Date: January 2021

Secrets of Thermo-oxidative and Thermal Stabilization of Polypropylene and Polyethylene

The degradation of polyolefins is well established.

Thermal processing degradation of polypropylene is a dominant chain scission reaction by free radicals that attack the polymer and increase melt flow (decrease viscosity) during melt processing. Standard additions of primary antioxidants with various key acid acceptors provide the optimum performance. However, once the chain scission mechanism has altered the molecular weight and distribution there is no turning back. Furthermore, any degradation that has occurred during processing remains while long term radical migration perpetuates in the dark as long term thermo-oxidative damage and radical build up over time.

Thermo-oxidative degradation as measured by ASTM rotary oven at temperatures from 150C to lower temperatures is accomplished with mainly ten mil compression molded plaques suspended on a rotary rack in a circulatory air oven until failure. Failure being indicated at 150C by the onset of powder decomposition, while at 125C and below embrittlement. Thermo-oxidative degradation measured by accelerated oxygen induction techniques on 10 mg samples is regulated by the temperature and NOT oxygen diffusion limited. Therefore, typical O.I.T. temperatures are 200C or 190C and exceed the melt temperature of polypropylene. OIT is typically done in the melt while ASTM testing is done on solid molded plaques of various thicknesses. The differences in the results are dramatic and neither technique has been sufficiently correlated. Degradation in the melt of stabilized polyolefins occurs by a different overall mechanism than degradation on molded samples.

Control of both thermal and thermo-oxidative degradation of polyolefins requires a full understanding of all the variables that control all mechanisms. A few of these variables include but not all inclusive:

- **Temperature**
- **Residence Time**
- **Thickness**
- **Orientation**
- **Acid acceptors and Concentration**
- **Type and Mw of the antioxidants used.**
- **Primary versus secondary antioxidants**
- **Environment of test.**
- **Venting or recycling of air in test chambers**
- **Sources of pro-degradants**
- **Cross over contamination**
- **Sample preparation used for testing**
- **Handling of samples-gloves vs no gloves**
- **Volatility of antioxidants**
- **Migration of antioxidants**

Clearly the variables dictate the limits of stabilization and degradation of the polymer. For recycled plastics called litter the challenge becomes broader. Initial design of the plastic depends on the end use requirements of the customer dictated to the manufacturer who designs the system for the end use requirements. In most instances the engineering of the formulation is cost benefit performance based and has limits. These limits are cost and performance and rarely include benefits beyond cost performance by the customer. Differentiation of the plastic by resin manufacturers is mainly focused on cost performance. However, down stream the customer may add additional formulation upgrades by masterbatch that benefit their needs.

Plastic litter on the other hand has no such guidelines. The plastic ends up in land fills and immediately exposed to environmental conditions

that start to compromise the plastics. These factors were not part of the original guidance by the customer to the resin manufacturer and become new variables. These include cross over contamination by various foods, food ingredients that contaminate the polyolefin waste. Oils and fats promote degradation of polyolefins and reduce thermal and thermo-oxidative stability.

Other variables include photo-oxidative degradation of exposed plastic litter that further degrades the plastic.

