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THE JOURNEY TO STABILIZATION OF AUTOMOTIVE PLASTIC APPLICATIONS

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Abstract

This paper will treat to expose the complexity of stabilization of plastics in automotive applications.

First, we will review some basics on stabilization, the use of phosphites and phenolic antioxidants. We will cover the different aspects of polymer stabilization: during processing and along the service life of the parts. This will involve discussion around light stabilization too. Along this paper, we will see some examples of outstanding chemistries than can lead to combine several benefits to achieve the performances required by OEMs.

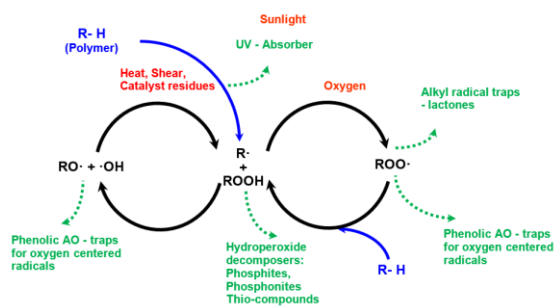
Polymer degradation

We call degradation all effects that damage polymer integrity, either in the bulk and/or on the surface, and which result in a change in

- mechanical or physical properties,
- color and appearance.

Many parameters can cause the degradation of plastic articles.

Polymer degradation process may be visualized by the so-called Polymer Auto-oxidation Cycle:



In red are the degradation inducers and in green the additives that are meant to inhibit it.

These negative factors, participate or even catalyze the auto-oxidation reaction and may act at different steps of the plastic conversion:

- **Storage** of the resin, or even finished product
- **Processing** of the plastic material
- **End use** of the plastic part

Basics on stabilization

Challenges in Automotive applications are increasing drastically for plastics. Main driver is to replace metal by plastics for various reasons behind weight reduction, such as energy and cost saving but also sustainability.

I. Processing conditions

During processing, several parameters can have a negative impact on the final quality of the plastic article.

Gain in productivity can be achieved through two ways:

- extrusion speed increase, reaching high pressure levels for injection molding, or by using latest high yield conversion machineries
- temperature increase in order to reach a higher flowability

These conditions will induce stress to the polymer caused by high shears and heat in the extruder, and also pressure build-up.

Secondary factors, such as cost saving by using high amounts of regrinds of polymer recycling as well as quality issues by reprocessing of MB or compound to adjust color or improve dispersion, may further affect the long term stability of produced parts.

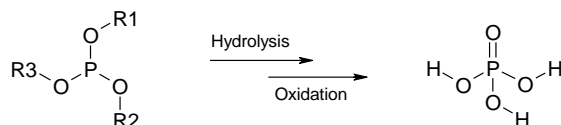
Heat and shear, combined with oxygen, are, unfortunately, the right and best/worst combination for accelerating the polymer degradation by oxidation and cause polymer structure damage by either chain scission or cross linking. This will have directly an impact on molecular weight distribution and viscosity.

Consequences would be as diverse as counterproductive: yellowing shift in color, bad processability, blooming of small molecules, VOCs, odor, emissions and loss of the mechanical properties.

Standard additive package is usually optimized of for a direct and single conversion and leaves very limited space for reprocessing.

II. Phosphorous based processing stabilizers

Phosphites are the benchmark for basic processing stability but may affect color appearance. The antioxidative reaction results in formation of phosphoric acid:

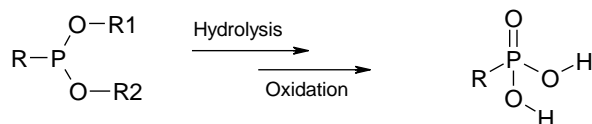


Addition of significant amount of acid scavenger (stearates) may be necessary, inducing risk of blooming and water carry over, critical issues in film production.

Additionally stearates show very poor performance in term of color protection.

By choosing the right additives package for such extreme process conditions, major part of those a.m. inconveniencies can be avoided.

Phosphorous based products such as phosphonites reduce these disadvantages significantly which can be explained by generation of less aggressive entities:



Beside the central phosphonite function, a special attention has also to be taken on substitution groups, these moieties can also damage polymer by further reacting, and create undesired black specks in the plastic.

