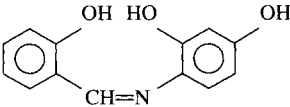
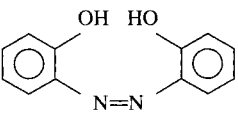
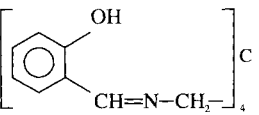


Figure 7.6

Manganese, copper, iron, cobalt and nickel ions can all initiate oxidation. Untinned copper wire can have a catastrophic effect on natural rubber compounds with which it comes into contact. Inert fillers for use in rubbers are usually tested for traces of such metal ions, particularly copper and manganese. The problem is perhaps less serious in saturated hydrocarbon polymers but still exists.

Where there is a danger of contamination of a hydrocarbon polymer with such ions it is common practice to use a *chelating agent* which forms a complex with the metal. It is, however, important to stress that a chelating agent which effectively slows down oxidation initiated by one metal ion may have a pro-oxidant effect with another metal ion. *Table 7.5* summarises some work by

Table 7.5 Catalytic and deactivating effects of ligands on metal-catalysed autoxidation of petroleum. (After Pedersen²)

Metal oleate ($1.6 \times 10^{-8} M$) Chelating agent (0.002%)	Deactivating efficiency, E_D				
	Mn	Fe	Co	Ni	Cu
	-103	-43	-833	-	100
	-	0	-96	100	100
	-84	100	96	-55	100
	-73	100	-	-124	100
	100	100	100	100	100

Pedersen² on the effect of various chelating agents upon the autoxidation of petroleum (a useful 'model' system) catalysed by various transition metals. The deactivating efficiency E_D is the percentage restoration of the original induction period observed with a control sample of petroleum without metal or deactivator. Only N,N',N'',N''' -tetrasalicylidene tetra(aminomethyl)methane was effective against all of the metals, all others having a negative effect with at least one ion.

Amongst other materials sometimes used as deactivators are, 1,8-bis(salicylideneamino)-3,6-dithiaoctane and certain *p*-phenylenediamine derivatives. It is interesting to note that the last named materials also function as chain-breaking antioxidants and in part as peroxide decomposers.

Ultraviolet light absorbers will be discussed in more detail under another section. Suffice it to say that their incorporation into a polymer can provide a useful antioxidant function.

Antioxidants are today often used in combination. One reason for this is that certain combinations can exhibit in a polymer an effect sometimes found with other additives, that known as *synergism*. In these circumstances two antioxidants may exhibit a co-operative effect and be more powerful than either antioxidant used alone, even when the total antioxidant concentration is the same. Certain terms are sometimes encountered here and these are defined in *Table 7.6*.

Table 7.6 Definition of terms associated with combinations of additives

Description of effect	Additive concentration (arbitrary units)		Effect
	[X]	[Y]	
Additive effect	1	—	x
		1	y
	2		$2x$
		2	$2y$
	1	1	$x + y$
Antagonism	1	1	$<(x + y)$
Synergism	1	1	$>(x + y)$
Practical synergism	1	1	$>(x + y)$ and also $> 2x$ and $> 2y$

In commercially practical terms it may be that although synergism occurs, one additive may be sufficiently less expensive for more to be used to achieve the required stability and still give the lowest overall cost.

In antioxidants, synergism appears to arise either from one antioxidant effectively regenerating another so that the latter does not become consumed or by the two antioxidants functioning by differing mechanisms. The latter is more important and it is easy to see how effective a combination of peroxide decomposer and chain-breaking antioxidant can be.

The peroxide decomposer will drastically reduce the number of radicals, which can then be more effectively 'mopped up' by the chain-breaking materials. A widely used combination is 4-methyl-2,6-di-*t*-butylphenol and dilauryl thioldipropionate. It is possible to envisage most powerful combinations where a chain-breaking antioxidant, a regenerating agent, a peroxide decomposer, a metal deactivator and an ultraviolet absorber are all employed together.