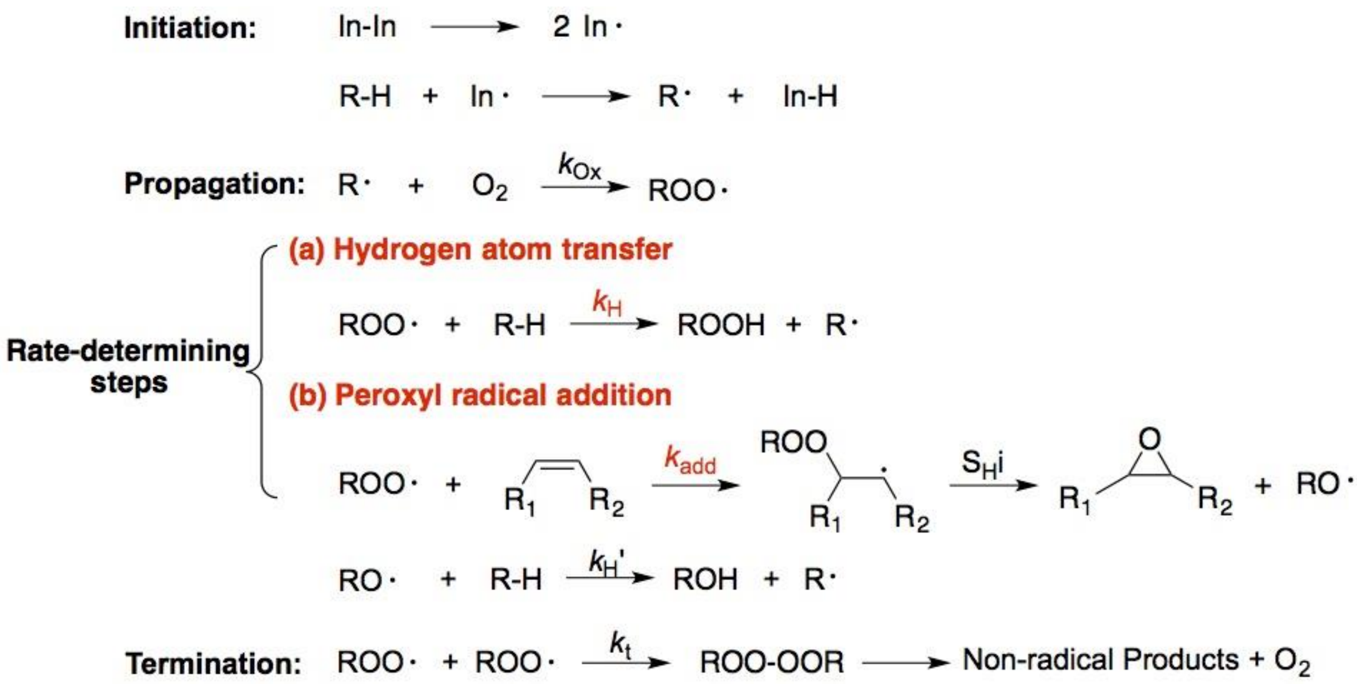
Cross contamination of the polyolefins with other plastics used in packaging that are not compatible in the melt make sorting more prevalent to prevent recycling from being perfect.

These factors all contribute to various unknowns that require further clarification prior to upcycling of the recycled polyolefin waste streams. Blending of polypropylene and polyethylene is not the problem. Both are miscible. However, less

compatible plastics combined with polyolefins is possible it can be costly when using IPN networks, and grafting techniques. However, SCF techniques today are looking promising if done correctly under proper guidance.

