Vitamin E - A New Choice for Polyolefin Stabilization

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Summary: Vitamin E based systems provide an alternative way to stabilize polyolefins, instead of the current state-of-the-art stabilizers, for certain niche applications. Its very positive public perception together with its excellent ability for melt flow control at a very low concentration can be utilized to a great extent, particularly for special applications like food and medical packaging. Thus, it's use can lead to an overall reduction in the total amount of additive required compared to a traditional stabilization system in certain applications. Other potential benefits, resulting from the positive attributes of Vitamin E, include low migration, high extraction resistance, very good organoleptics, gel suppression, and longer shelf-life of products. This study examines the performance of Vitamin E based systems in LDPE, LLDPE, HDPE and PP.

Introduction

The packaging industry is competitive, dynamic and growing. Consumers are looking for greater convenience such as improved package design and longer product shelf life, higher levels of package security, and there is an increasing awareness of the chemical additives used in the food and food-packaging.

Vitamin E has a positive public perception and is enjoying market awareness which led to its increasing inclusion in consumer products in the food and cosmetic industry. Vitamin E offers an attractive alternative to traditional stabilizers such as BHT (butyl hydroxyl toluene), due its GRAS (Generally Recognized As Safe) status by the FDA when used as a polymer stabilizer, and its worldwide approvals for use in food contact applications.

As the data demonstrates, vitamin E is an excellent polymer antioxidant providing superior melt flow control at low concentrations. Data also indicate that Vitamin E improves gel suppression during film manufacturing, particularly in resins which are prone to gel formation. Some studies have also indicated that packaging formulations stabilized with vitamin E have a positive effect on the organoleptic (taste and odor) properties of the product. Other testing suggests that the shelf life of the product may be improved through the use of a packaging material stabilized with Vitamin E **[5,7,8]**. Finally, though more costly than traditional stabilizers on a "per kilogram" basis, Vitamin E can be a cost effective stabilization system due to its significantly reduced use concentration.

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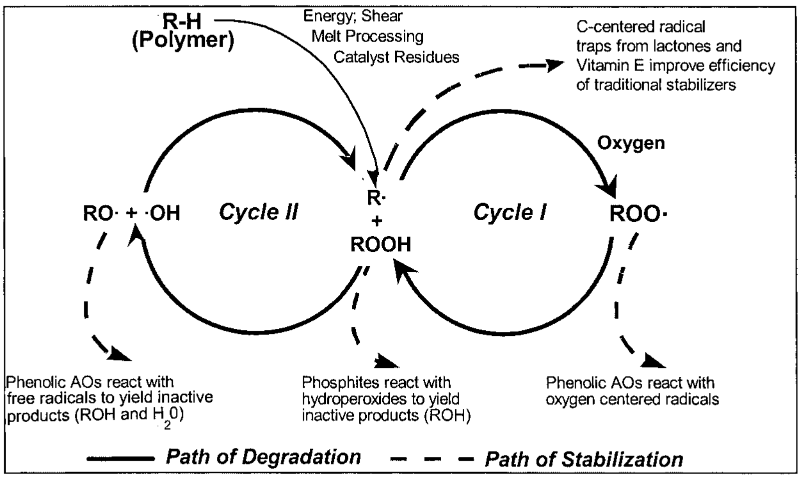
Autoxidation of Polymers

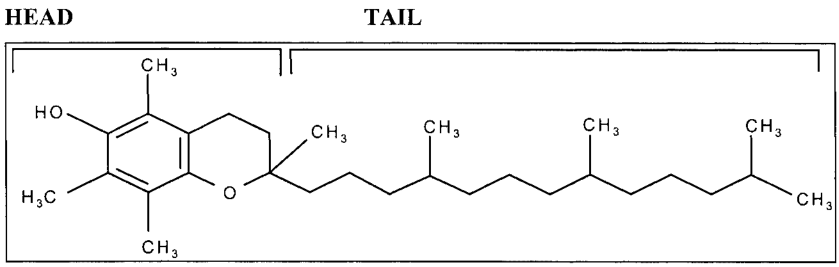
A simplified model for the inhibited autoxidation cycle for polyolefins is shown in Scheme A. The cyclical process represents polymer oxidation throughout its life cycle whereby the polymer is subjected to variety of energy sources, stresses, high temperatures and shear rates from the multiple melt extrusion steps and contaminations. Furthermore, catalyst residues, entrapped oxygen and other types of impurities play a role in promoting further degradation of the polymer [1].

