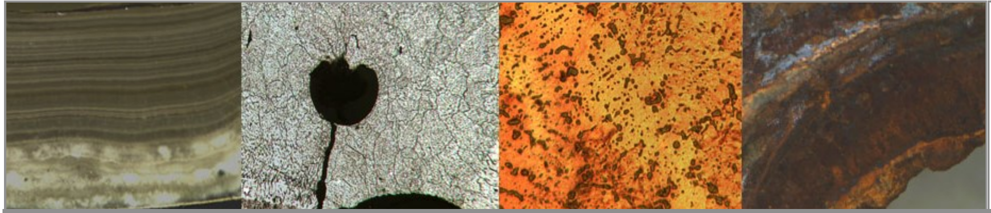
NUTS & BOLTS



New Hampshire
MATERIALS
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POLYMER STABILIZATION AGAINST UV DAMAGE **SEPTEMBER 2014 SUPPLEMENT**

Welcome to New Hampshire Materials Laboratory

Us here at NHML, hopes that everyone had a wonderful and relaxing Labor Day weekend. We want you all to know that we are continuously thankful for your continued business because without you there wouldn't be an us.

Do you ever find yourself wondering if the ultra violet radiation coming from the sun can damage products that we buy and use everyday just like it can damage our skin (sunburn) or damage furniture (fading, drying and cracking)? Plastics and polymers are not left out in this dilemma. This months Nuts & Bolts Supplement covers polymers and the molecular reactions that happen when exposed to UV radiation and some informative steps on how these molecular reactions can be avoided or stabilized.

For more information or to find out more on how we can be "Your Problem Solving Partner" or if you have any questions regarding the article, please visit our website at www.nhml.com or feel free to call our toll free number 800-334-5432.

Timothy M. Kenney

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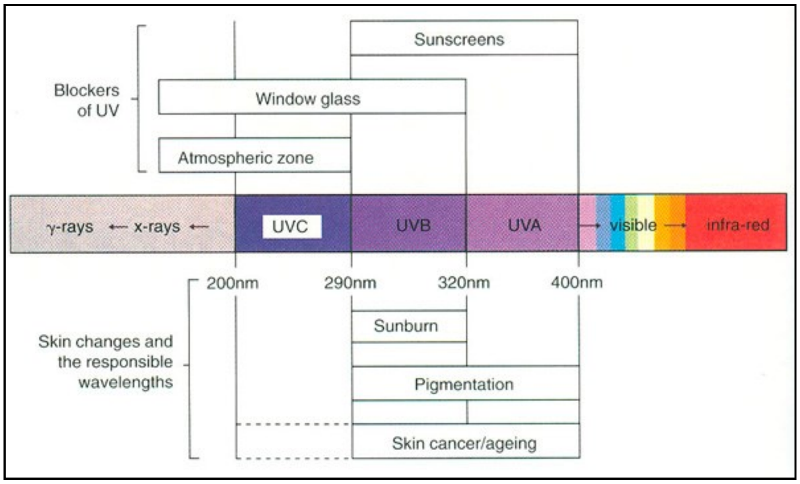
Polymer Stabilization Against UV Damage

by Jeffrey Masse

Ultra-violet radiation is just that, it consists of wavelengths *below* violet in the visible spectrum, and is therefore invisible to the human eye. Most people are aware of the effects this energetic radiation has on their skin, i.e., a suntan or a sunburn. Normal human skin responds to exposure of small doses of UV by increasing the amount of protective melanin in the skin's outer layers; thus, for small doses, we have a built in protective mechanism against UV radiation. However, everyone who has experienced a sunburn knows that too much exposure to UV can cause some painful cellular damage. Long term exposure can lead to more significant cellular damage and even to skin cancer. Just as the energy available in the ultraviolet region of the electromagnetic spectrum is capable of causing many degradative reactions in our skin, similar degradation occurs when polymers and plastics are exposed to UV radiation, and they have no built-in protective mechanisms where our skin does.



The UV radiation from the sun is partly absorbed by water vapor, the O-zone and carbon dioxide in the atmosphere. The remaining UV radiation is scattered by dust particles and clouds. However, the scattering does not decrease the total amount of UV light reaching the ground level. Approximately 6% of the total radiation that reaches the surface of the earth is in the UV region of the spectrum and varies with daily weather conditions. The "longer" wavelengths of light are not sufficiently energetic enough to cleave covalent bonds in organic molecules (namely polymers). However, the shorter more energetic radiation with wavelengths lower than 300 nm (UV radiation) will selectively excite electrons in polymer chains. The excited electrons may lose energy by fluorescing, phosphorescing, or increasing the vibrational and rotational energy of the covalent bonds in the polymer chain. From a chemists point of view, these interactions are very complicated, but the end result is that these energy transfers ultimately cause bond cleavage and formation of

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free radicals which themselves cause further damage. On a macroscopic scale the cumulative effect of these molecular reactions can be embrittlement of the plastic and degradation of its physical (and engineering) properties.

For polymers intended for outdoor use, exposure to such UV radiation is difficult or impossible to avoid. But is it possible to somehow stop this chain of reactions at the molecular level? Polymer chemists would need to know the details of how these steps propagate to figure out how to stop the process. I will spare you the gory chemical details, but it turns out that there are four possible ways to hinder or stop this degradation using some smart chemistry:

1. The first approach incorporates additives into the plastic that absorb UV light BEFORE it can contact the degradation-initiating center. The harmful radiation is absorbed by the stabilizer and the energy is dissipated as heat.
2. The second technique DEACTIVATES the excited state of the initiating center. Such reactions produce energy which is generated either in the form of heat or as fluorescent radiation.
3. The third method transforms the hydroxyperoxides that have been generated into other stable forms that do not generate free radicals. Metal complexes of Sulfur containing compounds are very efficient in this regard and can be effectively used at low concentrations.
4. A fourth technique incorporates additives that react with the free radicals that have formed TO STOP FURTHER REACTION, i.e. to break the chain.

(The exact mechanism by which commercial stabilizers perform is not precisely known and they probably operate by the simultaneous action of more than one mechanism)

Of these four possibilities, this article focuses on the fourth technique. Ultraviolet light stabilization of PP and other polymers can be achieved by a reduction in the rate of photo-initiation and reduction in the length of the propagation stage of this multistep mechanism. This can be achieved by “free radical trapping” which takes place at the molecular level. Among the first chemical compounds used to trap free radicals were Phenolics and Phosphites. These compounds do the job of preventing UV damage, however they undergo “sacrificial radical trapping”, meaning that they can react and trap only a single free radical and they are spent. Further research led to the discovery of Hindered Amine Light Stabilizers (HALS) which turn out to be much more efficient at trapping free radicals than their Phenolic and Phosphite predecessors. The exceptional efficiency of HALS

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(provide structure) in various polymers, especially in Polylefins, is attributed to their ability to trap multiple radicals and also different radicals, thereby inhibiting or stunting the photodegradation process more efficiently and in a greater variety of Polymers. As was mentioned, Phenolics and Phosphites undergo sacrificial radical trapping, however the HALS provide a ***regenerative radical trapping*** process in which Nitroxyl (>N-O) and its derivatives capture a number of free radicals before they are converted into inert derivatives. This essentially multiplies the effectiveness of HALS in preventing UV damage to polymers and means that lower levels of these additives are necessary to provide a given level of UV protection and, of course, less additives means monetary savings.

Common sense dictates that it is more important to UV protect polymers specifically intended for outdoor use since indoor “white light” of an ordinary incandescent bulb does not contain much UV in comparison to sunlight and its spectrum is rather biased towards the red (longer wavelength) end of the spectrum.