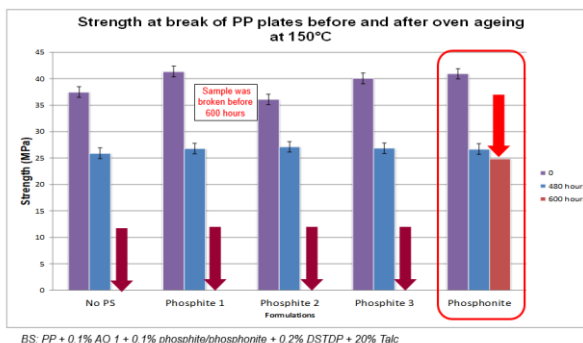
A proper product design has allowed to achieve higher level of solubility in even very low crystallinity polymers. Aryl groups were preferred for high compatibility in both standard and engineering plastics. Dimeric structure is also favoured in term of efficiency and higher molecular weight, to reach higher performance and lower migration.

As consequence of using high molecular weight diphosphonite as processing stabilizer, both color and transparency are protected and resin benefits from a good retention of initial properties.

Here below is a comparison in oven aging at 150°C

Phosphonite vs phosphites

Mechanical properties retention at 150°C

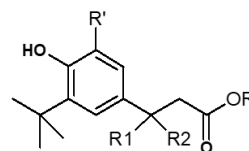


Using a phosphonite instead of a phosphite protects the polymer better during processing, delaying the long term degradation. In the example, we see a boosting effect of 25% between the phosphites (or no phosphite!) and the phosphonite.

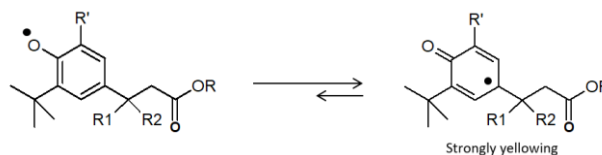
III. Phenolic antioxidants

One of the most frequent reason for polymer discoloration is the yellowing induced by the reaction product of antioxidants.

A general structure for phenolic antioxidants can be drawn as below:



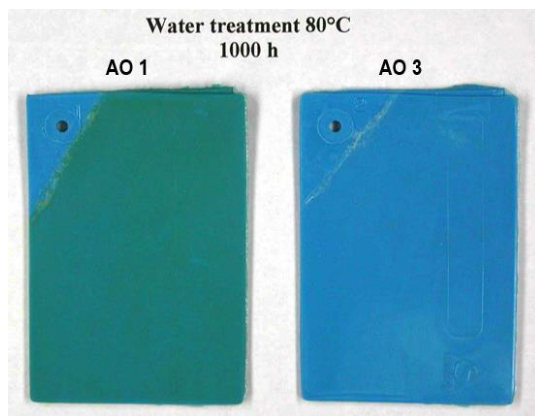
Yellowing of the polymer is coming from a radical rearrangement of the structure forming a quinone radical, strongly yellow colored.



This latter is likely to be formed if R1 and R2 are hydrogen, as a stable quinone radical which will be able to graft on the polymer chain.

When R1 and R2 are not hydrogen, radical position on C4 is difficult due to alkyl groups, the quinone radical formation will be unfavored against the desired phenolic radical, which will be the most stable entity. In addition, if hydrogen is at the position of R', phenolic radical is less sterically hindered and thus more reactive.

A comparative study by immersion in water shows the discoloration phenomenon after only 3 months.



The market situation is nowadays such that most of the resins are stabilized with antioxidants rather prone to quinone structure formation resulting in a yellowing resin depending of course on the amount of phenolic antioxidant, the temperature, the storage duration.



However alternative solutions exist to avoid such an inconvenience.

While an end article is stored for a significant period, hydrolysis of the phenolic antioxidant can take place in the matrix.

The ester group will cease and give 2 entities free to move in the polymer, one alcohol and one acid. A special attention should be taken on structures which can release pentaerythritol, a well-known char generating agent in flame retardancy domain, which could result in “undesired” insoluble residues. If those residues are not a trouble for most of the molding applications, they can be a critical problem for film application whenever they affect film quality, by showing black specs in the film or even resulting in film breakage.

For the acid part, the higher the molecular weight of the component is, the slower is the migration to the surface of the plastic part, which would avoid unaesthetic blooming effect affecting article appearance.

Potential side effects of stabilizers

Gas fading

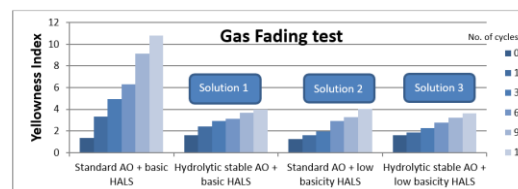
A particular case, but often underestimated, of degradation during storage or service life is related to gas fading. Such a phenomenon is related to the accumulation of exhaust gases from forklifts in the warehouse, or from a car in a garage for instance.

