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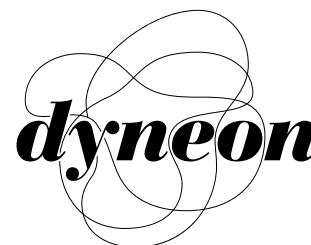
Title:

The Influence of Polymer Process Additives (PPAs) and Hindered Amine Light Stabilizer (HALS) Combinations in LLDPE Blown Film - Part IIA

Abstract:

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**The Influence of
Polymer Process Additives (PPAs)
and Hindered Amine Light Stabilizer (HALS)
Combinations in LLDPE Blown Film - Part IIA**

Susan S. Woods
Dyneon LLC

Rick E. King III, Ph. D.
Ciba Specialty Chemicals

Claude Lavallée
3M Canada

ABSTRACT

Polymer Process Additives (PPAs) are used to improve the melt extrusion of polyolefins. Hindered Amine Light Stabilizers (HALS) are used to prolong their ultra-violet (UV) stability in outdoor applications. These two types of additives are often used together in linear low density polyethylene (LLDPE) blown film applications where melt fracture free films with good UV stability are needed: for example, agricultural films and some heavy duty shipping sacks. The potential interaction between PPAs and some HALS has been examined previously.¹ This paper builds on that earlier work and looks at new HALS products developed specifically for markets where attempts to minimize the potential interaction between PPAs and HALS has been explored.

INTRODUCTION

PPAs have been added to LLDPE resins even before their widespread introduction in the late 1980s^{2,3}. Around this same time HALS were being adopted in LLDPE to provide light stability to film products. Within a few years of the introduction of these two types of additives, it became clear that under certain circumstances the ability of the PPA to eliminate melt fracture could be affected by the presence of certain types of HALS. This interaction was first studied and reported soon afterward^{4,5}.

Part I of our work¹ was a practical range-finding study which further investigated the HALS-PPAs interaction not only with regard to the effect of the HALS on the PPA's effectiveness, but also with regard to the nature of the PPAs on the HALS' effectiveness. (We found no effect on the latter.) Plausible mechanism interactions were also discussed. Part I demonstrated that a careful selection of the correct types of PPAs and HALS can help address the potential interaction from a practical point of view. Part I also gave recommendations on the optimum fabrication conditions required to minimize the impact of the potential interaction.

Part II (A and B) builds on our earlier work and looks at additional modes (separate versus combined masterbatches) as well as at new HALS products developed specifically for markets where attempts to minimize the potential interaction between PPAs and selected HALS has been explored. The reader is referred to Part IIB as a complement to this paper⁶.

EXPERIMENTAL

The experiments conducted in this Part IIA study included:

- Blown film experiments evaluating PPA-1 Dynamar™ FX 9613 (previously shown as being preferred over PPA-2 Dynamar™ FX 5920A in the area of HALS interactions) with

various HALS products.

- Blown film experiments evaluating combined and separate masterbatches.
- Analysis of the coating on the die surface.
- Further evaluations on the potential mechanism. Part I evaluated what this mechanism for the HALS-PPA interaction might be, albeit with limited success. This paper explores the potential mechanism further. Part IIB⁶ will present the extension of UV weathering studies on our original samples and the start of these new ones.

Materials

Additives:

PPA-1 = Dynamar™ FX 9613

HALS 1 = Tinuvin® 622

HALS 2 = Chimassorb® 119

HALS 3 = Chimassorb® 944

HALS 4 = CGL 116

HALS 5 = Chimassorb® 2020

HALS 6 = Tinuvin® 111

HALS 7 = Tinuvin® 783

HALS 8 = High Molecular Weight NOR• HALS

Masterbatches for Blown Film Work:

The PPA masterbatch was a 3% target concentration in a 2.0 MI LLDPE. The HALS masterbatches were all a 10% target concentration in a 2.0 MI LLDPE.

Resins:

The resin used for this study was a commercially available 1.0 MI, 0.920 density octene-LLDPE.

Fabrication

For the melt fracture evaluations, the formulations were blown into film on a Kiefel blown film line. The film line consisted of a 40 mm grooved feed extruder, 24/I Length/Diameter (L/D), 18/35/60 mesh screen pack, 40 mm die, 1.14 mm die gap (except for the films for the light stability testing where a die gap of 2 mm was used in order to provide a baseline film free of surface melt fracture and containing no PPA), and a single lip air ring. The output was approximately 30 lbs./hr. to give a shear rate of approximately 600 sec⁻¹ on the narrower die gap. Melt temperature was maintained at approximately 230°C.

