Effect of Titanium Compounds on Thermooxidative Properties of Stabilized Polypropylene

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Synopsis

The effect of titanium compounds on thermooxidation stability of stabilized polypropylene was studied. It was found that the presence of titanium compounds shortens the induction period of PP oxidation. This phenomenon is brought about by the thermal reactions of titanium compounds with antioxidants which take place during polymer processing. The first step is the reaction of Ti—Cl with OH groups of phenolic antioxidant, which gives rise to a colored titanate and HCl. Hydrogen chloride functions as a Friedel-Crafts catalyst for degradation and dealkylation of phenolic antioxidants. The products of degradation have a very low stabilization efficiency. Hydrogen chloride acceptors suppress antioxidant degradation and increase the polymer stability even in the presence of small amounts of titanium compounds.
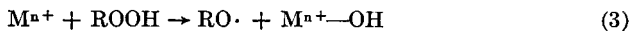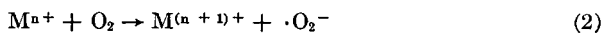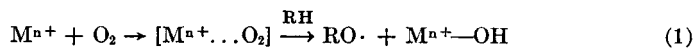
INTRODUCTION

Polypropylene (PP), owing to its chemical structure, exhibits a low thermooxidative stability and therefore, in contrast to polyethylene, has to be protected with a synergistic system of antioxidants. The efficiency of thermooxidative stabilization is strongly influenced by the presence of residues from Ziegler-Natta catalysts, which, if not thoroughly removed by extraction, cause a shortening of induction periods of oxidation and also a yellow discoloration of PP. Deterioration usually results from a titanium component of the catalyst which is hard to remove from the polymer. The effect of titanium compounds on the thermooxidation of polypropylene is the subject of this paper.
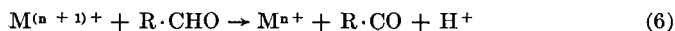
THEORETICAL

Isotactic polypropylene is prepared by polymerization of propylene with Ziegler-Natta catalysts which contain, as a rule, an aluminum organometallic component and a titanium (III) compound. The interaction of both components in the course of polymerisation has been studied by many authors.[1–9] The reaction of α-TiCl$_3$ with organoaluminum compounds was studied in more detail by Rodriguez et al.[3–5] The last-mentioned authors have concluded that catalytic residues are not well defined compounds since their constitution depends not only on the conditions

under which the polymerization was carried out (the ratio of the components, the nature of the defect on α-TiCl$_3$ surface, the temperature etc.) but also on the ensuing processes (extraction, drying etc.) during which the compounds can come into contact with oxygen and water. Generally, it can come into contact with oxygen and water. Generally, it can be said that after polymerization the residue from a Ziegler-Natta catalyst contains titanium in its lower valencies (Ti^{3+}, Ti^{2+}) and that also Ti—Cl bond has to be considered.

The effect of transition metals on thermooxidative stability of polymers is ascribed to initiation reactions in which electron or ligand transfer between organic substrate and transition metal ions takes place. In these reactions the transition metal ions can act either as electron donors or as electron acceptors. The first reaction type involves a direct interaction of transition metal ion with oxygen[10] and hydroperoxides:
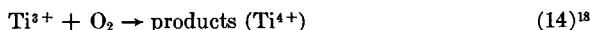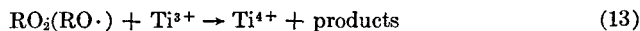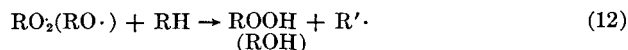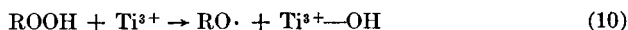
$$M^{n+} + O_2 \rightarrow [M^{n+}\ldots O_2] \xrightarrow{RH} RO\cdot + M^{n+}\text{—OH} \tag{1}$$

$$M^{n+} + O_2 \rightarrow M^{(n+1)+} + \cdot O_2^- \tag{2}$$

$$M^{n+} + ROOH \rightarrow RO\cdot + M^{n+}\text{—OH} \tag{3}$$

The interactions of transition metal compounds with RH or polymer[11,12] and its oxidation products—polymeric alcohols,[13] aldehydes,[14,15] ketones, and hydroperoxides—comprise the second type:

$$M^{(n+1)+} + RH \rightarrow M^{n+} + R\cdot + H^+ \tag{4}$$

$$M^{(n+1)+} + R\cdot CH_2\cdot OH \rightarrow M^{n+} + R\cdot\overset{.}{C}H\cdot OH + H^+ \tag{5}$$

$$M^{(n+1)+} + R\cdot CHO \rightarrow M^{n+} + R\cdot\overset{.}{C}O + H^+ \tag{6}$$