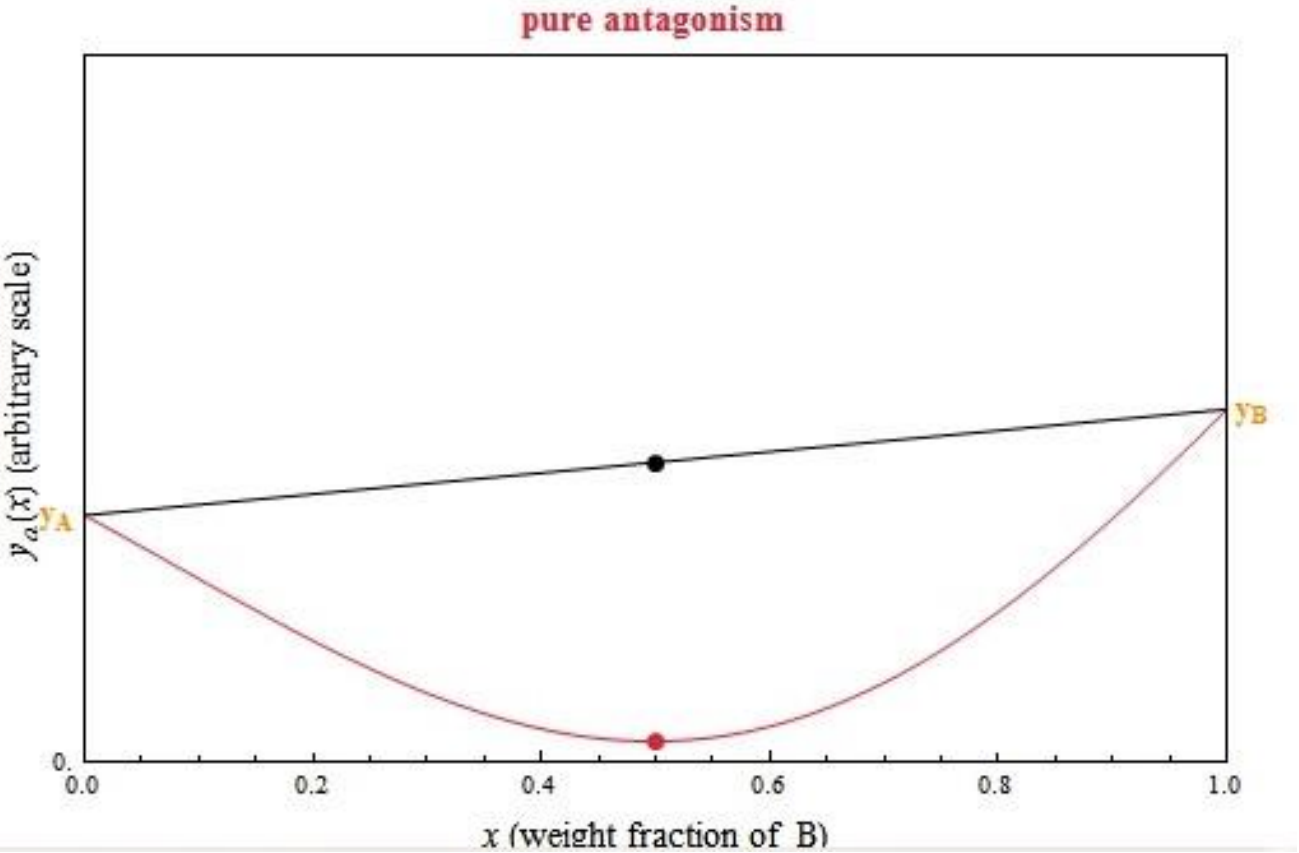
Furthermore, a common failure among recyclers and upcycling of waste is ignoring the existing state of the plastics before melt blending alone or with other plastics. Free radical damage and existing free radical reactions dominate in organic polymers and occur more rapidly and are longer lived. These radical reactions are prevalent in polyolefins and do greater damage in a shorter time than occur in condensation polymers.

We know from several years of study that the free radical mechanism see below continues after melt processing and after molding and increase rapidly in the dark period:

