



Acid Acceptors a Historical Perspective

The term Acid Acceptor or Acid Scavenger or Acid buffer has its roots to a time when Polyvinyl chloride (PVC), was one of the most dominant resins during the scale up transition of polyolefins. During this period flexible and rigid PVC were evolving and stability issues were focused on both antioxidant and transition metal fatty acid derivatives transition metal oxides in an effort to control acids from the plastic. The dominant acid in this case was hydrochloric acid. The acid was a by product of processing PVC and fabrication. The corrosion by the acid attacked both compression and injection molds and equipment related to processing at the time.

From these studies the foundation for future studies in polypropylene and polyethylene were used to correct for the acids remaining from polyolefin manufacturing. Considering the type of catalyst systems at the time the natural focus was on chloride and titanium and aluminum residues from catalyst that remain behind from the process. Unfortunately, among each manufacturer the rapid development of new catalyst systems significantly outpaced research and development efforts to properly study the consequences of the catalyst residue.

Besides the known adverse consequences of acids in polyolefins the choice, concentration and type of acid acceptor to control the damage from the acid also created side reactions that were unknown or predicted at the time.

The same rules used in PVC mediation were not comparable for polyolefins especially with the concentration and type of acid acceptor used for the known catalyst systems at the time.

In addition to each new acid acceptor being tested the new chemistries provided its own set of challenges with regard to side reactions.

During the period we will call Phase 1 of Acid Acceptor Development (1964-1974) the use of metallic stearates was a dominant form of acid acceptor for polyolefins and the logical choice based on work done in PVC. However, what was not predicted were the many chemical forms from various manufacturers at the time that created many problems. These changes in chemistry from the structural characteristics known at the time gave marginal performance as an acid acceptor. This performance was measured by corrosion testing a method well adopted for its time and correlated with mold insert corrosion.

Instead of solving the problem metallic stearates of many forms caused of plate out, rancidity, odor, volatiles, voids, increases in discoloration initially and during storage, interactions with primary and secondary antioxidants of this period, and filterability problems especially during fiber spinning of polypropylene a growing market at the time. However, metallic stearates provided for mold release during injection molding.

It should be noted during the ten year period all polyolefin manufacturers were positioning their individual manufacturing with their type of catalyst system on select markets which at the time included injection molding, blow molding, thermoforming, sheet, fiber, slit tapes and film as the dominant markets. Each manufacturer segmented their production volumes into these markets based upon melt flow and their perception of the performance of their resins against their competitors.

The groups within each manufacture responsible for issues of stabilization and controlled degradation of the resins were also charged with acid acceptor studies and the consequences of these chemistries on down stream marketing of the resins.

The shape of these studies determined the competitiveness of each company and the dominance of the vendors supplying these additives for study.

What few knew at the time was the interconnection between acid acceptors and the overall stability and performance of the resins being manufactured. This was made more complicated by the way in which the additives were added to the manufacturing platforms at the time. Some added the additives in the process at different stages of production while others added them post drying and isolation or at the very end of the process during the extrusion stage of

palletization. Each method provided for a series of interesting outcomes that only added to the mystery of acid acceptors.

In Phase II (the period between 1974-1984) was in our opinion the most critical period and the most exciting for the history of acid acceptors.

By this time conferences were publishing papers and reports daily on academic and corporate studies including the military on the effects of both stabilizers and acid acceptors. The dominance of new primary and secondary antioxidants to study with the same acid acceptors was growing and little time to fully understand the interactions.

Acid Acceptors finally were recognized as not just additive acid scavengers but key factors in the overall performance and stabilization of the plastic. This was shown in processing stability studies of Rheocord and Single and Twin screw multiple pass studies of melt flow (melt index) changes and especially in long term thermo-

oxidative degradation studies in a circulatory air oven and from oxygen induction time (O.I.T) studies by Differential Scanning Calorimetry.

During this period new findings and new problems with acid acceptors became more evident based on new end use application for the plastics globally.

Polyolefins were growing and the need for new solutions to existing problems grew in proportion to the market. Finding solutions to problems that did not exist were not as prevalent and priorities on new threats to the market share dominated daily research and development.

New problems with crystallization and nucleation were mounting. The connection between chemical interactions and addition methods were beginning to affect performance and major disagreements prevailed based on ignorance at the time of the complex chemistries formed.

Nucleation of polypropylene using the existing Generation 1 and 2 catalysts provided consistent and predictable performance but the new Generation 3 and 4 type catalysts were becoming a new problem. The new catalyst or called Super High Activity Catalyst used new supports and a selectivity control agent (SCA). Therefore, deviations from the conventional Ziegler Natta catalyst at the time and new manufacturing methods both created new problems for polyolefins. With increasing yields came additional problems with thermo-oxidative stabilization and induced crystallization changes not seen in conventional catalysts. The catalyst residues were different in form and their activities were much higher than conventional Ziegler Natta. We now had hotter catalyst residues. Although the levels were lower than in conventional Ziegler Natta catalyst we had more activity. We now saw major changes in the functionality of Aluminum and its new form while Magnesium residues were

unknown at the time and considered minor compared to Aluminum residues. The SCA used created its own problem especially with odor and nucleation.