$$M^{(n+1)+} + ROOH \rightarrow M^{n+} + RO_2^- + H^+ \tag{7}$$
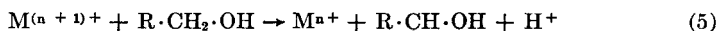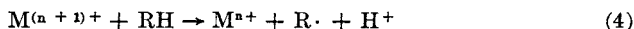
To function as an active oxidation catalyst, a transition metal compound must undergo a reversible change in its valency states (e.g., the reaction sequence eqs. (3), (7) or eqs. (3), (6) etc.). It has been shown that titanium compounds react by mechanism (3).[16] In our previous communication[17] we have stated that in the reaction of polypropylene oligomers with oxygen in the presence of α-TiCl$_3$ an induction period is observed if concentration of [Ti (III)] > [ROOH]. The length of the induction period increases with increasing concentration of α-TiCl$_3$ in the system. Oxidation of Ti (III) to Ti (IV) occurs during the induction period. The appearance of the induction period is evidence for the occurrence of termination reactions of Ti^{3+} with RO$_2^-$ and RO$\cdot$ radicals. Within this time limit the following reactions occur [the bimolecular termination of RO$_2^-$ radicals can be neglected in comparison with the reaction (13)]:

$$RH + O_2 \rightarrow radicals \tag{8}$$

$$\text{Ti}^{3+} + \text{O}_2 + \text{RH} \rightarrow \text{radicals} \tag{9}$$

$$\text{ROOH} + \text{Ti}^{3+} \rightarrow \text{RO}\cdot + \text{Ti}^{3+}\text{---OH} \tag{10}$$

$$\text{R}\cdot + \text{O}_2 \rightarrow \text{RO}_2^{\cdot} \tag{11}$$

$$\text{RO}_2^{\cdot}(\text{RO}\cdot) + \text{RH} \rightarrow \text{ROOH} + \text{R}'\cdot \tag{12}$$
$$(\text{ROH})$$

$$\text{RO}_2^{\cdot}(\text{RO}\cdot) + \text{Ti}^{3+} \rightarrow \text{Ti}^{4+} + \text{products} \tag{13}$$

$$\text{Ti}^{3+} + \text{O}_2 \rightarrow \text{products (Ti}^{4+}) \tag{14)[18]}$$

From the above equations it is evident that under steady-state conditions,

$$\frac{d([\text{RO}_2^{\cdot}] + [\text{R}\cdot])}{dt} = 0; \qquad \frac{d[\text{ROOH}]}{dt} = 0$$

the rate of polymer radical formation according to reactions (8) and (9) is lower than the rate of radical termination W_t in reaction (13). The experiments with model compounds have shown that Ti (IV) compounds are not as active catalysts as are compounds of Co, Mn, Fe, and Cu. Because of these results we proposed that the thermooxidative stability of polypropylene is influenced to a greater extent by the reactions between titanium compounds and antioxidants than by the redox reactions of titanium compounds occurring during the oxidation process.

EXPERIMENTAL

Chemicals

Isotactic polypropylene (VÚMCH Brno) prepared by the α-TiCl$_3$-Al(Et)$_3$-catalyzed polymerization of propylene. The catalyst residue was extracted with 5% isopropanol solution of HCl. The viscosity number of PP was 288 and the polymer contained 89.8% of isotactic fraction. The content of titanium is stated in the text.

α-TiCl$_3$ (VÚMCH Brno) was prepared by reduction of TiCl$_4$ with hydrogen. The isopropanol solution was used for impregnations.

Ti(OiPr)$_4$ was prepared according to Bradley.[19] The fraction 104–104,5°C/10 mm Hg was collected.

Ti(CH$_3$COO)$_2$Cl$_2$ (Dynamit Nobel), pure grade.

Antioxidants were purified by decantation with petroleum ether and by fourfold recrystallization from 80% ethanol. Pure compounds were checked by chromatography.

Antioxidant A (ICI): 1,1',3-tris(2-methyl-4-hydroxy-5-*tert*-butylphenyl)butane mp 185°C.

Antioxidant B (American Cyanamid Co.): 2,2'-methylene-bis(4-methyl-6-tert.butylphenol) mp 132°C.

Antioxidant C: 4,4'-butylidene-bis(3-methyl-6-*tert*.butylphenol) mp 210°C.

Antioxidant D: 4,4'-isopropylidene-bis(2-*tert*.butylphenol).

2-*tert*.Butyl-5-methylphenol (ÚMCH Praha), pure grade.

Dilaurylthiodipropionate, DLTDP (ICI) mp 41°C.

Phenoxypropenoxide (VÚSPL Pardubice), pure grade, bp 129°C (25 torr).

n-Butoxypropenoxide (VÚSPL Pardubice), pure grade, bp 69.3°C.

Di-*n*-butyltin di-2-ethylhexylmaleinate (VÚOS Rybitví).

Di-*n*-octyltin dilaurate (VÚOS Rybitví).

