Stabilizing Additives for Polypropylenes Prepared by Solventless Processes

One feature of gas phase or bulk (liquid pool) polymerization techniques for preparing poly-α-olefins with Ziegler-type catalysts is that catalyst residues and low-molecular-weight and amorphous polymers are not separated completely or at all from the crystalline polymeric product prior to commercial use. This may create various problems in the further treatment of the commercial polymer (molding, film-making, fiber preparation, etc.), including, *inter alia,* die-smoking during film extrusion, thermal degradation during extrusion or shaping operations, yellowing, decreases in brightness, and decreased clarity in polymer films. In view of this, polyolefins made by solventless processes require stabilizers capable of forming complexes with ionic catalyst residues and negating the adverse effects of unseparated materials, in addition to the stabilizers usually added to polyolefins made by slurry or solution techniques (which involve removal of catalyst residues and amorphous polymer).[1]

Special interest in these laboratories has attached in the negation of the adverse effects of the essentially inorganic catalyst residues on polypropylenes prepared by solventless processes (bulk or gas phase), and a method for the dechlorination of these residues by including phosphate or phosphonate methyl esters in the stabilizer package was previously reported.[2,3] The present communication deals with our studies aimed at the stabilization of the polymer by using complexing agents to tie up the cationic species (Ti^{3+}, Ti^{4+}, Al^{3+}) present in the catalyst residue in metal complexes that are colorless, thermally stable, and compatible with the polyolefin.[1] Logical choices were ligands of types similar to those used as conventional stabilizers of slurry polypropylene, such as polyalcohols and their partial or complete esters with long-chain fatty acids,[4-7] phosphite or thiophosphite esters,[8,9] and combinations thereof.[10] Accordingly, work in this direction was undertaken by using relatively low yield (3500–4000 g/g $TiCl_3$) bulk polypropylenes prepared with a catalyst system based on AA $TiCl_3$ (Stauffer) and Et_2AlCl. Polymer powders of this type contain about 3.5% boiling hexane extractables, 60–70 ppm Ti and varying levels of Al, depending on the Et_2AlCl-to-Ti molar ratio employed (e.g., from 60–70 ppm Al for a 1.5:1 to 210–250 ppm Al for a 6:1 molar ratio). Initial work with various polyalcohol stabilizers showed significant improvements in polymer yellowness, but some adverse effects were also observed, i.e., pentaerythritol [$C(CH_2OH)_4$] and sorbitol, because of their relatively low thermal stability,[11-15] caused severe discoloration of the polymer at 500–550°F (spiral flow test), while the thermally more stable trimethylolethane and trimethylolpropane [$CH_3C(CH_2OH)_3$ and $C_2H_5C(CH_2OH)_3$, respectively] were satisfactory in the latter test but caused moderate to severe die-smoking during extrusion of the polymer into film. Subsequent research was directed to the use of the even more thermally stable[12,14,15] partial esters of various polyalcohols (pentaerythritol, sorbitan, glycerol, diglycerol, polyethylene glycol) with long-chain fatty acids, and their combination with organophosphorus, organotin, and $Ca(OH)_2$ stabilizers (on top of conventional stabilizer packages of slurry polypropylene).[1] Among these partial esters, pentaerythritol monostearate (PMS) was studied to a larger extent and found to be suitable for all polypropylene grades. In fact, during molding and extrusion studies of bulk polypropylene formulations containing PMS, only a few minor disadvantages (i.e., plate-out of small amounts of PMS in the water bath during extrusion of the polymer into film and contribution to somewhat increased water carryover and static) were observed.