In order to effectively deal with the issue acid acceptors had to evolve again. The new generation acid acceptors had to be multi-functional and not only provide acid scavenging but deal with new forms of acid. Bronsted acid theory was acceptable for old generation catalyst residues and the process at the time but now we introducing Lewis Acid theory into the mix. The new form of acid and residues created issues of nucleation problems with processing especially in slit tapes and fiber orientation. This was not an issue for Injection molding but for other applications where deliberate addition of nucleating agents were tailored for an end use application, the presence of a resin that was self-nucleated complicated the introduction into markets where nucleation was not needed nor welcomed.

This problem today continues to persist globally especially for those manufacturers who have licensed the new catalyst technologies.

So, de-nucleating agents were developed around the multi-functional frame work of a total systems approach. During this period of development an industry had to deal with the issues of thermo-oxidative stability of polypropylene affected by these new catalyst residues and the new primary and secondary antioxidants the time.

In Phase III (from 1984-1994), we saw further catalyst development and improvements in the SCA used in high activity catalyst resins. Methods of manufacturing changed and so did the addition methods and post treatments of the resin powder prior to palletization. We also saw a surge of new secondary antioxidants affected by the catalyst residues not seen with primary antioxidants in the past.

These new problems included “Black Specks”, char formation in the extruder of secondary antioxidants, excessive plate out and corrosion problems from the in-situ decomposition of secondary antioxidants referred to as aliphatic and aromatic phosphites. Secondary antioxidants from the group called thioesters (thioethers) also became problematic. Odor generation by these additives was limited by processing in old conventional catalyst systems now we found the new high activity catalyst and the new acid acceptors being introduced to deal with the new catalyst were causing major interactions with sulfur based chemistries.

While these findings were being discovered we saw vendors who sold primary and secondary antioxidants as their core competency adopting the same problem acid acceptors in their technical brochures with their additives. This only helped to perpetuate the problems further. This was especially common among compounders and master-batch producers, a growing dominance in the market that only complicated the problem for the manufacturer.

While polyolefin manufacturing in the United States drove additive growth the internal technologies found to solve these problems was constantly challenged by those using the resins without knowledge of the sophistication of the additive systems designed by the manufacture. Additive systems developed by each resin manufacture is specifically tailored for the application intended. Therefore, compounders and master batch convertors using the same resins for their own design of systems for their customers end use failed to recognize the additives present that interacted with the additives being compounded in larger quantities. Thereby creating new problems and these same problems continue globally to this day and appear to be growing with a rapidly shrinking technical staff with a historical perspective.

Phase IV (1994-2018) saw rapid changes in licensing of catalyst technologies, a gradual change in the vendors selling additives and few new additive developments but rather re-branding and blending technologies of old additive technologies. There appeared to be far

more improvements in light stabilizer technologies beyond the scope of conventional ultraviolet absorbers into the realm of hindered amines. Primary, Secondary, Tertiary, amino ethers, acetylated hindered amines. Monomeric, oligomeric, and true high molecular weight versions of hindered amines were introduced with their own set of problems that required new acid acceptors to deal with the interactions between primary and secondary antioxidants and the acids that would deactivate or neutralize the HALS and other in-situ reactions that caused plate out problem.

By this time the additive industry had introduced and eliminated many additives from the market that were either grand-fathered into resin systems for years or phased out due to patents or regulatory issues by EPA, REACH and ECHA.

However, by this period acid acceptors had dramatically evolved conventional metallic stearates e.g. calcium stearate to other metallic fatty acids from stearic acid to behenic acid and many more carboxylic acid groups.

The metal ion had changed dramatically from calcium to sodium, zinc to magnesium, lithium and exotic metallic stearates like iron, cobalt, cerium and manganese were used in for controlling degradation of the plastic.

In addition to an evolution of fatty acid derivatives as acid acceptors changes in manufacturing techniques and raw materials used to produce these derivatives all become relevant in the stabilization and performance of the polyolefin. The fatty acid used and its purity and the reaction mechanism used to produce the additive all have profound consequences on performance.

New acid acceptors using more simplistic chemistries beyond the scope of hydrotalcites and other layered clays will limit the interactions between other additives and the in-situ transformation products produced.

The problems facing the global plastic industry today appear to be the same as recognized by resin manufactures in the last twenty years. This trend appears to show how it reinvents the same problems over and over again.

As catalyst changes continue with manufacturing protocols and techniques to improve on a process the need to constantly improve on acid acceptor technologies becomes even more important.

The next phase of development will most certainly be predicated on the technical expertise remaining from those with a historical perspective of past problems and lessons learned from their solution to these problems. The expansion of global manufacturing outside the United States and Europe has shown the same problems experienced over twenty years ago are currently being experience in these countries.

Therefore, the problems never go away they are recirculated to a new generation with less experience.

- **The purpose of this article stem from a persistent theme we continue to observe globally in the polyolefin industry related to the perception of acid acceptors and stabilization of plastics. Mistakes today are being repeated because of a lack of understanding and consistent leadership and total lack of curiosity and innovation. Future articles will key on the various natures of acid acceptors and the complicated chemistries involved. No one acid acceptor can be utilized for any one additive system. It is a matter of understanding the end use application and requirements for that application that determines the additive systems used.**

