

4.3.4 Acceptor and Donor Types of Antioxidant

Two recognised subcategories of primary antioxidant are the donor type (such as hindered phenols) and the acceptor type (such as quinones). The donor type converts the reactive hydroperoxide $\text{ROO}\cdot$ radicals to ROOH , typically by donating a hydrogen atom, and although this also leads to a new free radical, consisting of the antioxidant molecule minus the donated hydrogen atom, this is not a problem because the antioxidant is carefully chosen so that the newly formed radical it generates is a stable one that will not assist chain propagation.

Another type of primary antioxidant is the *acceptor* type of chain-breaker. It may itself be a stable free radical, i.e., such an unreactive one that it does not interact with hydrocarbon polymers. Fortunately, it does react fairly easily with other free radicals, forming harmless non-radical products.

New stabilisers for polypropylene have recently been designed that contain more than one type of stabilising group. One category consists of a phosphite stabiliser containing a hindered amine and a free hydroxyl group. In another approach, two stabiliser molecules were linked together by reaction with isophorone di-isocyanate. In one example, the stabilisers that were combined in this way included both a phenolic compound and a hindered amine. The compounds tried showed good thermo-oxidative protection, especially when they contained two hindered amine groups in the same molecule, linked by isophorone di-isocyanate. Combinations of hindered amines and phenolic compounds were also effective. Some combinations were able to protect 0.1 mm thick PP films from thermo-oxidative degradation for more than 14,000 hours at 110 °C, with additive levels of 0.2 wt%.

4.4 Antistatic Agents

4.4.1 Introduction

Plastics are mostly electrical insulators. The development of a static charge on two plastic film surfaces during their mutual contact occurs by the transfer of electrons from one film surface to the other during rubbing or rapid separation. It is an undesirable consequence of insufficient conductivity, especially in polymers with a very low tendency to absorb moisture, and static discharges can reach several thousand volts per centimetre. This leads to:

- (i) sparking, bringing the risk of fire or explosion
- (ii) difficulties with high speed packaging machinery
- (iii) blocking or sticking of film surfaces
- (iv) pigment swirling or streaking in rotational moulding, caused by friction between the powdered mix and the mould
- (v) dust accumulation and loss of film transparency
- (vi) risk of damage to electronic components or devices, caused by high voltages.

Products especially affected by static include packaging film, automotive fuel tanks and lines, electronic device housings and associated furniture and flooring, videocassettes, domestic appliances, televisions and mobile phones, conveyor belts and chemical process equipment, or any materials used in the vicinity of flammable atmospheres.

The cellulose have little need of antistatic protection because they absorb moisture more than polyethylene, polypropylene and (to a lesser extent) PET. Polystyrene is difficult to protect effectively against static.

Antistatic agents are incorporated in plastics to prevent or reduce the build-up of static charges on the surface of a product. They must be able to stand the processing temperatures used and not interact negatively with other additives (some cationic and anionic antistats interfere with PVC heat stabilisers). They must also satisfy food contact regulations, and not adversely affect performance in other ways.

Organic polymers with no electrically significant additives usually have surface resistivity values higher than 10^{14} ohms/square, whereas the resistivities of static dissipative materials generally lie between 10^6 and 10^{12} ohm/square. Much lower surface resistivities (10^3 to 10^5 ohm/square) enable a material to be called electrostatically conductive, and they can be achieved by incorporating carbon black or carbon fibres, although the concentration of carbon used may have to be kept within narrow limits for various reasons. Even lower resistivities of the order of 50 ohm/square are required for electromagnetic shielding.

Volume resistivities of static dissipative materials are usually between 10^5 and 10^{10} ohm-cm, with lower values implying conductive behaviour.

The time for a static charge to decay is measured to rate the effectiveness of static dissipation additives. One way is to measure the time required for a voltage of 1000 V to decay to 100 V. It should take less than two seconds, and preferably less than one.

A US test measures the time for the induced charge produced by 5000 volts DC to disappear on grounding. Electronic packaging requires 99% dissipation in less than two seconds at 12% relative humidity, whereas fire protection standards stipulate 90% discharge in less than half a second at 50% RH.

4.4.2 Blooming Antistatic Agents

Certain partially compatible substances such as glyceryl monostearate (GMS), ethoxylated amines or alkyl sulfonates bloom to the surface of the plastic article and bond to moisture attracted from the atmosphere, providing a conducting pathway. The migration depends on the degree of compatibility. Migration is also accelerated by high temperature and by slip agents such as erucamide, but decreased by absorbent fillers and pigments. The time required for migration will also depend on the molecular weight of the antistatic agent, the crystallinity of the resin and the prevailing relative humidity.