EXPERIMENTAL

Bulk polypropylene powder was admixed with various stabilizer additives (conventional and experimental additives), blended, extruded at 420°F, and pelletized. Polymer pellets were used as such for the melt flow rate and spiral flow tests, but were injection-molded into 2.25-in. diameter and 0.125-in. thickness discs (plaques), by using a miniinjection molder operated at

TABLE I

Improvement of Yellowness Index of Bulk and Slurry Polypropylenes through Stabilization with Pentaerythritol Monostearate

Bulk polypropylenes				Slurry polypropylenes			
Sample no.[a]	PMS (wt %)	Yellowness (%)	Brightness (%)	Sample no.[a]	PMS (wt %)	Yellowness (%)	Brightness (%)
1	None	11.1	65.7	2	None	12.4	62.3
1	0.25	5.2	66.5	2	0.25	11.8	62.3
3	None	9.8	69.5	4	None	6.2	69.1
3	0.1	5.9	69.5	4	0.1	4.3	69.6
3	0.3	5.4	69.5	4	0.3	4.3	69.6
3	0.5	5.6	69.4	4	0.5	3.9	69.8

[a] Additional stabilizers in samples 1 and 2: 0.05 wt % Ca(OH)$_2$ and 0.7 wt % of proprietary stabilizer package A. Samples 3 and 4 were compounded with PMS alone at a lower than normal temperature (400°F).

465°F for the yellowness, brightness, and oven stability tests. Yellowness and brightness determinations were made by using the ASTM Test No. D-1928, while for melt flow rate determinations the ASTM Test No. D-1238 (condition G) was used. In oven stability tests at 300°F or 320°F, failure (h) is given at the point where 10% of the surface of the test disc shows substantial darkening and powdering. Spiral flow is measured in a plunger injection-molding machine, and the effects of changes in cylinder temperature and injection pressure upon flow are measured (in.) of flow in a spiral flow mold; increases (in.) of flow are indicative of increased degradation of the treated polymer. Finally, multiextrusion tests are made by subjecting the polymer pellet to successive extrusions at 550°F; repelletizing is accomplished by using a 0.5-in. single-stage screw compounding extruder.

Among the pentaerythritol esters used, PMS was a product of S. C. Johnson and Sons, Inc. (Jonwax-12), while the monooleate (PMO) and distearate (PDS) esters were reagent grade materials as were also the glycerol and diglycerol monoesters used. Sorbitan and polyethylene glycol (PEG) monoesters were products of Emery Industries, Inc. Reagent grade $Ca(OH)_2$ and organophosphorus stabilizers were used, with the exception of diphenyl isooctyl phosphite, which was a product of Cincinati Milacron Chemicals, Inc. (Advastab CH-90). Finally, two organotin stabilizers were studied: di-n-octyltin maleate (T-813; Thermolite 813 of MIT Chemicals, Inc.) and di-n-octyltin S,S'-bis(isooctylmercaptoacetate) (OTM; Argus Mark OTM of Argus Chemical Corp.). The above experimental stabilizers were used in conjunction with conventional proprietary stabilizer packages for slurry polypropylene.

RESULTS AND DISCUSSION

Before describing the effects of the various experimental stabilizers investigated, it is considered necessary to demonstrate that the effects of partial esters of polyalcohols on polymer yellowing are particularly beneficent for polypropylenes made by solventless processes rather than slurry polypropylenes. The data given in Table I show that PMS has indeed a much larger effect on improving the yellowness index of bulk polypropylenes, relative to slurry polymer samples. This type of response was, of course, expected, since polyalcohol partial esters are known to function as complexing, and possibly chelating agents[16] and the bulk polymer contains much higher levels of metal ions than slurry polypropylene (and especially

TABLE II
Yellowness and Brightness Indices of Bulk Polypropylenes Stabilized with 0.25 Wt % of a
Polyalcohol Monoester

Ester[a]	Yellowness (%)	Brightness (%)
PMS	6.6	66.1
PMO	6.6	65.9
Diglycerol monooleate	6.1	65.7
Glycerol monostearate	6.7	65.2
Glycerol monooleate	6.6	65.5
Sorbitan monooleate	7.0	66.0
Sorbitan monolaurate	6.8	65.0
Sorbitan monostearate	8.1	65.7
Sorbitan monopalmitate	9.3	65.9
PEG-400 monostearate	6.7	66.4
PEG-400 monolaurate	6.0	66.6
PEG-400 monooleate	6.7	66.2
PMS[b]	2–2.5	66–67

[a] Additional stabilizers: 0.05 wt % $Ca(OH)_2$, 0.05 wt % T-813 or OTM and 0.7 wt % of proprietary stabilizer package A.