In an effort to eliminate these types of reactions, a variety of stabilization chemistries have been developed[2,3] and commercialized. These stabilizers concurrently work to help preserving the original molecular architecture of the polymer both above and below its melting point as it moves through its life cycle, see Scheme A.



Scheme A: Autoxidation of polyolefins and points at which antioxidants can interrupt the oxidation cycles

Antioxidants interrupt the degradation process in different ways, depending on their structure. The two major classifications are: (i) chain terminating primary antioxidants, and (ii) hydroperoxide decomposing secondary antioxidants; vitamin E belongs to the first class. Like classical hindered phenols such as AO-1, AO-2 or BHT, vitamin E is also a sterically hindered phenol, though has a lower degree of sterica hindrance, Scheme B.



Scheme B: Structure of Vitamin E

The radical scavenging ability of vitamin E, as is the case with the lactone antioxidant, L-1[4], has been suggested to involve reactions with both oxygen-centered as well as carbon-centered radicals[5] The roles of different classes of antioxidants, e.g. Vitamin E, phosphates, lactones, is illustrated in Scheme A [6].

Current Stabilization Practice in Polyolefins

Autoxidation affects the initial molecular architecture of all polymeric materials. For example, in LDPE and LLDPE films autoxidation results in cross-linking of the resin leading to difficulty in film processing and gel formation, whereas, in PP the dominant reaction is chain scission. In HDPE polymers, either cross linking or chain scission would result depending on the catalyst technology used in their polymerisation. Autoxidation can also cause yellowing of the polymer products. Degradation of physical properties, as a result of autoxidation, can lead to unacceptable product performance characteristics.

For LDPE and LLDPE, the current standard systems are widely based on traditional binary blends of high molecular weight di-tertiary butyl phenols (AO-1/ AO-2) and phosphites (P-1/ P-2). New high performance ternary blends involving lactones (L-1) together with traditional phenols and phosphites are being utilized more and more for demanding applications. Vitamin E based systems provide an alternate solution for food, medical and cosmetic packaging. It can meet or exceed the performance standards of traditional stabilizers with little or no cost premium.

Potential applications for vitamin E in HDPE are blow molded and film products for food and medical packaging. For Ziegler catalyzed HDPE, the traditional choice is a binary phenol/phosphite blend (combination of AO-1 or AO-2 with P-1) while in more demanding applications ternary blends of L-1 with AO-1 (or AO-2) and P-1 are used. In very color critical applications instead of P-1, more desirable phosphites like P-2 are used. In Chromium catalyzed grades similar systems are used, but with a relatively higher proportion of the phosphite antioxidant.

Stabilization packages for PP are generally based on phenol/phosphite binary blends as well, but used typically at higher levels, with the most common ones based on AO-1 and P-1. High performance ternary blends of L-1, AO-1 and P-1 offer considerable performance advantages over binary blends at low concentrations in applications with severe processing conditions like BOPP films, thermoforming or fibers. For PP film grades in food and medical packaging applications, vitamin E based systems offer an alternate choice for stabilization.

For extremely color critical applications like fibers, phenol-free stabilization systems are provided by combination of Hindered Amines (HAS-1 or HAS-2) used either with hydroxylamine (NOH) or with a mixture of lactone (L-1) and phosphite (P-1).