Two final points should be made while considering antioxidant synergism. Firstly, some antioxidants which function by more than one mechanism are in all probability autosynergistic. Secondly, certain additives which appear to act

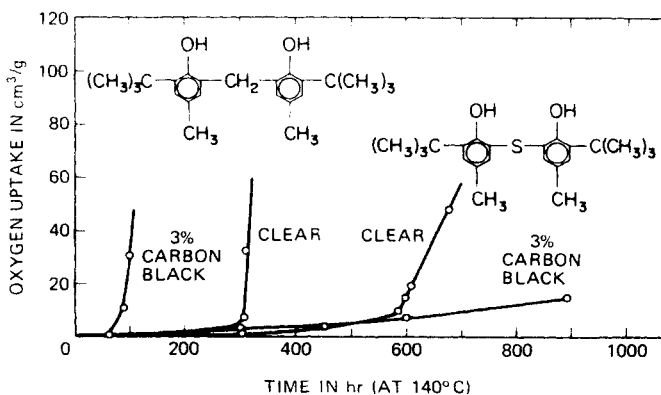


Figure 7.7. The synergism of sulphur antioxidants with carbon black as contrasted to the adverse effect shown with conventional antioxidants (in polyethylene)

synergistically with one antioxidant may be antagonistic to a second. The most well-known and important example of this is carbon black, which has an adverse effect with many phenols and amines but which is synergistic with some phenolic sulphides. This is illustrated clearly in *Figure 7.7*.

Antioxidants may be assessed in a variety of ways. For screening and for fundamental studies the induction period and rate of oxidation of petroleum fractions with and without antioxidants present provide useful model systems. Since the effect of oxidation differs from polymer to polymer it is important to evaluate the efficacy of the antioxidant with respect to some property seriously affected by oxidation. Thus for polyethylene it is common to study changes in flow properties and in power factor; in polypropylene, flow properties and tendency to embrittlement; in natural rubber vulcanisates, changes in tensile strength and tear strength.

7.5.2 Antiozonants

When diene rubbers are exposed to ozone under stressed conditions cracks develop which are perpendicular to the direction of stress. Whilst ozone must react with unstressed rubber no cracking occurs in such circumstances nor when such rubber is subsequently stressed after removal of the ozone environment. For many years such rubbers were protected by waxes which bloomed on to the surface of the rubber to form an impermeable film. This was satisfactory for static applications but where the rubber was operating under dynamic conditions the wax layer became broken and hence less effective.

Since the mid-1950s several materials have been found effective in combating ozone-initiated degradation, in particular certain *p*-phenylenediamine derivatives. The actual choice of such antiozonants depends on the type of polymer and on whether or not the polymer is to be subject to dynamic stressing in service. Since antiozonants are not known to have any use in plastics materials, even those which may have certain rubber particles for toughening, they will not be dealt with further here. Anyone interested further should consult references 3–5.

7.5.3 Stabilisers Against Dehydrochlorination

Whilst such stabilisers have found use in many chlorine-containing polymers their main application has been with poly(vinyl chloride). These additives will be considered in Chapter 12.

7.5.4 Ultraviolet Absorbers and Related materials

On exposure to ultraviolet light, particularly in an oxygen-containing atmosphere, physical and chemical processes may occur leading to such effects as discolouration, surface cracking, hardening and changes in electrical properties. Because polymers vary in their chemical nature the effects differ from one polymer to another. For most purposes the effects are undesirable but occasionally may be utilised in a positive manner—for example, to effect cross-linking or deliberately to initiate degradation.

The greatest damage is caused by shorter wavelengths, i.e. less than 400 nm, but as the earth's atmosphere absorbs most light rays shorter than about 300 nm the main damage is done, in terrestrial applications, by rays of wavelength in the range 300–400 nm (*Figure 7.8*).

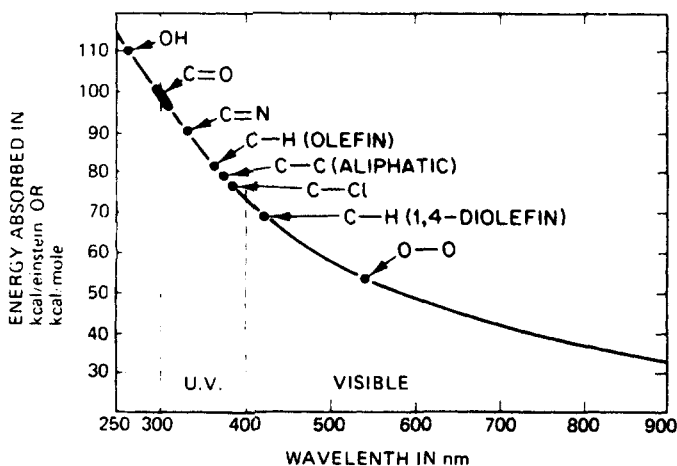
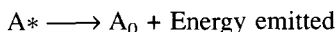