[b] In these cases 0.05 wt % $Ca(OH)_2$ and 0.9 wt % of proprietary stabilizer package B was used along with relatively high yield (7000–9000 g/g $TiCl_3$) bulk polypropylene samples, prepared by using a high activity, chemically modified, unsupported $TiCl_3$ catalyst (yellowness indices of these polymers without use of PMS were 4–5%).

Ti which is present at the 60–70 ppm level in the bulk polymer samples investigated, but at less than 30 ppm in slurry polypropylene samples).

Comparative studies of a number of pentaerythritol stearate esters [i.e., PMS, PDS, and pentaerythritol tetrastearate (PTS)] revealed that PMS is somewhat superior to PDS, reducing the yellowness index from 11–15% down to 6–9% vs. 8–10% for PDS; PTS, which does not contain free hydroxyl groups, does not contribute to any improvement of the yellowness of the bulk polypropylene. From that point on, our studies were limited to the monoesters of various polyalcohols. Table II lists the effects of a series of stabilizers of this type on the yellowness and brightness indices of bulk polypropylenes with yellowness indices of 15–18% in the absence of polyalcohol esters. Most of the monoesters examined can reduce yellowness down to 6–7%. It is also noteworthy that PMS reduces the yellowness of higher yield bulk polypropylenes down to 2–2.5%. The relative superiority of PMS was later demonstrated in a series of studies of the combined effects of various esters on yellowness and oven stability at 300°F (Table III). During the same study it became obvious that both yellowness and oven stability are improved when an organotin stabilizer (OTM or T-813) is included along with the ester in the stabilizer package.

During subsequent studies, the effects of organophosphorus vs. organotin stabilizers for use along with PMS were investigated. As shown in the data of Table IV, use of diphenyl isooctyl phosphite (Advastab CH-90) offers significant advantages in that it improves yellowness, brightness, spiral flow, and melt flow rate rise, relative to either OTM or T-813; on the other hand, the organotin stabilizers may contribute to higher oven stability at 320°F in comparison to the organic phosphite. The overall conclusion from the data of Table IV is that combination of diphenyl isooctyl phosphite with PMS is advantageous over that of an organotin stabilizer with the same monoester. In view of the favorable effects of diphenyl isooctyl phosphite, a number of other phosphites (0.05 wt %) were later investigated with respect to their contribution on yellowness improvement in bulk polypropylenes containing PMS (0.25 wt %), Ca(OH)$_2$ (0.05 wt %), and 0.9 wt % of proprietary stabilizer package B, with the following results: Yellowness % (brightness %): diphenyl isooctyl phosphite 5.1 (66.4); trilauryl thiophosphite 5.1 (66.4); triisooctyltrithio glycolyl phosphite 4.7 (66.3); dioctyl phosphite 5.3 (66.0);

TABLE III
Oven Stability Studies at 300°F of Bulk Polypropylenes Stabilized with Polyalcohol Esters