Die Surface Studies on Slit Die Rheometer

In this case, the PPA masterbatch and the samples at the final level were prepared in a 1 MI, 0.918 density butene resin. The PPA masterbatch was at a 2% target concentration. The HALS masterbatches were the same as for the blown film work.

Formulations for slit rheometry testing were prepared using a Haake Rheocord™ System 90 torque rheometer and Rheomix™ 3000 mixing bowl attachment fitted with roller blades. The mixing sequence began with a two minute material loading period at 15 rpm. During the third minute the rotor speed was increased to 50 rpm and held constant for the rest of the duration of the sequence. The set point temperature of the bowl was initially programmed at 210°C for two minutes and then decreased to 180°C during the third minute and held constant for the rest of the duration. The entire mixing cycle lasted for eight minutes. Total batch size was 190 grams; final melt temperatures of the samples were in the range of 180°C to 200°C.

Rheometry experiments were performed on an Instron 4202 frame with a 3210 rheometer barrel using a flat entry slit die with a 3.81 mm width, a 0.25 mm gap and a 13.2 mm length. The die was set up with removable shims that could be removed for analysis. The die shims (stainless steel or copper) were cleaned and polished before each test.

For each sample, the die was coated by extruding the composition at a shear rate of 300/s until constant pressure was reached. The pressure reduction provided by the PPA was reported as a percentage of the pressure of the resin without PPA.

TECHNICAL CHALLENGE

As mentioned earlier, the phenomena of adding more PPA to achieve a melt fracture free film product in the presence of certain type of HALS has been widely experienced in the field. Having said this, it should be emphasized that this is not a ubiquitous occurrence. The effect of the interaction can be measured in terms of the rate of elimination of melt fracture or the amount of PPA required to completely eliminate melt fracture. In those occasional cases where it is observed, there is a straightforward set of remedies such as: adding a little more PPA, or changing the type of PPA. In the cases where this is specifically identified as a HALS-PPA interaction, changing the type of hindered amine, or its concentration relative to the PPA may also be pragmatic approaches. Other practical steps include lowering the melt temperature as much as possible.

RESULTS AND DISCUSSION

The data set collected was composed of three parts:

1. Blown film experiments where the percent of melt fracture was visually assessed over time.
2. Slit rheometry data looking for evidence of the site competition mechanism.
3. UV light stability testing of the blown film samples. (Reported in part IIB)

Blown Film Results

Part I of our work showed that with some HALS, higher melt temperatures required higher levels of PPA to clear melt fracture. Part I also showed the ranking of various HALS with PPA. This data set is continued here by expanding the HALS

species evaluated with PPA-1. The results, illustrated in Figure 1, show that again HALS 1 is the additive of choice as far as enabling the PPA to effectively eliminate melt fracture. HALS 3 is the most challenging. HALS 6 and 8 are intermediate and essentially equivalent to each other from the aspect of this performance element. HALS 7 is perhaps slightly improved over HALS 6 and 8 but is not as good as HALS 1. We chose 3000 ppm as the HALS level in order to make the test on the PPA more stringent than in Part I of our study.

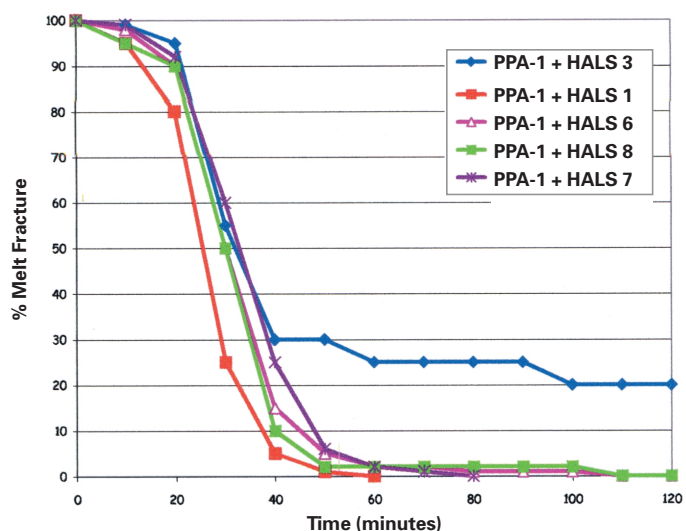


Figure 1 – Showing least to most interference with HALS + PPA-1

It is of interest to note that HALS 7 (which is a blend of HALS 1 and HALS 3) lies approximately midway in performance between the two blend components. HALS 6 (which is a blend of HALS 1 and HALS 2) is expected to behave in a similar fashion.