Vitamin E as Polyolefin Stabiliser

Vitamin E is also known as α-tocopherol (ATP) [9] with four types of tocopherols found in nature, α, β, γ and δ, differ only by the number and position of the methylation of the arene ring. α-Tocopherol has been shown to have very strong free radical scavenging activity [10]. Its mode of action has been extensively documented in the open literature [11-22] . Basically three factors account for the high activity of α-tocopherol [6].

1. Simple (methyl) alkyl substitution at both ortho- and meta- positions resulting in less sterical hindrance.
2. No electron-withdrawing groups bonded to the oxygen atom in the para-position of the arene ring, and
3. Good overlap between the 2p orbitals of the lone-pair on the para-oxygen atom and the aromatic π-electron system.

These factors lead to a thermodynamically stable phenoxyl radical (tocopheroxyl radical) derived from the abstraction of the phenolic hydrogen atom of α-tocopherol which accounts for its high activity.

α-Tocopherol and its transformation products provide excellent melt processing stability by functioning as a H-atom donor, an oxygen-centered radical scavenger, and as carbon-centered radical scavenger. α-Tocopherol transformation products have also been shown to be very effective radical scavengers and that is part of the reason for its activity even at low concentrations [22] .

Since the ramifications of a poorly stabilized polyolefin resin can be rather diverse due to autoxidation (as described above), selection of appropriate stabilizer systems is of utmost importance to ensure that the performance requirements of the end users are met by preserving the original architecture of the molecule. In order to differentiate the efficiency of the various stabilizer systems, multiple pass extrusion experiments were carried out to assess melt processing stability, both in terms of melt flow rate and color control, see Appendix II for structural identification of the various stabilizer systems used in this study.

Experimental

Melt Flow Measurement: Multiple pass extrusion and melt flow measurements were carried out under conditions described in the different figures. Color Measurement: Yellowness Index (YI) was measured on 1^{st}, 3^{rd} and 5^{th} pass polymer extrudates according to ASTM-1925-77. 125 mil compression molded plaques; ACS Spectrophotometer; Large Area View; Spectral Component Included; C Illuminant, 2^{o} Observer. Long Term Heat Aging (LTHA): To determine LTHA characteristics, compression molded 40 mil samples were oven aged to measure color development and embrittlement characteristics with a 90^{o} bend test. The aging temperature varied depending on the substrate.

Results and Discussions

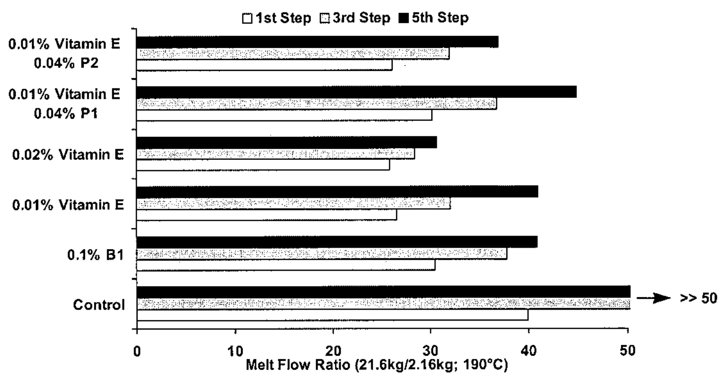
LLDPE

Figures 1 and 2 show a comparison of the performance of vitamin in E by itself as well as in binary systems in combination with different phosphites, and that of a conventional formulation based on 1000 ppm of the binary blend B1. A very small concentration, 100 ppm only, of vitamin E could match the melt flow control offered by 1000 ppm of the blend B1, although the former leads to stronger discoloration. Addition of 400ppm of a high performance phosphite, P-2, to 100ppm of vitamin E improves the melt flow control over that of the B-blend and also improves the color versus the use of 100 ppm of vitamin E alone. One interesting observation is the fact that the effectiveness of vitamin E, compared to B1, is more evident in the 1st pass, which may be due to a greater percentage consumption of vitamin E during the earlier passes compared to the B-blend. This phenomenon is more pronounced when the extrusion is done open to air. In a nitrogen-blanketed environment the propensity of the Vitamin E to be consumed at a higher rate would be reduced.