These exhaust gases interact with ingredients used to produce the polymer.

As a case study, we are showing how phenolic antioxidants, due to their chemical structure, have a significant impact on discoloration (color change) of the polymer article and a low stability towards environmental effects (water, gases, ...)

In contact with pollutants such as NO_x gases, standard phenolic antioxidants present two major issues: tendency to volatilize due to low molecular weight and yellowing due to the formation of a colored product (quinonoid family), caused by NO_x addition on *para*-position to phenolic OH, *ortho*-position being blocked by tBu moieties.

Moreover, light stabilization system may further add a negative contribution to the yellowing effect, a special care should be taken in light stabilizers selection, beside the antioxidant.



Gas Fading Exposure using ISO 105 G02
100 µm PP films (compression molded)

This gas fading study shows that there are 2 ways to solve the issue:

- Use of a phenolic antioxidant with low degradation or migration behavior to stabilize the resin (Solution 1), this is an option for a resin manufacturer.
- When antioxidant is already in the matrix, the addition of lower basicity radical scavenger can reduce their discoloration tendency (Solution 2). This is the frequent case faced by masterbatches or compounds producers who cannot influence the selection of phenolic antioxidant in the resin.

Solution 1 can be further improved in term of color stability by replacement of basic HALS by a lower basicity radical scavenger (Solution 3)

Interactions stabilizers/metal ions

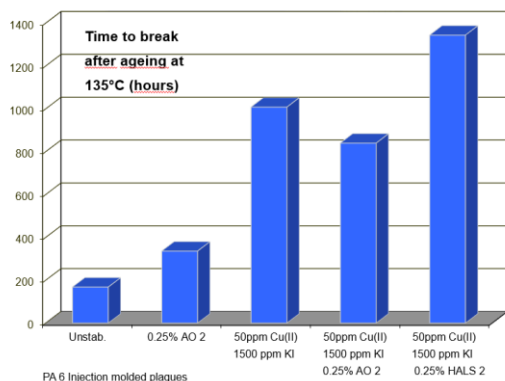
Another well-known example which can occur during storage is interaction among ingredients in the polymer matrix.

Combinations of additives can lead either to antagonism or synergism within the matrix.

Metal ions are usually a source of interactions with other constituents of the formulation.

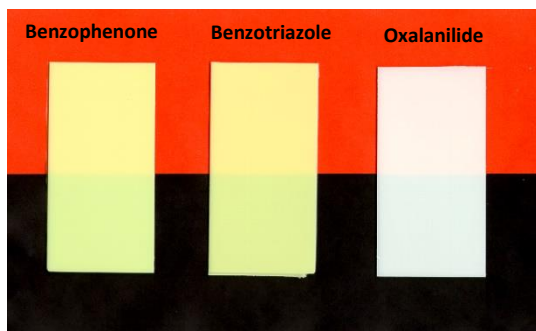
Here we will take some examples with copper halides present in nylon as heat stabilizers.

When combined with other chemistries, effects can be deteriorating for the overall stabilization of the polymer.



A study in solution can easily show that UV Absorbers may react strongly with metal ions, which can result from catalyst residues or any inorganic compounds added to the polymer.

Commonly used UV absorbers, namely hydroxyphenyltriazines, hydroxyphenylbenzotriazoles and hydroxyphenylbenzophenones present such a disturbance, building highly colored complexes with metal ions, contrary to oxalanilides or benzilidene malonates which show no interaction with such ions.



Additives: 0.005% Cu²⁺ + 0.5% UVA

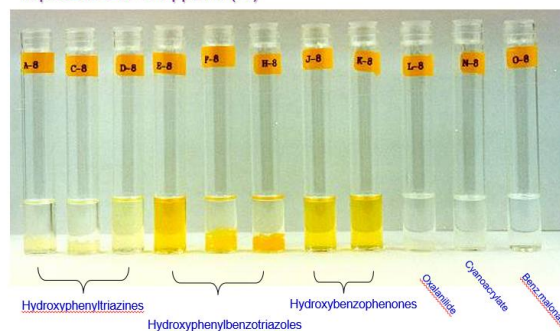
Injection molded plaques (1 mm thick) from PA-6 semi dull

A strong and initial yellowing is also observed when adding hydroxyphenyl benzotriazole or hydroxyphenyl benzophenone in presence of some ppm of copper ions in polyamide matrix. Stabilization with an oxalanilide instead did not affect the initial color of the resin.