Figure 7.8. Relationship of energy absorbed by molecule to wavelength of incident light. Dissociation energies of various bonds are indicated to show wavelength below which breakdown may occur. (After Scott¹)

When a molecule (A) absorbs a quantum of light it is activated to an electronically excited state A^* , after which a number of process may occur. These may be summarised as follows:

(1) *Photophysical processes*

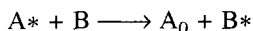
- (a) Emission of energy (e.g. phosphorescence or fluorescence)



- (b) Generation of heat (radiationless conversion)

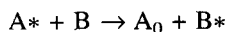


- (c) Energy transfer



(2) *Photochemical processes*

- (d) Consequent on energy transfer



└─ Products

- (e) Reaction of excited molecule equivalent to effect occurring with thermally excited molecules

Reactions (d) and (e) occur much less frequently than reactions (a)–(c) but do so at a sufficient rate to cause changes in most polymers. There are three methods available for combating such effects; light screens, ultraviolet absorbers and quenching agents.

Light screens

Light screens function by absorbing damaging radiation before it reaches the polymer surface or by limiting penetration of the radiation into the polymer mass. Coatings including pigment-loaded paints have been long used to protect a natural polymer composite, wood. It is also possible to coat a polymer with a layer of polymer containing a high concentration of an ultraviolet absorber or alternatively with a polymer which itself is capable of absorbing radiation without undergoing a deleterious chemical change. In addition to coatings light screens may be dispersed as powders into the polymers. Such materials should not scatter radiation and for this reason carbon black, which is also something of a thermal antioxidant, is uniquely effective. Such carbon black must, however, be of fine particle size (15–25 nm), used in concentrations of at least 2% and very well dispersed.

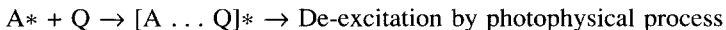
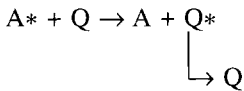
Ultraviolet absorbers

Ultraviolet absorbers are a form of light screen which absorb primarily in the ultraviolet range. It is a requirement for most ultraviolet absorbers that absorption in the visible range should be negligible; if this were not so the resultant instant colour formation could be worse than that experienced after prolonged exposure of the polymer.

The ultraviolet absorber could dispose of absorbed energy by radiation, by conversion into heat or by chemical changes leading to stable products. The most important commercial absorbers, such as the *o*-hydroxybenzophenones, *o*-hydroxyphenylbenzotriazoles and salicylates, appear to function by conversion of electronic energy into heat. The properties of the main types of ultraviolet absorbers are summarised in *Table 7.7*.

Quenching agents

Such agents are not in themselves powerful absorbers of ultraviolet light. They are, however, capable of reacting with activated polymer molecules by the following mechanisms:



In the above scheme A represents the excited polymer, Q the quenching agent and [A.....Q]* an excited complex.

The use of quenching agents in polymers is a recent development. Of particular interest are the nickel(II) chelates in polypropylene film and fibre and the even newer hindered amines which appear to combine the roles of antioxidant and quenching agent.

7.6 FLAME RETARDERS

For some applications of plastics, such as in packaging where disposability has to be considered, it may be desirable for plastics materials to burn without difficulty. There are, however, a number of uses such as in building, furniture and fitting

Table 7.7. Some commercial ultraviolet absorbers

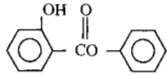
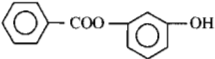
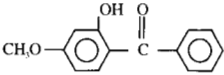
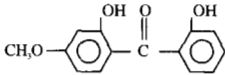
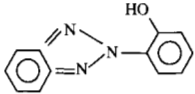
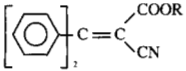
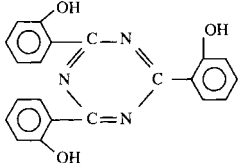
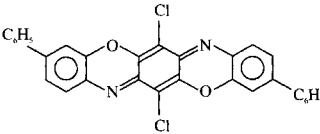
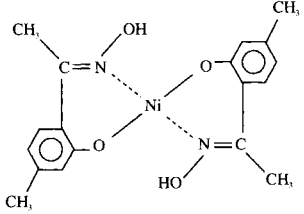
<i>Ultraviolet absorber</i>	<i>Formula</i>	<i>Type</i>	<i>Comments</i>
Phenyl salicylate		Salicylate	Rather weak.
Resorcinol monobenzoate		Benzoate	Converted in sunlight to a dihydroxybenzophenone. Used in celluloses.
2-Hydroxy-4-methoxybenzophenone		Substituted monohydroxybenzophenone	Negligible absorption in visible range.
2,2'-Dihydroxy-4-methoxybenzophenone		Substituted dihydroxybenzophenone	Stronger than the monohydroxy compound but some absorption in the visible range.
2-(2-Hydroxyphenyl)benzotriazole		Benzotriazole	Powerful.
		Substituted acrylonitrile	Some use in PVC and polyolefins.

