

# Neutral Organophosphoryl Methyl Ester–Metal Chloride Interactions as Applied to the Dechlorination of Catalyst Residues in Polypropylenes Prepared by Solventless Processes

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## Synopsis

A novel method of dechlorinating catalyst residues in polypropylenes prepared by solventless processes is reported. The method is based on the reaction of the metal chlorides present in these residues with neutral organophosphoryl methyl esters, such as trimethyl phosphate and dimethyl methylphosphonate. These reactions lead to the formation of  $M[OP(O)(OCH_3)_2]_n$  or  $M[OP(O)(CH_3)(OCH_3)]_n$  complexes, with evolution of the chloride in the form of methyl chloride. Experimental evidence presented demonstrates that inclusion of one of the preceding esters in the stabilizer package of polypropylene powders prepared by the bulk polymerization process and containing 300–650 ppm Cl, followed by extrusion and pelletization, can result in practically complete dechlorination (Cl content less than 5 ppm) of the polymer.

## INTRODUCTION

Reactions of metal chlorides with diorganophosphinate, -phosphonate, or -phosphate alkyl esters  $[(RO)R_2P=O, (RO)_2R'P=O, \text{ and } (RO)_3P=O, \text{ respectively; where } R = \text{alkyl; } R' = \text{alkyl, aryl, } -N(CH_3)_2, -Cl, \text{ etc.}]$  at elevated temperatures (30–200°C, depending on the metal ion) result in the elimination of alkyl chloride and precipitation of polymeric metal complexes with  $R_2POO^-$ ,  $(RO)R'POO^-$ , or  $(RO)_2POO^-$  ligands,<sup>1–5</sup>



$M = Al^{3+}, Ti^{3+}, V^{3+}, Cr^{3+}, VO^{2+}, ZrO^{2+}$ , for example;  $X, Z = RO$  or  $R'$ . When  $R$  is ethyl or higher alkyl, part of the alkyl chloride produced decomposes to alkene and  $HCl$ .<sup>1–5</sup> The latter reaction is presumably catalyzed by the decomposing metal chloride–organophosphoryl ester adduct,<sup>6,7</sup> which is formed as an intermediate. On the other hand, for  $R = CH_3$ , the methyl chloride produced remains intact.<sup>1–5</sup> It should be noted that reactions of type (1) do not take place when  $R = \text{aryl}$ , at least at temperatures of up to about 300°C.<sup>8</sup>

During studies aimed at the dechlorination of catalyst residues in polypropylene prepared by solventless (liquid pool or bulk and gas phase) processes, it was felt by these laboratories that advantage of the preceding information could be taken. Several organophosphoryl methyl esters were investigated and were found to substantially reduce or practically eliminate the chloride present in the catalyst residues of the poly- $\alpha$ -olefin.<sup>9</sup> Use of the corresponding ethyl or higher

alkyl esters was avoided, since the anticipated elimination of HCl would probably create corrosion problems for the extrusion equipment and might also adversely affect the stability of the polymer. Our studies in this direction are reported in the present article.

A few comments on the importance of dechlorinating polypropylenes prepared by solventless processes are in order at this point: In low-yield polypropylenes prepared by the conventional slurry process by using a low-activity Ziegler-Natta catalyst (e.g., Stauffer's AA  $\text{TiCl}_3$ , which has the composition  $\text{TiCl}_3\text{-}\frac{1}{3}\text{AlCl}_3$ ) and  $\text{Et}_2\text{AlCl}$  as cocatalyst, part of the residual chloride remains in the hydrocarbon diluent (hexane or heptane), while the rest is converted to alkali metal chloride during the subsequent catalyst deactivation treatments with alcohol and aqueous alkali metal hydroxide. In contrast, the solventless processes are designed for use with high-activity and high-stereospecificity unsupported<sup>10,11</sup> or supported<sup>12-14</sup>  $\text{TiCl}_3$  catalysts, so that the costly atactic removal and catalyst deactivation treatments are either eliminated completely or greatly minimized. Consequently, the polymers produced by solventless processes contain residual chloride, part of which will be eventually evolved in the form of HCl and cause severe corrosivity and polymer degradation problems during extrusion and polymer powder or pellet storage. These problems may be alleviated by using stabilizer additives, but it is generally preferable to use a simple method for eliminating the residual chloride before or during extrusion.