Figures 3 and 4 show that a ternary system containing the vitamin, the phosphite P2 and the hindered phenol AO-1, used at 200 ppm, improves the melt flow control significantly. Due to the additional amount of the synthetic phenol used, the polymer discoloration due to the system vitamin E/B2 is somewhat stronger than that of vitamin E when used alone. This indicates that the right choice of the phenol and also the phenol/phosphite ratio is important to obtain the desired performance.

Additionally, the use of a high performance phosphite such as P-2 could help to further improve the color behavior of these types of ternary systems.

Fig 1: Melt Flow Control of LLDPE During Processing
Vitamin E and Combinations with Phosphites



LLDPE Butene Type; Gas Phase Process
Single Screw Extruder/Maddock Mixing Head; 24:1 L/D; max 450°F; 40rpm

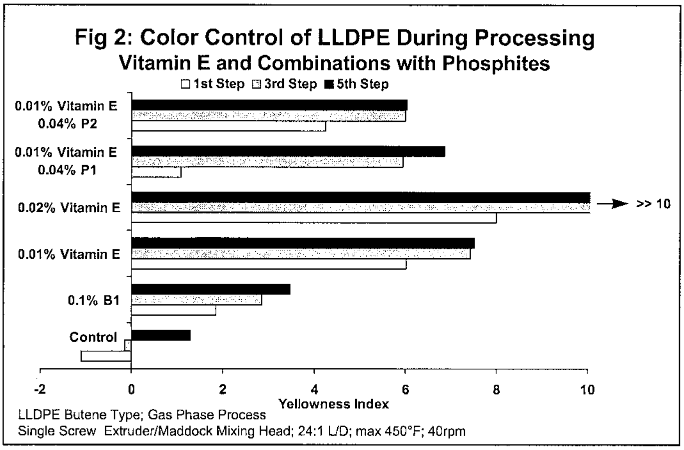


Fig 2: Color Control of LLDPE During Processing
Vitamin E and Combinations with Phosphites
1st Step 3rd Step 5th Step
0.01% Vitamin E 0.04% P2
0.01% Vitamin E 0.04% P1
0.02% Vitamin E
0.01% Vitamin E
0.1% B1
Control
>> 10
-2
0
2
4
6
8
10
Yellowness Index
LLDPE Butene Type; Gas Phase Process
Single Screw Extruder/Maddock Mixing Head; 24:1 L/D; max 450°F; 40rpm

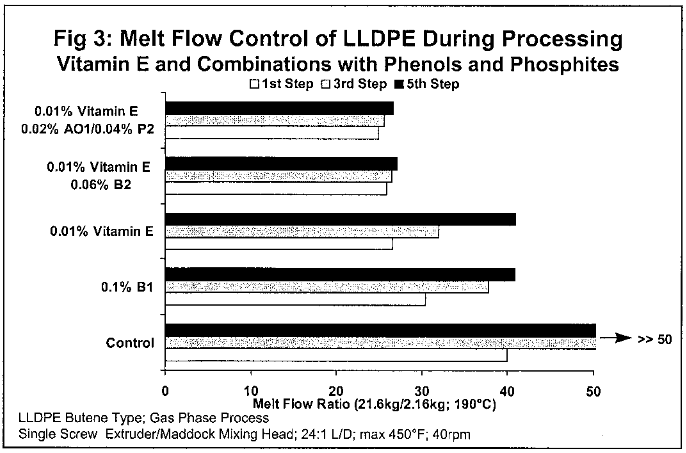


Fig 3: Melt Flow Control of LLDPE During Processing
Vitamin E and Combinations with Phenols and Phosphites
1st Step 3rd Step 5th Step
0.01% Vitamin E 0.02% AO1/0.04% P2
0.01% Vitamin E 0.06% B2
0.01% Vitamin E
0.1% B1
Control
>> 50
0
10
20
30
40
50
Melt Flow Ratio (21.6kg/2.16kg; 190°C)
LLDPE Butene Type; Gas Phase Process
Single Screw Extruder/Maddock Mixing Head; 24:1 L/D; max 450°F; 40rpm