Figures 2 and 3 illustrate the effect of combining HALS and PPA-1 into one masterbatch instead of adding them separately.

It is obvious from the previous two figures that in order to minimize the interaction one would want to use separate, and not combined, masterbatches.

Possible Mechanisms

We would like to propose two likely mechanisms for the HALS-PPA interaction:

- Site competition (between the HALS and the PPA at the polymer metal interface)
- Potential for acid/base chemistry (chemical reaction between the HALS and PPA)

Both of these mechanisms have been discussed in some detail in Part I. This discussion is a summary from that paper, included here for the reader's convenience.

In regard to competition for the metal surface, additives that strongly compete with the PPA are undesirable as they

negatively impact the elimination of melt fracture. This interference can be an issue since one of the primary mechanisms for the processing additive to function is based on establishing, and then maintaining, a coating of PPA on the metal surface. If other additives prevent or impede the coating process, it will take longer to establish the coating, or take more PPA to maintain the coating.

Separate and Combined PPA-1 & HALS 1 Masterbatches

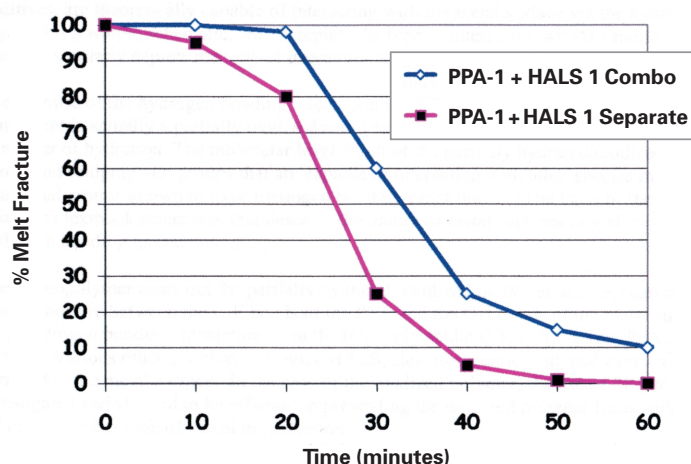


Figure 2– Melt Fracture clears faster if the HALS 1 and PPA-1 are added as separate masterbatches

Separate and Combined PPA-1 & HALS 3 Masterbatches

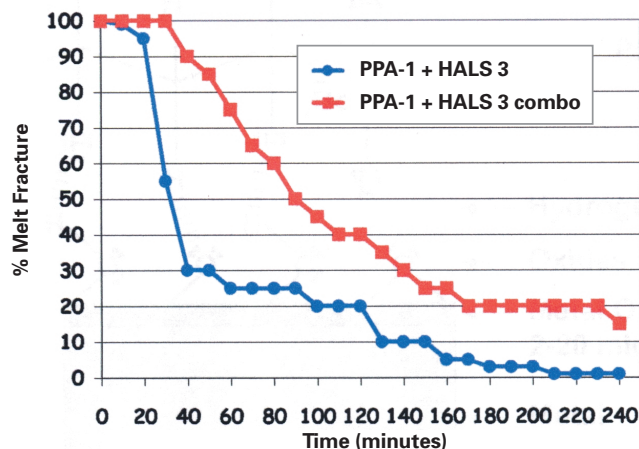


Figure 3– Melt Fracture clears faster if the HALS 3 and PPA-1 are added as separate and combined masterbatches

One of the primary mechanisms for bonding to the metal surface is thought to be (multiple) hydrogen-bonding sites between the various additives and the partially hydrated/partially oxidized metal surface. HALS, as well as other additives, are theoretically capable of interacting with the metal surface via the hydrogen bonding interactions. Figure 4 is a simple schematic, which depicts the type of interaction with the metal surface that can occur with PPAs. Figure 5 similarly depicts the type of interaction that can occur with HALS.