Table 7.7 (continued)

<i>Ultraviolet absorber</i>	<i>Formula</i>	<i>Type</i>	<i>Comments</i>
1,3,5-Tris-(2-hydroxyphenyl)-triazine		Triazine	Powerful but some absorption in visible range
6,13-Dichloro-3,10-diphenyltriphenodioxazine		Oxazine	Excitation dissipated by radiation (fluorescence). Very effective in cellulose acetate-butylate but reddish brown in colour
-		Nickel(II) chelate	Appears to function as a quenching agent in polypropylene

applications where products from plastics materials should have an adequate degree of fire resistance. Whilst such an adequate resistance is often shown by products from unplasticised PVC, phenolic resins and aminoplastics, other materials, notably the aliphatic polyolefins, polystyrene and polyurethanes, are deficient. This has led to the progressively increasing use of flame retardants.

Whilst the development of flame retarders has in the past been largely based on a systematic trial-and-error basis, future developments will depend more and more on a fuller understanding of the processes of polymer combustion. This is a complex process but a number of stages are now generally recognised and were discussed in Chapter 5.

From what was said in that chapter it will be seen that flame retardants might be capable of acting at several stages in the process and that a combination of retardants might be employed, different components acting at different stages. In industrial practice flame retardants may be divided into two classes, reactive components and additives. The 'reactives' are used primarily with thermosetting plastics and are special intermediates which are inserted into the polymer structure during cross-linking. Used largely with polyesters, epoxides and polyurethanes, such materials are usually either highly halogenated or are phosphorus compounds. Whilst such reactives do not lead to problems of leaching, migration and volatility which can occur with additives they do suffer from certain disadvantages. Firstly, it is often difficult to incorporate enough bromine, chlorine or phosphorus into the structure to give sufficient flame retardance; secondly, such systems are often lacking in flexibility; and thirdly, such highly specialised chemicals produced in small quantities tend to be expensive. For this reason the bulk of flame retardants are of the additive type and these will be dealt with below. Reactives specific to a given class of polymer will be considered in the appropriate chapter.

Flame retardants appear to function by one or more of four mechanisms:

- (1) They chemically interfere with the flame propagation mechanism.
- (2) They may produce large volumes of incombustible gases which dilute the air supply.
- (3) They may react, decompose or change state endothermically, thus absorbing heat.
- (4) They may form an impervious fire-resistant coating preventing access of oxygen to the polymer.

In volume terms the most important class of fire retardants are the phosphates. Tritolyl phosphate and trixylyl phosphate are widely used plasticisers which more or less maintain the fire-retarding characteristics of PVC (unlike the phthalates, which reduce the flame resistance of PVC products). Better results are, however, sometimes obtained using halophosphates such as tri(chloroethyl) phosphate, particularly when used in conjunction with antimony oxide, triphenyl stibine or antimony oxychloride.

Halogen-containing compounds are also of importance. Chlorinated paraffins have found use in PVC and in polyesters and like the halophosphates are most effective in conjunction with antimony oxide. Bromine compounds tend to be more powerful than chlorine compounds and a range of aromatic bromine-containing compounds, including tribromotoluene and pentabromophenyl allyl ether, is available. Such halogen-based systems appear to function through the diluting effect of HCl, HBr or bromine.

The role of antimony oxide is not entirely understood. On its own it is a rather weak fire retardant although it appears to function by all of the mechanisms listed above. It is, however, synergistic with phosphorus and halogen compounds and consequently widely used. Other oxides are sometimes used as alternatives or partial replacements for antimony oxide. These include titanium dioxide, zinc oxide and molybdenic oxide. Zinc borate has also been used.

Where the polymer does not have to be subjected to high processing temperatures aluminium trihydrate may be used. One very large area of use for this material is in polyester laminating resins. An inorganic material which has been particularly successful as a flame retardant in the nylons is, perhaps surprisingly, red phosphorus. This material conferred a V-0 rating for the Underwriters Laboratories UL 94 specification (see Chapter 5) even with glass-filled grades (which are not self-extinguishing like unfilled nylons). Although the mouldings were dark in colour there was little loss in toughness or electrical insulation characteristics.