Blooming antistatic additives fall into four categories: (i) non-ionic, (ii) anionic, (iii) cationic, and (iv) amphoteric.

Nonionic antistatic agents include GMS, the ethoxylated alcohols (widely used in plasticised PVC) and the diethanolamides (used in electronic packaging). GMS needs to be present at about the 1% level in polyolefins and it is approved for food packaging film, but its antistatic action does not last long in thin walled products, because it has poor compatibility with polyolefins and migrates too quickly. To prolong the antistatic action, GMS can be combined with a second, long-acting additive such as an ethoxylated amine. The diethanolamides are not always approved for food contact.

Anionic antistatic agents include the sodium alkyl sulfonates, e.g., $\text{RO}(\text{SO}_2)\text{ONa}$, the sulphonamides, e.g., $\text{C}_{12}\text{H}_{25}\text{-N-SO}_2\text{NH}_2$ (where N is a benzene ring) and the sodium alkyl phosphates, e.g., $(\text{RO})_2\text{PONa}$, where R is a long hydrocarbon chain such as stearate.

Alkyl sulfonates are used at the 2 to 3% level in styrene polymers, unless good clarity must be maintained, in which case ethoxylated amines can be used. Alkyl sulfonates are also employed in rigid PVC, whereas flexible PVC uses high (2 to 6%) levels of ethoxylated amines and fatty acid esters such as GMS.

Cationic antistatic agents are exemplified by quaternary ammonium salts, e.g., $R(NR'_2)^+CH_2Cl^-$ where R is a long alkyl chain and R' is a small alkyl or aromatic group. They are used in PVC but not generally for food contact.

Amphoteric antistatic agents include the alkylbetaines. Modest thermal stability usually limits their use.

The effectiveness of blooming antistatic agents is dependent on the relative humidity, and its effects are neither permanent nor necessarily immediate. If they migrate too quickly, they are unlikely to remain effective for long – perhaps a few hours. If migration is too slow, it could take weeks before they can provide protection. Mixtures of fast and slow types can be used to overcome this.

4.4.3 Compatibility

If the polymer is a hydrocarbon, then an antistatic agent of appropriate compatibility is likely to contain a hydrocarbon-compatible group such as an alkyl group, and also a polar group. When the antistat migrates to the surface, the compatible groups are usually buried in the polymer and the polar groups are oriented outwards beyond the surface, as shown in Figure 4.2. To form a conducting layer on the surface, the incompatible group must attract a thin layer of moisture from the atmosphere. The polar groups may also attract and complex with ionic surface contaminants, such as those in dust.

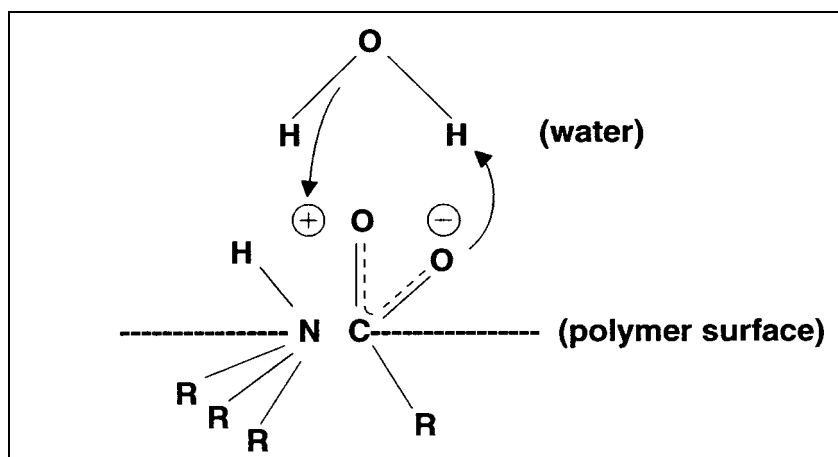


Figure 4.2 The chemistry of a tertiary fatty amine and its quaternary ammonium salt (trilaurylammonium stearate) blooming to the surface to attract conductive atmospheric moisture, creating a surface ESD effect while the underlying polymer remains insulating in nature

Source: S. Monte, Paper 25, Proc. Seventh Annual Conference, Addcon World, Berlin, Germany, October 2001, Rapra Technology Ltd., reprinted with permission

GMS behaves anomalously. In polypropylene it forms a surface film, with its polar groups (stearate) oriented within the polymer, and its non-polar groups (glyceryl) oriented away from the surface, the opposite of the usual trend. It is fast-acting but its antistatic effect dies away, typically after a few weeks. On the other hand ethoxylated amines can be slow to achieve their antistatic effect in low-density polyethylene.

Incidentally, commercial GMS is not necessarily all strictly monostearate, and samples may contain distearate and tristearate impurities.