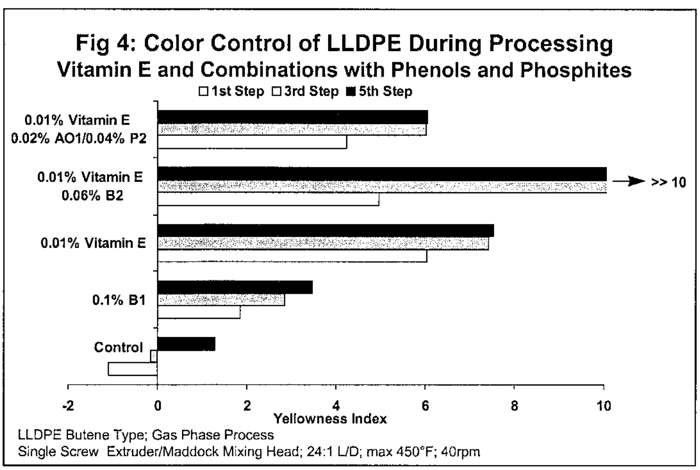


Fig 4: Color Control of LLDPE During Processing
Vitamin E and Combinations with Phenols and Phosphites
1st Step 3rd Step 5th Step
0.01% Vitamin E 0.02% AO1/0.04% P2
0.01% Vitamin E 0.06% B2
0.01% Vitamin E
0.1% B1
Control
>> 10
-2
0
2
4
6
8
10
Yellowness Index
LLDPE Butene Type; Gas Phase Process
Single Screw Extruder/Maddock Mixing Head; 24:1 L/D; max 450°F; 40rpm

LDPE

For LDPE, 100ppm of vitamin E could match the melt flow and color control of 500ppm of the binary blend of B-1 (Fig. 5) . Further addition of a phosphite to the vitamin offers only a marginal improvement in the melt flow control (Fig. 5) and no improvement in color (Fig. 6). One interesting observation in the case of LDPE was the good performance of a high performance ternary system based on lactone (L-1), hindered phenol (AO-2) and phosphite (P-1). 250ppm of such an antioxidant system could match the melt flow control (Fig. 5) and surpasses by far the performance of the binary phenol/phosphite system in terms of color stability (Fig. 6). Such systems are the right choice for demanding LDPE applications.