In order to test the value of the method herein reported, we have elected to attempt dechlorination studies of relatively low-yield (3500-4000 g/g  $\text{TiCl}_3$ ) and high-Cl-content polypropylenes prepared by the bulk polymerization process by using a catalyst system based on AA  $\text{TiCl}_3\text{-Et}_2\text{AlCl}$ . Polymer powders of this type contain about 3.5% boiling hexane extractables (Soxhlet extraction) and are characterized by melt flow rates of 2-6 g/10 min and a Cl content ranging between above 100 and up to about 650 ppm.

## EXPERIMENTAL

Bulk polypropylene powder was admixed with the dechlorinating agent and various appropriate stabilizers,<sup>9</sup> blended, extruded at 215.5°C (420°F), and pelletized. Chlorine content was determined by X-ray fluorescence spectroscopy, while corrosivity determinations were effected by exposing the polymer pellets to  $\frac{3}{4} \times 2$ -in. strips of mild, cold-rolled, 20-gauge steel (stored under acetone after cutting). During this test, the polymer was contacted with the steel strip for 15 min at  $260 \pm 5^\circ\text{C}$ . Corrosion is indicated by light gray or delustered areas on the strip. For other tests, the pellets were injection molded into  $2\frac{1}{4}$ -in. diameter and  $\frac{1}{8}$ -in. thickness discs (plaques) by using a miniinjection molder operated at 240.5°C (465°F). These discs were used for yellowness-brightness determinations (ASTM Test No. D-1928) and oven stability tests at 160°C (failure is given in hours at the point where 10% of the surface of the test disc shows substantial darkening and powdering).

The phosphoryl methyl esters used in the present study were trimethyl phosphate (TMP),  $(\text{CH}_3\text{O})_3\text{P}=\text{O}$ ; methyl diphenyl phosphate (MDPP),  $(\text{CH}_3\text{O})(\text{C}_6\text{H}_5\text{O})_2\text{P}=\text{O}$ ; and dimethyl methylphosphonate (DMMP),  $(\text{CH}_3\text{O})_2\text{CH}_3\text{P}=\text{O}$ . Other potential dechlorinating agents utilized for comparisons were propylene oxide (P.O.); trimethyl phosphite,  $(\text{CH}_3\text{O})_3\text{P}$ ; dimethyl

sulfite,  $(\text{CH}_3\text{O})_2\text{S}=\text{O}$ ; and dimethyl carbonate,  $(\text{CH}_3\text{O})_2\text{C}=\text{O}$ . It should be noted that no attempts were made to collect and identify the trace amounts of methyl chloride evolved during the dechlorination of catalyst residues in the polymer by using neutral organophosphoryl methyl esters. Gaseous  $\text{CH}_3\text{Cl}$  has been previously collected at  $-80^\circ\text{C}$  and identified by analytical techniques (gas chromatography, IR spectroscopy) as a by-product of the reaction of TMP with various metal chlorides ( $\text{M} = \text{B}^{3+}, \text{Ti}^{3+}, \text{V}^{3+}, \text{Cr}^{3+}, \text{Si}^{4+}$ ).<sup>5,15</sup>

## RESULTS AND DISCUSSION

Table I shows a series of experiments designed to establish the dechlorinating effect of the three phosphoryl methyl esters investigated and compare their superiority relative to other potential dechlorinating agents. From the data of this table, it is clear that both trimethyl phosphate and dimethyl methylphosphonate can reduce the residual chloride to below 5 ppm. Methyl diphenyl phosphate, on the other hand, was found to be inferior, reducing the Cl content to only about one-half of the original value. The three other esters investigated were definitely inferior to the phosphoryl esters; the order of increasing dechlorinating ability for the six esters studied is dimethyl carbonate  $\ll$  trimethyl phosphite  $<$  dimethyl sulfite  $<$  methyl diphenyl phosphate  $\ll$  dimethyl methylphosphonate  $\sim$  trimethyl phosphate. It is obvious that reactions analogous to (1) occur also with phosphite, sulfite, and carbonate methyl esters, as might be expected,<sup>16,17</sup> but these reactions are far from being quantitative, at least under the experimental conditions employed. Propylene oxide also proved to be a much inferior dechlorinating agent relative to the phosphoryl esters; it is likely that most of this

TABLE I  
Dechlorination of Catalyst Residues in Bulk Polypropylenes by Extruding in the Presence of Potential Dechlorinating Agents<sup>a</sup>