Also of interest are salts of melamine (see Chapter 24). In the nylons these can be used with bright colours (unlike red phosphorus) and do not adversely affect electrical properties. They do, however, decompose at about 320°C. Similar materials are very important in giving flame-retardant properties to polyurethane foams.

Many methods have been evolved in recent years for assessing flame retardants and the combustion characteristics of plastics and these have been the subject of comprehensive reviews.⁶⁻⁹

The use of fire retardants in polymers has become more complicated with the realisation that more deaths are probably caused by smoke and toxic combustion products than by fire itself. The suppression of a fire by the use of fire retardants may well result in smouldering and the production of smoke, rather than complete combustion with little smoke evolution. Furthermore, whilst complete combustion of organic materials leads to the formation of simple molecules such as CO₂, H₂O, N₂, SO₂ and hydrogen halides, incomplete combustion leads to the production of more complex and noxious materials as well as the simple structured but highly poisonous hydrogen cyanide and carbon monoxide.

There has also been considerable concern at the presence of toxic and corrosive halogen-containing fire degradation products in confined spaces such as submarines, mines, subways and aircraft. This is beginning to restrict the use of some chlorine-containing polymers in spite of the fact that they often have good flame retardant properties. For this and other reasons several of the halogen-containing flame retardants are no longer used with some polymers.

One possible solution to the problem is to make greater use of intumescent materials which when heated swell up and screen the combustible material from fire and oxygen. Another approach is to try to develop polymers like the phenolic resins that on burning yield a hard ablative char which also functions by shielding the underlying combustible material.

7.7 COLORANTS

There are basically four methods used for colouring polymers. These are surface coating (e.g. painting), surface dyeing, introduction of colour-forming groups into the polymer molecules and mass colouration. Surface coating involves extra processing and can substantially increase the cost of the product and is avoided where possible except in the case of fibres. Surface dyeing can be of limited use

with some polar polymers such as the nylons where only a small quantity of material is required to be coloured. Whilst academically interesting, the deliberate introduction of chromophoric groups is an inflexible and expensive method. Therefore, for most applications of rubbers and plastics the mass colouration approach is favoured.

Colorants are sometimes divided into two classes, insoluble colorants (pigments) and soluble colorants (dyestuffs). It should, however, be noted that many colorants have a low but finite solubility so that such a rigorous classification can be misleading. As explained previously, such a low solubility may in certain circumstances lead to blooming. One way of reducing blooming tendencies is to use colorants of high molecular weight. For a material to be a successful colorant it should meet all the requirements listed on p. 120.

For example, to be efficient they should have a strong covering power although in some circumstances a colorant of lower covering power than another might be favoured if it was so much cheaper that more of the colorant could be incorporated and still lead to a cheaper compound. Stability to processing covers not only the obvious aspect of heat resistance but also resistance to shear. Particles of some colorants break down under intensive shearing and as a result may change colour. When colorants are added before polymerisation they should not interfere with the polymerisation reaction nor should they be affected by the presence of some of the polymerisation additives. Blooming and bleeding can both be problems. Some colorants may also adversely affect polymer properties such as oxidation resistance and electrical insulation behaviour. Anisotropic pigments may become oriented during processing to give anomalous effects.

7.8 BLOWING AGENTS¹⁰

Many polymers are used in a cellular form in which the polymer matrix is filled with gas-filled cells which may or may not be intercommunicating. Over the years many methods have been devised for producing cellular polymers of which the most important are the following:

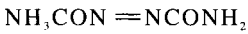
- (1) Incorporation of a chemical compound which decomposes at some stage of the processing operation to yield volatile reaction products. These are known as chemical blowing agents.
- (2) Incorporation of low boiling liquids which volatilise during processing. Such volatile blowing agents are important with polystyrene and polyurethanes and will be dealt with in the appropriate chapters.
- (3) Diffusion of gases into the polymer under pressure with subsequent expansion of the composition at elevated temperatures after decompression. Such a process can be employed with a wide variety of polymers.
- (4) Incorporation of powdered solid carbon dioxide which volatilises at elevated temperatures. This process has been used in conjunction with PVC pastes.
- (5) Chemical reactions of polymer intermediate during polymerisation and/or cross-linking. This is important with polyurethanes.
- (6) Mechanical whipping of polymers in a liquid form and subsequent 'setting' in the whipped state. The manufacture of latex rubber foam is the best-known example of this approach.
- (7) Incorporation of hollow or expandable spheres of resin or of glass (microballoons).
- (8) Leaching out of soluble additives.