The premise of the hydrogen bonding interaction is based on the assertion that the metal surface of the processing equipment is actually a partially oxidized metal surface. On top of the partially oxidized metal surface, there is a thin layer of hydration. At the molecular level, the result of the partially hydrated/oxidized metal surface is a series of $-OH$ bonds and bridging $-O-$ groups that are capable of interacting with other species (in the polymer matrix) that contain functional groups known to have hydrogen bonding capabilities. (The basis of these interactions can be found in numerous textbook references that describe the nature of metal surfaces as well as the principles involved regarding hydrogen bonding interactions.)

The fluoropolymer coats out the partially hydrated oxidized metal surface. As can be seen from Figure 4, the interactions are between the C-F bonds of the PPA and the $-OH$ bonds of the metal surface. There is also a potential for a hydrogen bonding interaction from the relatively acidic C-H bonds of the PPA and the $-OH$ bonds of the metal surface. Various other additives (phenols, HALS, stearates/stearic acid and even oxidized polymer) can also be attracted to the metal surface. In the case of the oxidized polymer, the use of PPA to reduce this effect has been investigated and shown to be efficient in preventing the oxidized polymer from building up and sloughing off as a gel or some other type of visual imperfection⁷.

For the hindered amine, a representative example of the hydrogen bonding interaction could potentially be formed between the $-NH$ of the piperidinyl group and the $-OH$ on the metal surface. In regard to the HALS, since hindered amines are not recognized as melt processing stabilizers, the molecule is not involved in polymer stabilization. Therefore, there is no net gain from the molecule interacting with the metal surface and maybe limiting polymer-metal interactions. In fact, if the HALS-metal interaction is strong, it will inhibit the fluoropolymer from coating out on the metal surface.

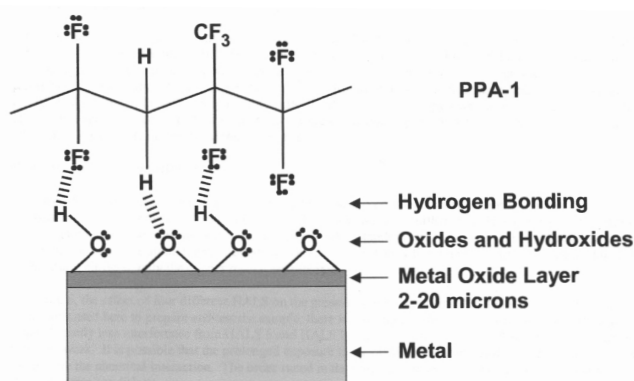


Figure 4– Potential Interaction (PPA) via Hydrogen Bonding Mechanism

Potential for Chemical Reactivity

The potential for chemical reactivity between the relatively 'acidic' PPA and the relatively 'basic' HALS has been previously discussed in some detail'. Despite the demonstration of the POTENTIAL for chemical interaction by oven aging and TGA testing, there was no conclusive scientific evidence that proved that such an interaction did in fact occur in the blown film extrusion experiment. Should an acid-base type reaction have occurred, one would expect to find a double bond in the fluoropolymer. Both IR and Raman spectroscopy scans failed to detect any double bonds. However, it should be noted that if the interaction were solely due to site competition, there would be no difference between using separate or combined masterbatches.

Potential for Site Competition

Capillary rheometry testing, which had previously been used to establish that site competition was occurring between additives, was also included in Part I. In this study, we have further investigated this site competition concept through the use of metal 'shims' composed of either stainless steel or copper. The results for both copper and stainless steel were similar. Because stainless steel interferes with the analytical techniques used to detect fluorine and nitrogen, only the copper results are reported.

In Figure 6, the effect of four different HALS on the pressure reduction obtained at 300/s is reported. Under the conditions used here to prepare and test the sample, there is a strong interference from HALS 3 and HALS 1. There is significantly less interference from HALS 6 and HALS 8. This is slightly different than what was observed in the film line work. It is possible that the prolonged exposure to elevated temperature (200°C) used in these experiments exacerbated the chemical interaction. The order stated in the previous section is probably more relevant to most film manufacturing conditions.