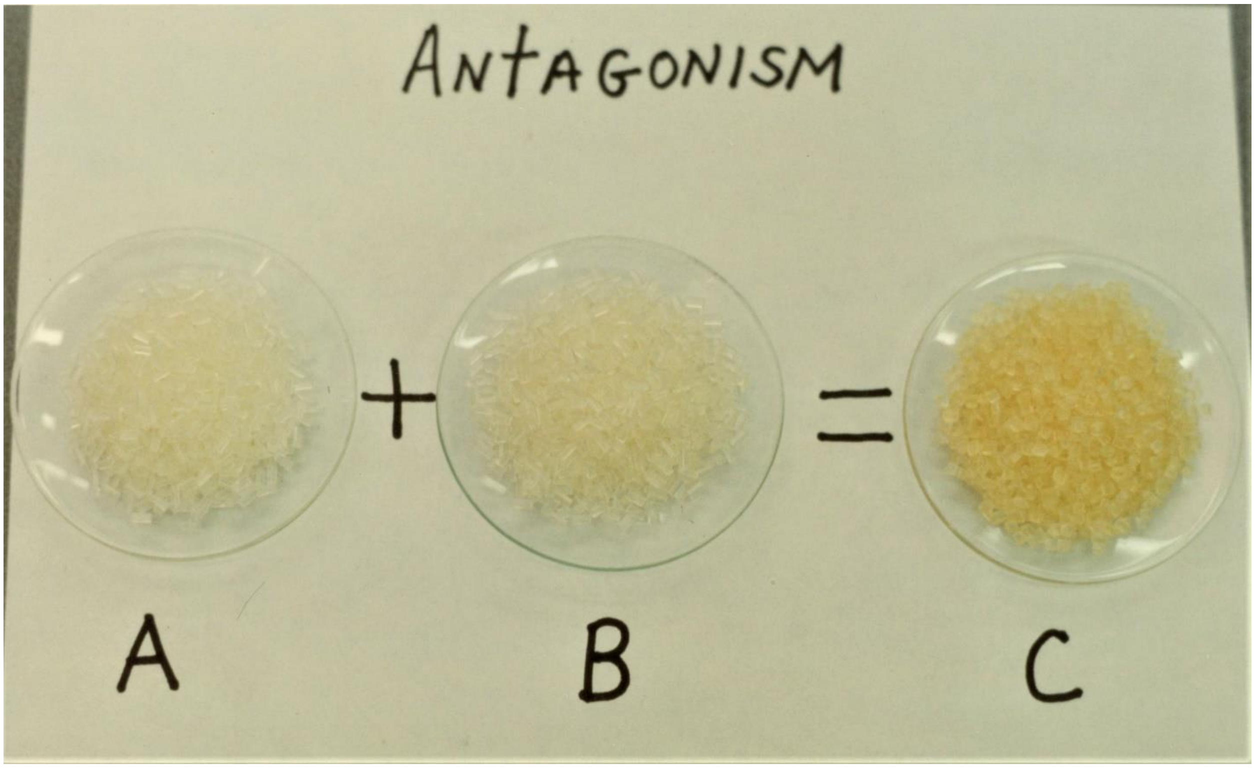


To control free radical mechanisms primary and secondary antioxidants which are consumed and fugitive over time also leave behind in-situ transformation products that in many cases are pro-degradants or can act as highly staining weaker stabilizers. Discoloration of polyolefins typically manifested as yellowing initially or over time has negative connotations for end use.

Recycled polyolefin waste streams globally contain highly diverse antioxidants, and the levels vary dramatically from a few hundred parts per million to over one percent depending on the end use application. What has been kept secret by the industry has added to the problem of recycling and upcycling!! This secret known among those versed in the field of stabilization and controlled degradation is called "Antagonism"