Same phenomenon is observed between Ti (IV) ions, commonly present in the polymer under TiO₂, and hydroxyphenyl benzotriazoles or hydroxyphenyl benzophenones.

Interaction of UV Absorbers with metal ions

Dichloromethane solution - 500 ppm UV absorber in presence of 100 ppm Ti (IV)



Oxalanilides and benzilidene malonates leave the polymer color unchanged, ready to be exposed to any light source, natural or artificial, in “real life” or in accelerated weathering chamber.

Lifetime of the parts – simulation with accelerated aging

In this section, we are only considering damages that can happen on the end article during its service life and how this can be avoided by selecting the suitable stabilizers.

The main factors that can accelerate discoloring and product aspect degradation are heat, sunlight, extraction media and environmental conditions such as pollution, humidity and natural phenomena.

Assuming that resin and pigment were selected properly, according to requirements, an efficient stabilization package is necessary for a good protection of plastic articles, otherwise they may undergo loss of mechanical properties (product integrity), deterioration of esthetical properties (surface crazing, chalking,...), change/loss of color.

Light-induced degradation can be inhibited by using a combination of HALS and often UV absorbers, while against temperature-induced degradation, plastics can be stabilized by specialty antioxidants, sometimes in combination with HALS, as additional radical scavengers.

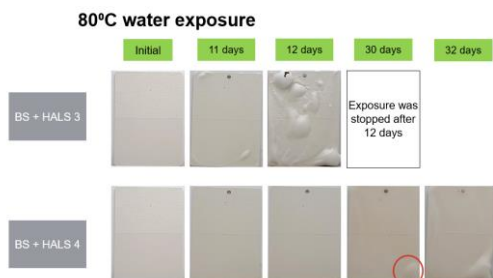
Generally, stabilization system for light protection also show nice resistance to heat degradation.

However, certain HALS under thermal exposure and in presence of pigments, can create interaction and color is shifted. This can be shown through performing an oven test. If HALS contains some heat sensitive groups, this will induce a yellowing of the article.

The choice of HALS will depend on the requirements, the polymer matrix and the other components of the formulations.

Stabilization of PC/ABS is problematic, a UV absorber is needed for the PC part but the addition of a HALS, needed for ABS part, may strongly accelerate the degradation of PC.

HALS 4 is a special UV graftable HALS that will selectively go on the ABS side and graft, being then a permanent HALS, difficult to extract as you can see in below figure.

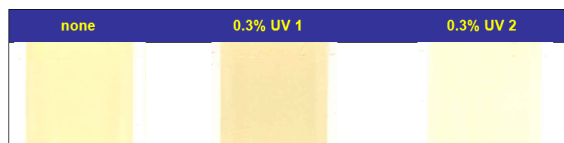


Especially for engineering plastics, the UV absorber selection must be driven by its heat resistance and its absorbance level in the critical wavelength of the polymer, otherwise a fast yellowing will occur.

Here below some examples of UV absorbers performance in polycarbonate. UV 1 (benzotriazole) shows a strong discoloration while UV 2 (benzylidene malonate) exhibits an excellent color retention, extremely important factor for this polymer used for its transparency but also its outstanding aesthetics properties.

Light Stabilization of Polycarbonate

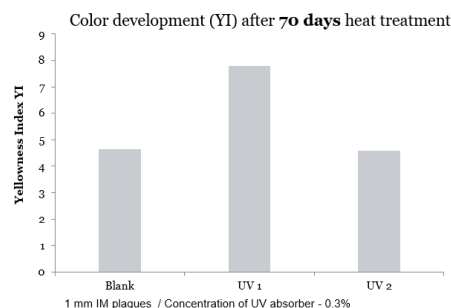
Color development during accelerated weathering (WOM / CAM-7) after 3000 hrs. exposure



Samples: 1M plaques, thickness 1mm.

As sunlight is generating constant heat (IR) exposure to exterior parts, it is important to look at the influence of additives, even light stabilizers, on heat resistance of such parts.

Influence on thermal stability of Polycarbonate Air-draft Oven at 135°C



Stabilization should then be thoroughly tested according every requirements stated by the OEMs in order to check if any antagonism or drawback could happen and compromise the whole evaluation of the performances of the plastic part to be approved.