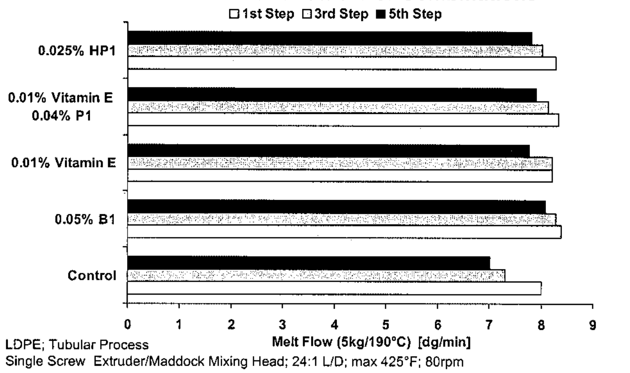
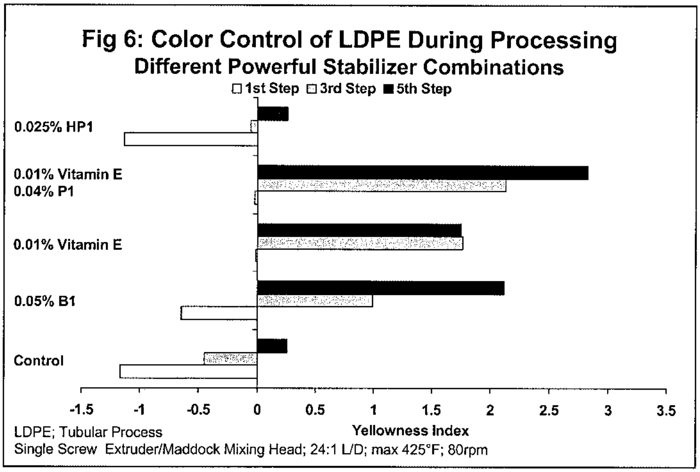
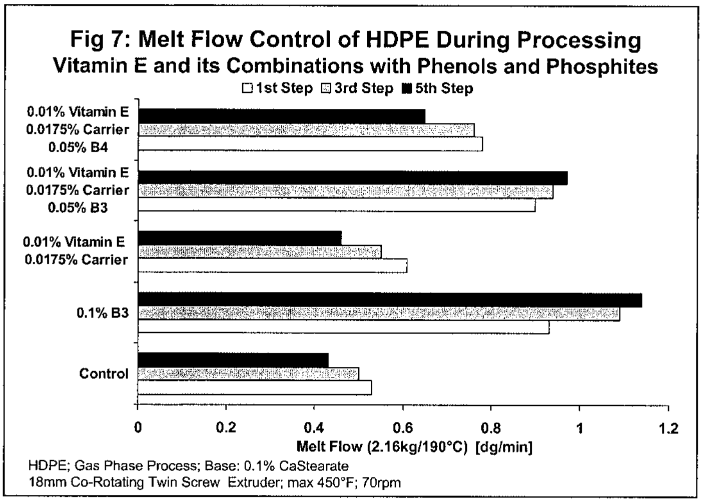


Fig 5: Melt Flow Control of LDPE During Processing
Different Powerful Stabilizer Combinations

HDPE

The work was carried out here using vitamin E on a carrier system in a blow molding grade HDPE resin. It was observed that vitamin E alone could not match the melt flow control of a standard benchmark phenol/phosphite blend (B-3). When used together with the binary blend B-3, the performance improved significantly (Figs. 7-9). All the systems containing B-3 showed strong discoloration. Changing the ratio of phenol to phosphite could improve this. As an example a combination of blend B- with vitamin E offered lower extent of discoloration, but slightly compromising melt flow control.





PP

For the particular PP grade used in this work, the base stabilization requirement was rather high, necessitating a phenol/phosphite binary blend in the 2000ppm concentration range. Like HDPE, the experimental work done here was conducted with vitamin E on a carrier system. Vitamin E alone was not adequate enough to stabilize the polymer at a reasonable concentration level. A binary phenol/phosphite blend, however, combined with vitamin E could match the melt flow control of 2000ppm of B3 with some improvement in color control (Figs. 10-11)