Additive package[a]	Initial yellowness (%)	Yellowness (%) prior to failure	Time (h) to failure at 300°F (two discs)
0.25 wt % PMS	7.0	41.2	1488, 1440
0.35 wt % PMS	6.9	41.6	1488, 1440
0.5 wt % PMS	7.1	43.2	1464, 1440
0.25 wt % PMO	7.7	47.3	1464, 1440
0.35 wt % PMO	7.1	47.3	1464, 1440
0.5 wt % PMO	7.5	49.2	846, 870
0.25 wt % PMS + 0.05 wt % T-813	6.6	47.2	1875, 2043
0.25 wt % PMS + 0.05 wt % OTM	6.6	46.5	2225, 2091
0.25 wt % PDS + 0.05 wt % T-813	8.0	43.4	2091, 2043
0.25 wt % PDS + 0.05 wt % OTM	7.9	48.1	2225, 2139
0.25 wt % PMO + 0.05 wt % OTM	6.6	42.5	1488, 1536
0.25 wt % sorbitan monooleate + 0.05 wt % OTM	6.9	47.9	1560, 1776
0.25 wt % sorbitan monolaurate + 0.05 wt % OTM	6.7	40.5	1608, 1656
0.25 wt % PEG-400 monolaurate + 0.05 wt % OTM	6.5	41.5	846, 1440
0.25 wt % PEG-400 monostearate + 0.05 wt % OTM	6.3	40.4	1440, 1536

[a] 0.05 wt % Ca(OH)$_2$ and 0.7 wt % of proprietary stabilizer package A were also included.

TABLE IV
Comparisons of Organotin and Organic Phosphite Stabilizers in Bulk Polypropylenes
Containing Pentaerythritol Monostearate

Additional stabilizer[a]	Yellowness (%) (brightness %)	Spiral flow (in.)	Polymer melt flow rate (g/10 min) after nth successive extrusion at 550°F			Time (h) to failure at 320°F (two discs)
			$n = 1$	$n = 2$	$n = 3$	
None	6.4 (69.7)	19.6	1.7	2.2	2.8	736, 736
OTM	4.6 (70.1)	25.7	3.5	6.5	10.5	834, 834
T-813	4.8 (69.9)	24.4	1.9	3.8	5.1	810, 834
Diphenyl isooctyl phosphite	3.7 (71.4)	19.2	1.4	1.9	2.7	749, 837

[a] 0.05 wt % of the additional stabilizer was used; samples also contained 0.25 wt % PMS, 0.05 wt % $Ca(OH)_2$ and the appropriate proprietary stabilizer package for each application (i.e., 0.7 wt % of stabilizer package A for multi-extrusion and oven stability studies, and 0.45 wt % stabilizer package C for the yellowness-brightness and spiral flow tests).

diphenyl isodecyl phosphite 5.8 (66.2); phenyl didecyl phosphite 6.5 (65.9). The effects of these phosphites on oven, spiral flow, and multiextrusion stability have not been investigated so far.

In conclusion, the present work establishes the beneficial effects of partial esters of poly-alcohols in general, and PMS in particular, as yellowness index improvers of polypropylenes prepared by solventless processes. Additional improvements in yellowness, accompanied by improvements in the thermal stability of the polymer, can be brought about by combining PMS with an organotin or, preferably, an organic phosphite additive. The PMS-organic phosphite stabilizer system should be used along with a suitable inorganic base such as $Ca(OH)_2$ (HCl neutralizer[2,3]) on top of a conventional stabilizer package for slurry polypropylene. The beneficent function of the stabilizers herein discussed is due to complexation or chelation of the monoester[16] and the organic phosphite[17] to the trace amounts of Ti and Al ions present in the bulk polypropylene. The PMS-organic phosphite system can find general application for the overall improvement of bulk or gas phase polypropylenes prepared with unsupported $TiCl_3$ catalysts, ranging from the low activity AA $TiCl_3$ to highly active chemically modified $TiCl_3$ catalysts[18-20] (see Table II). However, the usefulness of this stabilizer package for gas phase or bulk polypropylenes made with supported catalysts, which contain 1–5% Ti on a Mg-based support,[18] is questionable. In fact, polymer made with supported catalysts contains very low levels of residual Ti (1–5 ppm), which is believed to be the main contributor to polymer yellowing.

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