Case of a new additivition development for automotive interior TPO compounds

Additives are, in essence, chemicals, interacting with the matrix, with the components of the compounds, with each other to protect the polymer.

This reactivity between entities could have also some antagonist effects, such as deactivation of HALS, yellowness of parts, blooming, adsorption on inorganic components, etc...

It also can induce synergies when chemistries are working together to get optimum results.

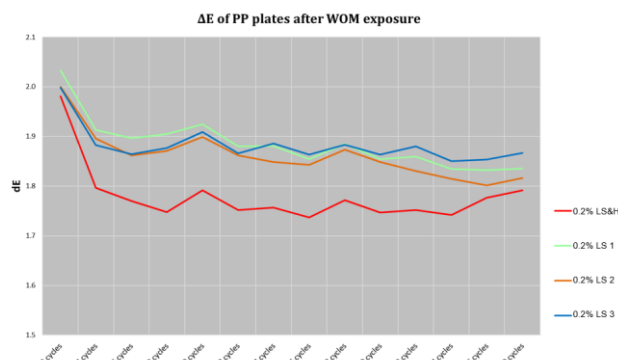
It is essential to control all steps of development of such solution, especially when some components are having multiple actions in the matrix.

Here below is shown the performance of a heat and light stabilization solution for automotive polypropylene compounds (TPO) without phenolic antioxidant to reduce emissions of any sorts. Processability stabilization is supported by another type of radical scavenger in combination with a high performance processing stabilizer.

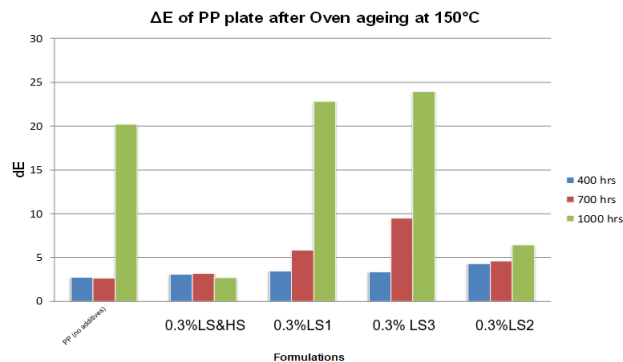
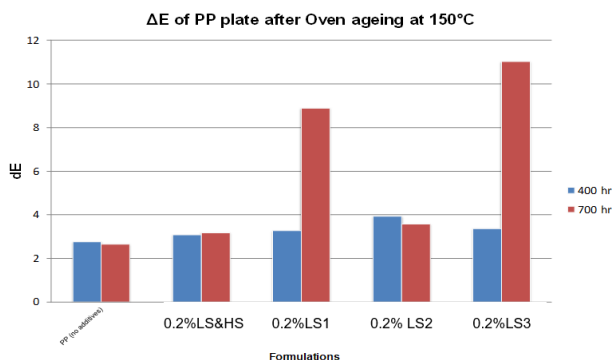
Combination of several benefits, critical for automotive interior applications, are comprised in the same additive solution:

- Light stabilization
- Heat stabilization
- Odor management

Using this solution, light stabilization of TPO compounds may reach thousands of hours of artificial weathering, according standard from OEMs, without significant color shift, comparable or higher performance than any alternatives in the market:



Excellent color retention for heat stabilization at 150°C of same TPO compounds can reach 700 hours or even 1000 hours, depending on other components, thickness of the parts and dosage of the solution, without the addition of phenolic antioxidant or sulfur-based additives. Standard antioxidant package in the base resin was sufficient, no additional antioxidants were needed to achieve the automotive OEMs requirements in heat stability for interior applications.



These results make this synergistic solution highly recommended for automotive interior TPO applications.

Odor evaluation was also performed for comparison and validation of a complete solution for stabilization of automotive TPO applications.

Results we obtained were reaching as low as 1.5 (on the 6 grades scale) at room temperature testing and as low as 2.5 for high temperature testing

Conclusion

Standard stabilization packages (included in the resin or available in masterbatch form) are normally suitable for the resin protection under standard conditions of use but fail when facing severe processing or usage conditions.

Selection of an additive or additive package can be critical and, if improperly done, may lead to unexpected side effects particularly when other components are included in the resin.

Additives package may be added directly in the resin or in compounding step, as masterbatches or more recently as “ready-to-use” solution.

Development of specific solutions regarding color and aesthetics, heat and light stability require high performance specialty additives in order to provide outstanding protection to plastics parts for the demanding automotive industry.