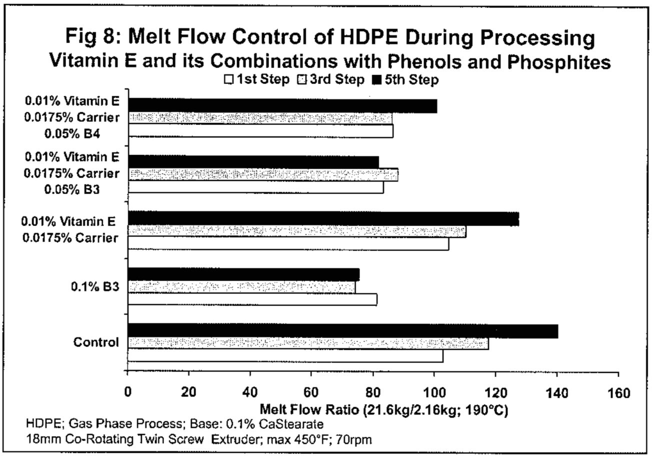


Fig 8: Melt Flow Control of HDPE During Processing
Vitamin E and its Combinations with Phenols and Phosphites
1st Step 3rd Step 5th Step
0.01% Vitamin E
0.0175% Carrier
0.05% B4
0.01% Vitamin E
0.0175% Carrier
0.05% B3
0.01% Vitamin E
0.0175% Carrier
0.1% B3
Control
0
20
40
60
80
100
120
140
160
Melt Flow Ratio (21.6kg/2.16kg; 190°C)
HDPE; Gas Phase Process; Base: 0.1% CaStearate
18mm Co-Rotating Twin Screw Extruder; max 450°F; 70rpm

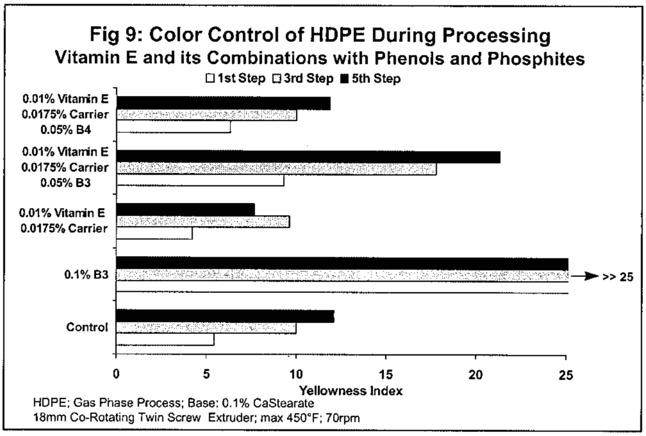


Fig 9: Color Control of HDPE During Processing
Vitamin E and its Combinations with Phenols and Phosphites
1st Step 3rd Step 5th Step
0.01% Vitamin E
0.0175% Carrier
0.05% B4
0.01% Vitamin E
0.0175% Carrier
0.05% B3
0.01% Vitamin E
0.0175% Carrier
0.1% B3
>> 25
Control
0
5
10
15
20
25
Yellowness Index
HDPE; Gas Phase Process; Base: 0.1% CaStearate
18mm Co-Rotating Twin Screw Extruder; max 450°F; 70rpm

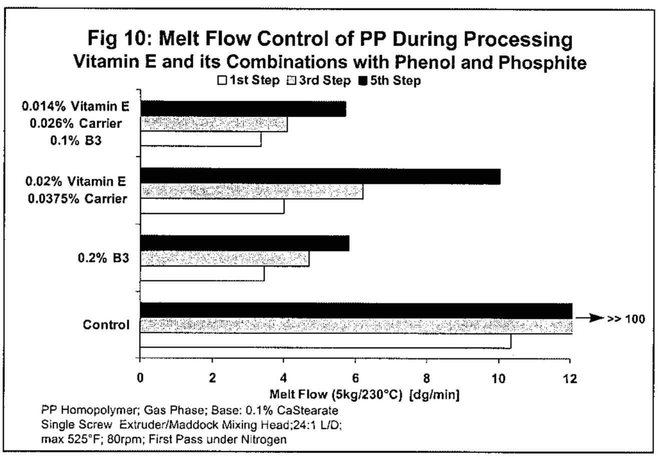
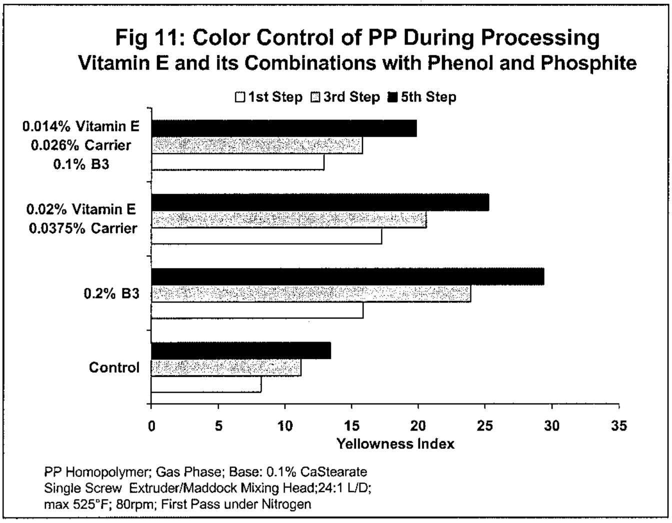


