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Equistar Technical Tip

tech.topic

Additives: Scavengers

Catalysts are used to increase the efficiency and economy of the polymerization process used to produce polypropylene (PP) and polyethylene (PE) resins. Most of the catalysts used today for PP and PE synthesis are of the Ziegler-Natta type; the names refer to the original discoverers of commercial PP catalysts.

Ziegler-Natta catalysts utilize transition metals (titanium, chromium, etc.) and chlorine-based co-catalysts. The transition metals have many available electron sites that aid in polymerization. The chlorine-based co-catalysts increase the efficiency of the Ziegler-Natta catalysts.

While the presence of transition metals and chlorine-based materials are essential for viable, commercial PP and PE polymerization, these catalyst residues can promote the degradation of the polymer chains in the finished material.

Transition metals are known to catalyze the free-radical decomposition of hydroperoxides which are formed by the reaction of atmosphehic oxygen with the carbon-hydrogen bond in the polymer (see Equistar Technical Tip, "*Additives*: *Antioxidants*"). The decomposition of the hydroperoxide [ROOH] by the transition metals [M^{+m} or M^{+n}] is believed to proceed by the following mechanisms:

$$ROOH + M^{+n} \longrightarrow ROO^{*} + H^{+} + M^{+m}$$

$$ROOH + M^{+m} \longrightarrow RO^{*} + OH^{-} + M^{+n},$$
where m=n-1

The mechanism by which the transition metal decomposes the hydroperoxide, and thus furthers the autoxidation process, also regenerates the transition metal so that the process can continue indefinitely. To combat this process, scavengers are added to the PP and PE reactor powder during pelletization which bind to the transition metals and deactivate them.

he most commonly used transition metal scavenger is calcium stearate [$Ca(O_2C_{18}H_{37})_2$]. Calcium stearate is a molecule consisting of a central calcium ion with two stearate groups attached. The stearate group is essentially a long-chain carbon molecule. As such, the stearate group is similar to, and therefore soluble in, the polymer chains.

Calcium stearate attacks the transition metals, usually found in the form of metal chlorides [MCl_2] by the following reaction:

$$Ca(O_2C_{18}H_{37})_2 + MCl_2 \longrightarrow CaCl_2 + MSt_2$$

The large stearate groups bond with the transition metal rendering the metal essentially inactive.

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Additives: Scavengers *(Continued)*

Scavenger additives are also added to bind up chloride [Cl^-] ions left from the co-catalysts. There are many chloride scavengers used with PP and PE; usually these materials contain magnesium [Mg], aluminum [Al], or calcium (Ca) ions that bind with the chloride ions, forming harmless salts:

$$Mg^{+2} + 2\ Cl^- \longrightarrow MgCl_2$$

$$Al^{+3} + 3\ Cl^- \longrightarrow AlCl_3$$

$$Ca^{+2} + 2\ Cl^- \longrightarrow CaCl_2$$

The presence of chloride ions in PP and PE can result in the formation of hydrochloric acid [HCl] and other acids if not properly scavenged. Hydrochloric acid can degrade the polymer and produce unwanted color formation (yellowing) in the pellets.

In summary, scavengers are added to PP and PE polymers to deactivate undesirable catalyst residues, such as metals and chlorides. While the transition metals and chlorine co-catalysts are necessary for efficient and controlled polymerization of PP and PE, their presence in the finished material can cause unwanted degradation and color change.

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