Polypropylene sample	Dechlorinating agent, wt %	Other stabilizers, wt % <sup>b</sup>	Cl content after treatment, ppm
A (Cl content 655 ppm)	None	PMS (0.25), $\text{Ca}(\text{OH})_2$ (0.05)	651
	TMP (0.25)	PMS (0.25)	25
	P.O. (0.20)	PMS (0.25)	449
	Dimethyl carbonate (0.25)	PMS (0.25)	570
B (Cl content 344 ppm)	TMP (0.20)	PMS (0.25), $\text{Ca}(\text{OH})_2$ (0.05)	5
	DMMP (0.20)	PMS (0.25), $\text{Ca}(\text{OH})_2$ (0.05)	4
	TMP (0.20)	$\text{Ca}(\text{OH})_2$ (0.05)	3
	TMP (0.20)	Ca and Zn stearates (1:1) (0.1)	5
	TMP (0.20)	—	26
	TMP (0.20)	OTM (0.025)	43
	DMMP (0.20)	OTM (0.025)	22
	MDPP (0.20)	OTM (0.025)	158
	Trimethyl phosphite (0.20)	OTM (0.025)	206
	Dimethyl sulfite (0.20)	OTM (0.025)	171

<sup>a</sup> Average results of three to four extrusions.

<sup>b</sup> All samples contained 0.7% of a proprietary stabilizer package; PMS = pentaerythritol monostearate; OTM = Argus Mark OTM (organotin stabilizer).

volatile reagent (bp 34.3°C) was evolved unreacted under our experimental conditions.

Since two of the phosphoryl methyl esters studied (DMMP and TMP) can remove almost all of the residual chloride from the polymer, it follows that reactions of these esters with all the metal chlorides present in the system are facile under our experimental conditions. With MDPP, dechlorination was not as effective; this may be attributed to the effects of the steric hindrance introduced by the two phenyl groups of this reagent. In fact, reactions of type (1) seem to occur at increasingly higher temperatures with increasing chain length or bulkiness of the substituents on phosphorus when solutions of metal chlorides in neat organophosphoryl ester are heated.<sup>1-4</sup> In contrast, our experimental conditions involve interaction between trace amounts of the metal chloride with small quantities of the dechlorinating agent in a polymer melt medium; hence, the effects of bulky substituents on phosphorus on partially inhibiting reactions of type (1) would become more pronounced under such conditions.

During our studies, it was established that, regardless of whether the deactivated bulk polymer powder was maintained in an inert atmosphere (dry N<sub>2</sub>) throughout its blending with stabilizers and extrusion or was exposed to the atmosphere prior to blending, DMMP or TMP can reduce the Cl content to below 5 ppm. This indicates that elimination of Cl<sup>-</sup> bound to either Ti<sup>3+</sup> or Ti<sup>4+</sup> and oxo (e.g., TiO<sup>2+</sup>), aqua, or hydroxo derivatives<sup>18,19</sup> is equally facile. The same seems to hold true for Cl<sup>-</sup> bound to the Al<sup>3+</sup> of the AlCl<sub>3</sub> present in AA TiCl<sub>3</sub> and of the Et<sub>2</sub>AlCl cocatalyst as well as their partially chlorinated aqua,<sup>20</sup> hydroxo,<sup>20-22</sup> and oxo(AlOCl)<sup>23</sup> derivatives. Use of neutralizing agents such as Ca(OH)<sub>2</sub> or a mixture of Ca and Zn stearates in the stabilizer package appears to improve the dechlorinating ability of DMMP or TMP (reduction of Cl<sup>-</sup> content to 3-5 ppm when these reagents were present vs. 23-43 ppm Cl<sup>-</sup> in their absence). A very tentative interpretation of this effect is that the neutralizing agents react with residual HCl, adsorbed on the polymer surface, to form CaCl<sub>2</sub> and ZnCl<sub>2</sub>, which in turn undergo reactions of type (1) with DMMP or TMP. In fact, the phosphoryl methyl esters would not be likely to drive off any residual HCl, but they would be expected to react with any metal chloride, yielding the corresponding methyl methylphosphonate or dimethylphosphato metal complex and CH<sub>3</sub>Cl.<sup>1-5,15,24</sup> The tendency of CaCl<sub>2</sub> or ZnCl<sub>2</sub> to undergo reactions of type (1) with phosphoryl methyl esters has been recently demonstrated in a study of reactions of methyl methylphenylphosphinate with various MCl<sub>2</sub> salts (M = Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn), which invariably led to the precipitation of the corresponding bis(methylphenylphosphinato) metal(II) complexes.<sup>24</sup>

