

## Thermal Degradation - Antioxidants

Polypropylene (PP) and polyethylene (PE) resins are inherently unstable and degrade when exposed to oxygen. The degradation is similar to the rusting (or oxidation) of untreated iron in that the polymers change colour to yellow-brown and begin to flake away until the material becomes useless. When PP or PE degrades, chain scission, or the breaking up of the polymer chains into smaller pieces, takes place. The physical properties of the polymer deteriorate and its average molecular weight (chain length) decreases, melt flow rate increases and a powdery surface eventually forms. Polymer degradation is a natural phenomenon that cannot be totally stopped. Instead, resin producers seek to stabilise the phenomenon by adding stabilisers such as antioxidants. The degradation of these polyolefin resins follows a cyclic oxidation process which involves initiation, propagation and termination which we expand upon below.

### Initiation

The initiation of thermal degradation involves the loss of a hydrogen atom from the polymer chain as a result of energy input from heat or light. This creates a highly reactive and unstable polymer 'free radical' ( $R\bullet$ ) and a hydrogen atom with an unpaired electron ( $H\bullet$ ).

### Propagation

The propagation of thermal degradation can involve a variety of reactions and one of these is where the free radical ( $R\bullet$ ) reacts with an oxygen ( $O_2$ ) molecule to form a peroxy radical ( $ROO\bullet$ ) which can then remove a hydrogen atom from another polymer chain to form a hydroperoxide ( $ROOH$ ) and so regenerate the free radical ( $R\bullet$ ). The hydroperoxide can then split into two new free radicals, ( $RO\bullet$ ) + ( $\bullet OH$ ), which will continue to propagate the reaction to other polymer molecules. The process can therefore accelerate depending on how easy it is to remove the hydrogen from the polymer chain.

### Termination

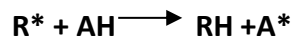
The termination of thermal degradation is achieved by adding countermeasures to stop or at least inhibit the process.

One way to terminate the oxidation process is by adding various antioxidants to the resin. An antioxidant (AO) can have varying chemical compositions. Antioxidants are generally classified into three types:

1. Primary AO: organic molecules consisting of hindered phenol and amine derivatives; generally, the higher the molecular weight of the additive, the better the performance.
2. Secondary AO: organic molecules consisting of phosphates and lower molecular weight hindered phenols; generally, the lower the molecular weight, the better the performance.

3. Thioesters: organic molecules containing sulphur which have acted synergistically with the primary AO.

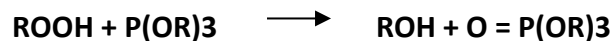
Primary antioxidants [AH] work as radical scavengers [R\*] by the following mechanism:



The phenol radical [A\*] can cause polymer degradation but is kept from doing so by the hindered physical structure of the primary AO.

Primary antioxidants are added to the polymer to protect against degradation during the service life of the finished product. Secondary antioxidants are added to the resin to reduce colour formation and to provide processing stability during the future thermal exposure the polymer may undergo during its lifetime.

Secondary A/Os [P(OR)<sub>3</sub>] decompose hydroperoxides [ROOH] to form stable alcohols [ROH] by the following mechanism:



Thioesters behave similarly to the secondary AO: they decompose the hydroperoxides [ROOH] into alcohols and other non-reactive species. But they also have a synergistic effect with primary AO, especially with those antioxidants with a high molecular weight. The particular method by which the thioesters decompose hydroperoxide radicals is not well known but is theorised to be similar to that of the secondary AO. Thioesters are usually used in end products with requirements that include long-term exposure to high temperatures, such as under-the-hood automotive applications and home appliances. Thioesters have been shown to be quite effective at temperatures greater than 50°C. Even at these high temperatures, these antioxidants can deactivate up to 55 molecules of hydroperoxide for every molecule of thioester.

A certain minimum amount of antioxidant is necessary to stabilise and protect polyolefins from degradation. Primary antioxidants and thioesters are added to the polymer to provide stability while secondary antioxidants are added to provide colour and processing stability during the polymer's future exposure to the effects of a thermal environment.

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