Fig 10: Melt Flow Control of PP During Processing
Vitamin E and its Combinations with Phenol and Phosphite
1st Step 3rd Step 5th Step
0.014% Vitamin E
0.026% Carrier
0.1% B3
0.02% Vitamin E
0.0375% Carrier
0.2% B3
Control
>> 100
0
2
4
6
8
10
12
Melt Flow (5kg/230°C) [dg/min]
PP Homopolymer; Gas Phase; Base: 0.1% CaStearate
Single Screw Extruder/Maddock Mixing Head;24:1 L/D;
max 525°F; 80rpm; First Pass under Nitrogen



Conclusions

Vitamin E represents an attractive choice to resin producers, converters, packaging manufacturers and consumer goods manufacturers to differentiate their products. The positive public perception of vitamin E, its broad regulatory approvals and its environmentally friendly appeal to consumers provide the opportunity for an alternate stabilizer system. Conclusions from this work are as follows:

1. Vitamin E based systems can provide comparable performance to the current state-of-the-art processing stabilizers. Approximately 100 ppm of vitamin E can match the melt flow control obtained with 1000 ppm of a traditional phenol/phosphite binary blend. Addition of phosphites improves the melt flow control and lowers color. High performance phosphites yield better results.
2. Ternary systems of vitamin E/phosphite/traditional phenol can lead to further improvement in melt flow control. The type of phenol and the ratio of the different additives influence both the melt flow control as well as the color development.
3. Vitamin E based systems provide a novel approach to differentiate products in food/medical packaging industry without sacrificing performance.
4. Vitamin E can address odor and taste requirements in specific applications.
5. Vitamin E can lead to suppression of gel formation and improvement of the shelf-life of packaged products.

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Appendix I

<table>
<tr>
<td>AO-1: IRGANOX 1010
Tetrakis(methylene(3,5-di-tert-butyl-4hydroxyhydrocinnamate))methane</td>
<td>AO-2: IRGANOX 1076
Octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate</td>
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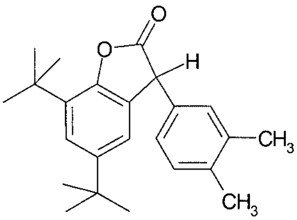
<td>L-1: HP-136
5,7-di-t-butyl-3-(3,4 di-methylphenyl)-3H-benzofruan-2-one

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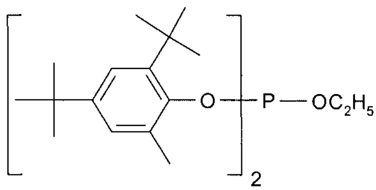
<td>P-2: Irgafos 38
Bis[2,4-di-tert.-butyl-6-methyl)phenyl]ethyl phosphite

</td>
</tr>
<tr>
<td>P-1: IRGAFOS 168
Tris(2,4-di-tert-butylphenyl)phosphite</td>
<td><u>Composition Of Different Blends</u>

<u>B1</u>: 1:2 blend of AO-2 and P-1
<u>B2</u>: 1:2 blend of AO-1 and P-1
<u>B3</u>: 1:1 blend of AO-1 and P-1
<u>B4</u>: 1:4 blend of AO-1 and P-1
<u>HP1</u>: Proprietary blend of AO-1, P-1 and L-1</td>
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