Table II shows corrosivity data for bulk polypropylene pellets prepared by extrusion in the presence or absence of neutral phosphoryl methyl esters. These results clearly indicate that inclusion of the phosphoryl esters in the stabilizer package results in noncorrosive polymer pellets. Comparative data show that by using Ca(OH)<sub>2</sub>, pellets ranging from noncorrosive to slightly corrosive can be obtained depending on the level of Ca(OH)<sub>2</sub> utilized, whereas use of propylene oxide as a substitute for the phosphoryl methyl ester leads to the production of slightly corrosive pellets.

Regarding yellowness index determinations, dechlorination with organophosphoryl methyl esters leads to lower yellowness percent values relative to dechlorination with trimethyl phosphite (Table III). The inclusion of Ca-Zn

TABLE II  
Corrosivity Data for Various Stabilizer Formulations in Bulk Polypropylenes<sup>a</sup>

Stabilizer additives, wt % <sup>b</sup>	Degree of corrosion <sup>c</sup>
None	1
Ca(OH) <sub>2</sub> (0.05)	0
PMS (0.125), Ca(OH) <sub>2</sub> (0.05)	1
PMS (0.25), Ca(OH) <sub>2</sub> (0.035)	1+
PMS (0.25), Ca(OH) <sub>2</sub> (0.05)	0
PMS (0.25), P.O. (0.10)	1-
TMP (0.15)	0
DMMP (0.15)	0

<sup>a</sup> Initial Cl content in these samples was 125 ppm.

<sup>b</sup> All samples contained 0.9% of a proprietary stabilizer package; PMS = pentaerythritol mono-stearate.

<sup>c</sup> Degree of corrosion is defined as follows: 0 = none; 1 = light; 2 = medium; 3 = severe.

stearate mixtures in the stabilizer package leads to further improvements in yellowness. Finally, oven stability data at 160°C for bulk polypropylenes dechlorinated with DMMP or TMP showed, at best, oven lives of 600–650 h; these values are low for commercial polypropylenes. Additional work is needed for the development of stabilizer packages that will improve both the yellowness and the oven stability of polypropylenes dechlorinated by the method herein described.

Prior to concluding, it should be pointed out that in view of the stoichiometries involved in reaction (1) (i.e., 1 mol ester required per Cl atom), relatively large amounts of phosphoryl methyl ester are required in order to perform the dechlorinations under study. Thus, for about 300 ppm Cl, more than 1000 ppm of the ester should be used (or about 2000 ppm in order to have an excess of the ester needed in the system). It is nevertheless anticipated that the initial chlorine content of polymer powder prepared with highly active unsupported or supported catalysts (yields in excess of 10,000 g/g catalyst),<sup>10–14</sup> and partially dechlorinated by an effective deactivation treatment, will have a Cl content of

TABLE III  
Yellowness and Brightness Indices for Bulk Polypropylenes Dechlorinated with Organophosphorous Compounds<sup>a</sup>

Dechlorinating agent, wt % <sup>b</sup>	Other stabilizers, wt % <sup>b</sup>	Yellowness, %	Brightness, %
TMP (0.20)	OTM (0.025)	10.4	65.0
DMMP (0.20)	OTM (0.025)	9.0	64.3
MDPP (0.20)	OTM (0.025)	8.4	65.2
Trimethyl phosphite (0.20)	OTM (0.025)	17.9	62.6
DMMP (0.20)	Ca and Zn stearates (1:1) (0.10)	6.0	64.9
TMP (0.20)	OTM (0.025)	7.2	64.8
DMMP (0.20)	OTM (0.025)	6.7	63.9

<sup>a</sup> Bulk polypropylene sample B of Table I (344 ppm Cl), except for the last two experiments, where a sample containing 282 ppm Cl was used.

<sup>b</sup> All samples contained 0.7% of a proprietary stabilizer package; OTM = Argus Mark OTM (organotin stabilizer).

less than 100 ppm. This will allow the use of substantially lower levels of TMP or DMMP for the effective dechlorination of the catalyst residue.

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