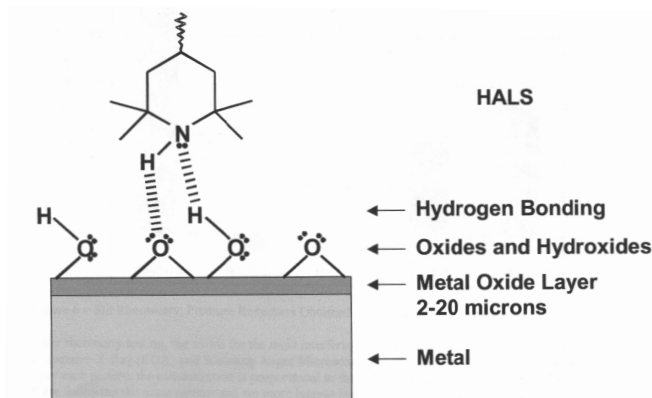


Figure 5– Potential Interaction (HALS) via Hydrogen Bonding Mechanism

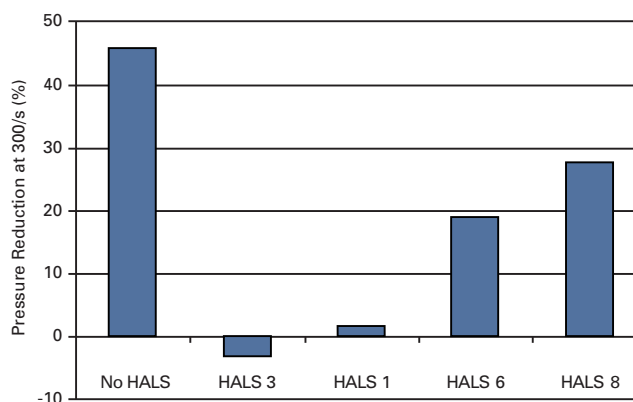
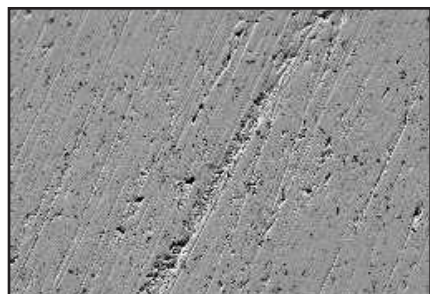


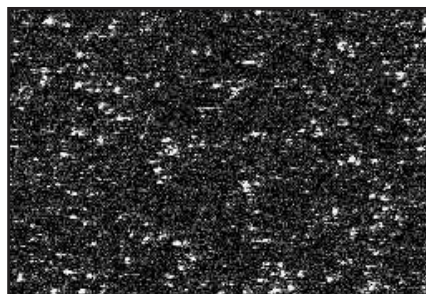
Figure 6- Slit Rheometry, Pressure Reduction Obtained with PPA-1 in the Presence of Selected HALS

After rheometry testing, the shims for the most interfering HALS were collected and sent for analysis by Energy Dispersive X-Ray (EDX) and Scanning Auger Microscopy (SAM). The EDX maps are given in Figures 7 and 8. For each picture, the concentration is proportional to the light intensity. On both figures, one can see that the C and F are following the same pattern and are more intense in the crevasses on the die. Similarly, aluminum and oxygen exhibit the same pattern. This is probably due to the use of aluminum oxide abrasive to polish the dies. The pattern of copper is the reverse of C and F indicating that less of the Cu is visible when the coating is thick. Also, in both cases, the fluorine is distributed evenly across the analyzed area. From this test, there is no evidence of competition.

It should be noted that, the intensity on these pictures is only a relative scale and a direct comparison between the two samples cannot be made.



