Coatings that stay looking good

BASF performance additives

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The Chemical Company

Background of light and heat stabilization

How UV radiation and heat promotes degradation of organic substrates

Light- or heat-induced oxidation of organic materials is a complex radical process characterized by initiation, propagation, chain branching, autocatalytic chain and termination reactions. Both initiation steps generate free radicals (R•) to enter this cyclic process.

The predominant initiation mechanism under normal service life conditions of polymers is the light-induced oxidation, the so-called photo oxidation (see fig.1). The initiation reaction is the photolysis ① where a chromophore CH (= UV-absorbing molecule or moiety) absorbs radiation energy (h·v). The absorbed energy leads to the formation of an excited state CH* (higher energy level). CH* molecules are highly reactive and can subsequently form free radicals (R•) by homolytic bond cleavage ③. Under high temperature conditions heat can accelerate the oxidation – the so-called thermal oxidation ② – by radical breakdown reactions and formation of free radicals R•. This heat-induced initiation step can occur during high-temperature processing, production and service life.

The free radicals R• generated during photo and thermal oxidation can subsequently react with oxygen (O_2) to form peroxy radicals (ROO•) ④, which can further attack the polymer (P-H) thereby forming unstable hydroperoxides (ROOH) ⑤. These hydroperoxides fragment due to UV radiation and/or heat and form additional free radicals ⑥. As the process continues, more and more molecular bonds break – a process which is autocatalytic in nature and is known as autoxidation.
Photo oxidation in the presence of light and O_2 is the predominant mechanism under interior and ambient conditions. As a result mainly discoloration (i.e., yellowing) of the substrate or fading of colorants (e.g., in wall paints or inks) are observed. Under exterior weathering conditions – water is the decisive factor – photo oxidation leads to photo-degradation resulting in additional surface defects of the coating such as loss of gloss, cracking, chalking etc. Heat exposure of organic substrates as encountered during processing steps such as synthesis, mixing, extrusion, curing or during high-temperature-baking cycles of coatings mainly cause yellowing, embrittlement or loss of other mechanical properties such as tensile strength.

In order to protect organic substrates against harmful UV-radiation and subsequent photo oxidation followed by photo degradation the use of appropriate light stabilizers such as UV absorbers (UVA) and free-radical scavengers such as hindered amine light stabilizers (HALS) is necessary. UV absorbers filter out the harmful UV light, thereby preventing color change of the resin, of the substrate underneath and of colorants in coatings, inks, adhesives and sealants. HALS trap free radicals once they are formed and are effective in preventing surface defects such as loss of gloss, cracking and chalking. While HALS are, technically speaking, a class of antioxidants or free-radical scavengers, the term “antioxidant” or “AO” generally refers to additives that are primarily used as heat stabilizers. Today the most commonly used AOs are based on sterically hindered phenol, thioether or phosphite technologies.

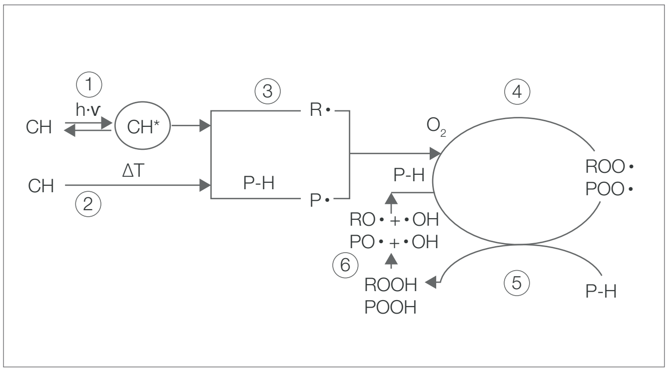

Fig. 1: Mechanism of light- and/or thermally induced oxidation

Tab. 1: Overview of existing light and heat stabilizer technologies

		Radical scavengers	
	UV absorbers (UVA)	hindered amine light stabilizers (HALS)	antioxidants
mode of action	converts UV light into heat	deactivation of free radicals	deactivation of free radicals
usage area	interior/exterior	exterior	interior/exterior
protect against	photo oxidation and degradation	photo degradation	thermal oxidation
protect what?	deeper coating layers substrate underneath	coating surface pigments in coatings	coating
protects against	yellowing blistering loss of adhesion	surface defects loss of mechanical properties loss of water impermeability pigment fading	yellowing embrittlement loss of mechanical properties
chemical classes	2-hydroxyphenyl-benzophenones (BP) 2-(2-hydroxyphenyl)-benzotriazole (BTZ) 2-hydroxyphenyl-s-triazines (HPT)	tetramethyl piperidine derivatives	sterically hindered phenols phosphites thioethers

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