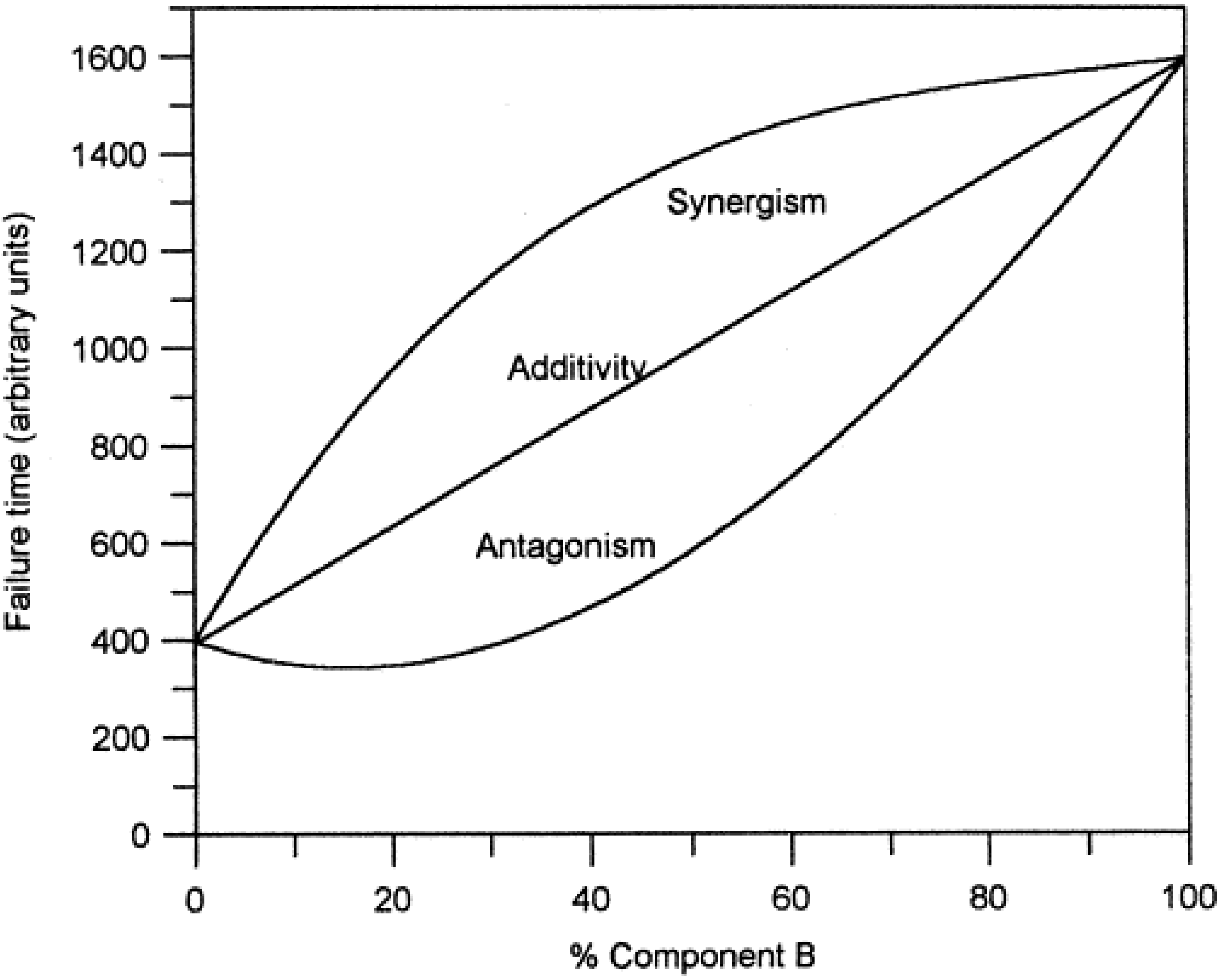
A photo of yellowing antagonisms between different types of antioxidants is seen in this photo.



Although yellowing antagonism is considered negative for sales of the polyolefin to the market it may also be a positive depending on end use requirements of thermo-oxidative stabilization.

However, avoidance of yellowing is a focus among polymer stabilization chemists. Therefore, designs among these chemists working at resin

manufacturing companies is focused on synergisms not antagonisms.



Synergisms provides for control of formulation cost and allows for better designed formulations that require higher limits on end use requirements.

Today to achieve new goals and end use applications we find the technology limited and restrictive and those vendors who manufacture antioxidants have not kept up with global demands. Therefore, what drives the market is lower cost, lower additive content and lower performance and greater liability. The days of R&D that gave us the products that met the requirements. Technical service and support are limited or eliminated and worse the information has been lost by downsizing the technical skill set that got us here over the last fifty years. This is resulting in the community re-inventing the wheel, mistakes are increasing that could have been avoided and costing the industry millions.

Although we are experiencing a global shift toward mediocrity the work continues to provide cheaper and clearer solutions to the real problems that exist in the global market including upcycling of plastic waste.

Our latest findings have discovered a new method to restore polyolefin waste by suppressing and terminating in-situ free radical mechanisms in the dark period and allowing for subsequent proper upcycling of the degraded waste products.

This technique starts by understanding the state of the waste and reverse engineering the type and level of stabilizers present. This includes primary, secondary, and acid acceptors and lubricants added and or cross contaminated in the litter stream.

Once this information has been gathered a course of action with predictive results as outcomes.

Elimination and suppression of the free radical mechanism is inexpensive and can be implemented on PCR and PIR and landfill waste that has been present in landfills for years.

This technology has been expanded in the last few years to condensation polymers. Polyamides and

Polyesters have been upcycled and part of a new global market. Depolymerization is no longer required for non-fiber applications like injection molding, roto molding, thermo-forming, sheet, or blow molding.

These new findings are now part of a global effort to alter the existing paradigms of stabilization and controlled degradation of polyolefins and condensation polymers that make up the bulk of global plastics today.

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