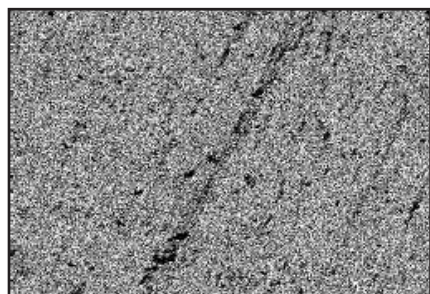
SEM image, 500X, 15kV



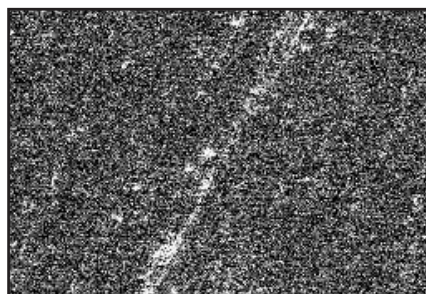
Aluminum



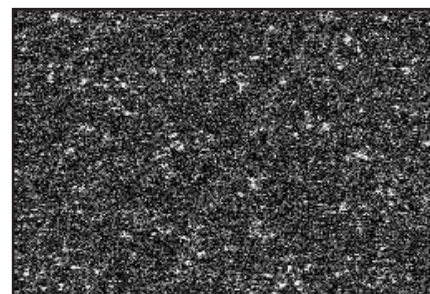
Carbon



Copper

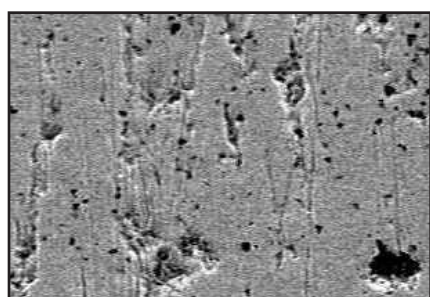


Fluorine

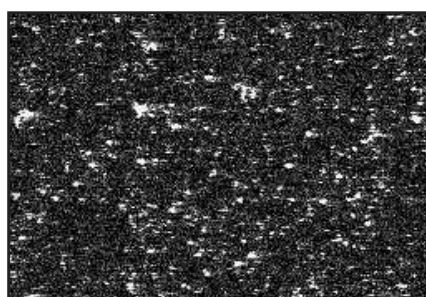


Oxygen

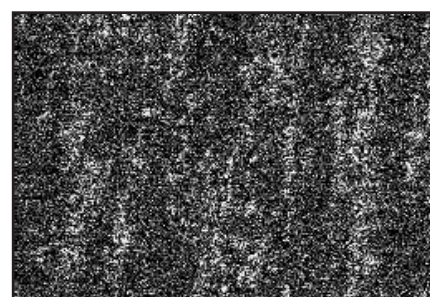
Figure 7 – EDX Map, 500x, 15kV, PPA-1 with No HALS



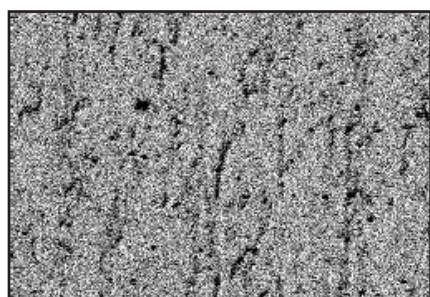
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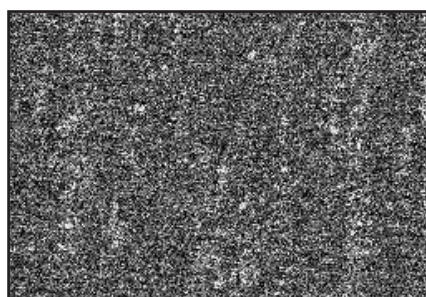
Aluminum



Carbon



Copper



Fluorine



Oxygen

Figure 8 – EDX Map, 500x, 15kV, PPA-1 with HALS 3

Because EDX cannot detect nitrogen SAM was, used to monitor the nitrogen. The SAM maps are given in Figure 9. The detection limit is lower in this case and the noise in the pictures makes the comparison difficult. However, the same trend is observed, where C and F are more intense in the crevasses of the die. The nitrogen map is the reverse of the fluorine map, suggesting that the HALS is coating the areas where there is no PPA. Table I shows the elemental composition of the die surface after coating with a PPA. In this case, the results clearly show fluorine on the surface when no HALS is present and very little fluorine when HALS is present. Also, there is nitrogen on the surface with HALS and no nitrogen without HALS. This strongly suggests that the HALS, at least in part, compete for the metal surface.

Although we have found conclusive evidence for mild site competition, the potential for a chemical reaction between PPA and certain types of HALS still exist¹, even though we have found only indirect evidence that it occurs. For these reasons, we believe that the interaction mechanism is likely some combination of site competition and chemical reaction, which may occur to different extents, depending on extrusion conditions.

RECOMMENDATIONS

From a practical perspective, the way to handle the interaction includes the following suggested steps:

- The concentration and relative concentration ratio of HALS and PPA need to be taken into consideration
- Keep your melt temperatures low
- Remember that PPA-1 is the PPA of choice for minimizing the reduction in melt fracture elimination rate penalties caused by interactions with some HALS
- Remember the order of increasing HALS interference (but keep in mind your whole additive package)
Least: HALS1 < HALS 6 < HALS 7 = HALS 8 < HALS 3 :Most
- Keep your PPA and HALS masterbatches separate