Table 7.8 Chemical blowing agents in commercial use

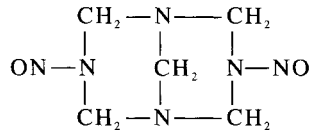
<i>Blowing agent</i>		<i>Class</i>	<i>Volatiles produced</i>	<i>Decomposition range (°C)</i>	<i>Gas yield (cm³/g)</i>	<i>Comments</i>
Azocarbonamide	(I)	Carbonamide	N ₂ , CO, CO ₂	190–230	220	Most widely used blowing agent in PVC and polyolefins. High decomposition temperature reduced by a variety of metal salts and oxides such as lead carbonate, lead phosphite and zinc oxide. High gas yield. Reaction products show little odour or discoloration*.
Dinitrosopentamethylene-tetramine	(II)	Nitrosoamine	N ₂ , NO, H ₂ O, CH ₃ , NH ₂	160–200	210	Widely used in natural and synthetic rubbers. Some use in polyolefins.
Benzenesulphonohydrazide	(III)	Hydrazide	N ₂ , H ₂ O	146	170–250	Blowing power affected by phthalate and phosphate plasticisers.
4, 4'-Oxybis(benzenesulphono-hydrazide)	(IV)	Hydrazide	N ₂ , H ₂ O	150	120–180	Faster decomposition rate than azodicarbonamide but low blowing power limits use.
<i>N,N'</i> -Dimethyl- <i>N,N'</i> -dinitrosoterephthalamide	(V)	Terephthalamide	N ₂ , H ₂ O, CO ₂	90–105	180	Low exotherm on decomposition but low decomposition temperature restricts use largely to open-cell foams.
Azoisobutyronitrile	(VI)	Azo	N ₂	95–98	136	Effective but decomposition products are toxic.
Sodium bicarbonate	(VII)	Inorganic	CO ₂	100–130	125–130	Low cost. Suitable for cellular rubber but insufficiently powerful for most plastics. Erratic in decomposition.
Terephthalazide	(VIII)	Acid azide	N ₂	85–112	207–311	Generates a di-isocyanate on decomposition which may cross-link some polymer species. Subsidiary reactions may increase blowing power.
Trihydrazinotriazine	(IX)	Hydrazine	N ₂ , NH ₃	275	225	Used with high softening point polymers, e.g. polycarbonates, nylons and glass-reinforced thermoplastics.

* Problems of corrosion and staining can occur under conditions of high melt pressure. Modified grades are now available that largely overcome these difficulties.

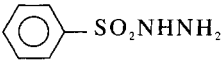
In volume terms annual production of cellular plastics products is of the same order as for non-cellular products and it is not surprising that the mechanisms of cell nucleation, growth and stabilisation have been extensively studied. As a result of this the texture and properties of cellular plastics can be widely controlled through such variables as average cell size, cell size distributions (including the possibility of some very large cells being present in a structure largely composed of small cells), degree of intercommunication between cells and the use of non-cellular skins. Such variables are in turn controlled by processing conditions and by the use of *cell nucleating agents* and *cell stabilisers* in addition to the *blowing agent*.



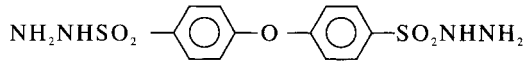
(I)



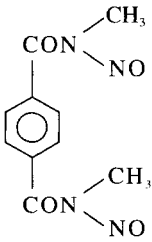
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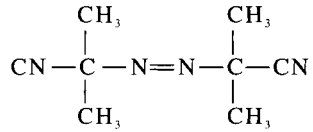
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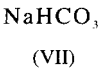
(IV)



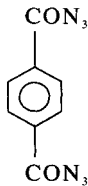
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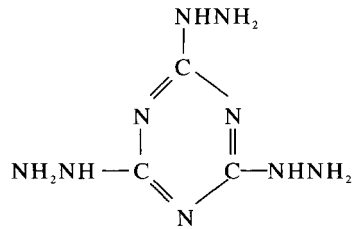
(VI)



(VII)



(VIII)



(IX)

Figure 7.9. Formulae of blowing agents listed in Table 7.8