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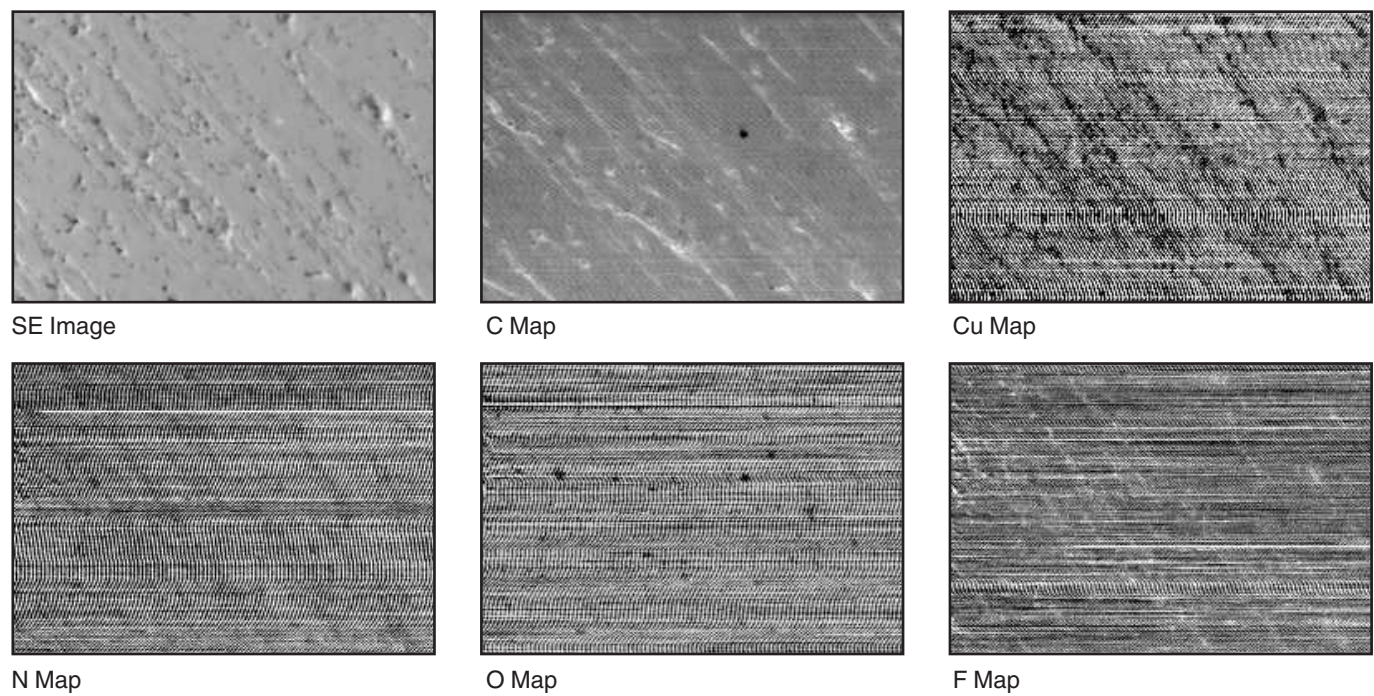


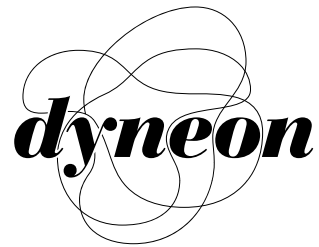
Figure 9 - SAM Map, 500x, PPA-1 with HALS 3

Table 1: SAM - Elemental Composition of the Die Surface After Coating with a PPA

	Cu	C	N	F	O	Cl
PPA-1	7.7	84	0	5.3	2.8	0.5
PPA-1 + HALS 3	7.4	82	8.3	0.5	1.8	0.3

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Dyneon Sales Offices:

Dyneon LLC
6744 33rd Street North
Oakdale, MN 55128
Phone: +1 800 723 9127
+1 651 733 5353
Fax: +1 651 737 7686

3M Canada Inc.
PO Box 5757
London, Ontario NGA 4T1
+1 519 451 2500

Dyneon GmbH & Co. KG
Hammfelddamm II
D-41460 Neuss/Germany
+49 2131 14 2524

Dyneon N.V.
Canadastraat 11, Haven 1005
B-2070 Zwijndrecht, Belgium
+32 3 250 7537

Sumitomo 3M Limited
33-1 Tamagawadai 2-chome
Setagaya-ku, Tokyo
158 Japan
+81 03 3709 8111

Product Information:

+ 1 651 733 5353
+ 1 800 723 9127

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