Nitrogen was dried with molecular sieve and oxygen was removed on Cu and Mn catalyst. Content of impurities: $[O_2] < 5$ ppm, $[H_2O] < 10$ ppm.

Other chemicals were of analytical or reagent grade purity.

Methods

Thermooxidative Stability Measurements. Thermooxidative stability of polypropylene containing antioxidants was evaluated by the induction period measured at 180°C.[20] The samples containing different concentrations of titanium compounds were prepared by impregnation. Polypropylene was at first impregnated with the synergistic mixture of antioxidants (0.3 part of DLTDP and 0.1 part of phenolic antioxidant); the 5-g samples were then weighed into the ampuls having a self-sealing closure and finally pure propane was distilled in. Oxygen from the polymer and ampul was forced out by a partial evaporation of propane. Isopropanol solutions of titanium compounds were dosed with a syringe through a self-sealing closure.

The mixture of propane and isopropanol under continuous shaking was evaporated through a syringe needle; the polymer was melted at 250°C. Then the ampul was broken and the induction period of oxidation was measured.

The samples containing HCl acceptors were prepared on a Brabender plastograph, which had the feeding hopper modified so as to permit work under nitrogen. 30 g of PP containing a synergistic mixture of antioxidants and HCl acceptors was molded for 30 min; the temperature of the endless screw was 230°C.

Interaction of α-TiCl₃ with Antioxidants. The interaction of α-TiCl₃ with antioxidants in an inert atmosphere was followed by means of the flow apparatus described in our previous communication.[21] Hydrogen chloride forces out of the liquid phase with nitrogen was determined potentiometrically.

Measurements of the Polymer Color. The polymer samples did not have a suitable form for optical measurement of a reflected light. Because new polymer pressing is always followed by a change of color, the polymer color was evaluated by comparing the polymer sample with a standard scale of color intensity.

Thermal Degradation of Antioxidants in an Inert Atmosphere. The reactions of antioxidants with HCl were followed at 250–300°C. Antioxidants (2 g) were weighed into 10-ml ampules; the ampules were flushed with nitrogen and then with HCl and sealed. Standard samples were prepared by the same procedure in the absence of HCl. The time of interaction was 15 min. The molecular weights were determined by a cryoscopic method using dioxane solutions, as substituted phenols are in this solvent only slightly associated. The liquid phase was analyzed by a descending paper chromatography using the systems containing dimethyl formamide.[22,23] The gaseous products were determined by means of GLC chromatography using a 1-m column filled with aluminum. The GLC apparatus was equipped with an ionization detector.

Infrared Spectra Measurements. Infrared spectra were measured with a UR-10 double-beam apparatus. The nujol technique was used for the antioxidant spectra measurements.

RESULTS

Effect of Titanium Compounds on the
Oxidative Induction Period of Stabilized PP

The dependence of the induction period of PP on the molar ratio of titanium compounds and phenolic antioxidants is given in Figure 1. It can be seen that these curves are identical for both $TiCl_3$ and $(CH_3COO)_2TiCl_2$
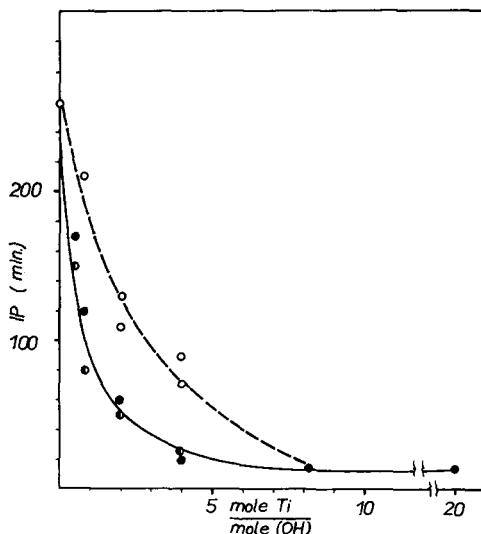

Fig. 1. The dependence of the induction period of oxidation of PP on the molar ratio of titanium compounds and phenolic antioxidant: T, 180°C; stabilization system, 0.3 p. DLTDP plus 0.1 p. antioxidant A; (◑) $TiCl_3$; (●) $(CH_3COO)_2TiCl_2$; (○) $Ti(OiPr)_4$.

but the curve for (iPrO)₄Ti descends more slowly.   The polymer discoloration increases simultaneously with increasing concentration of titanium compound.   These results indicate that, at low concentrations of titanium compounds, the type of groups (ligands) bonded to titanium is a far more important factor than the valency of titanium.   The Ti-Cl bond is very reactive and therefore its interaction with antioxidants can be expected.

Reaction of Ti-Cl With Antioxidants

The interaction of α-TiCl₃ with antioxidants at the temperatures above 100°C leads to the formation of HCl.   The rate of HCl formation from
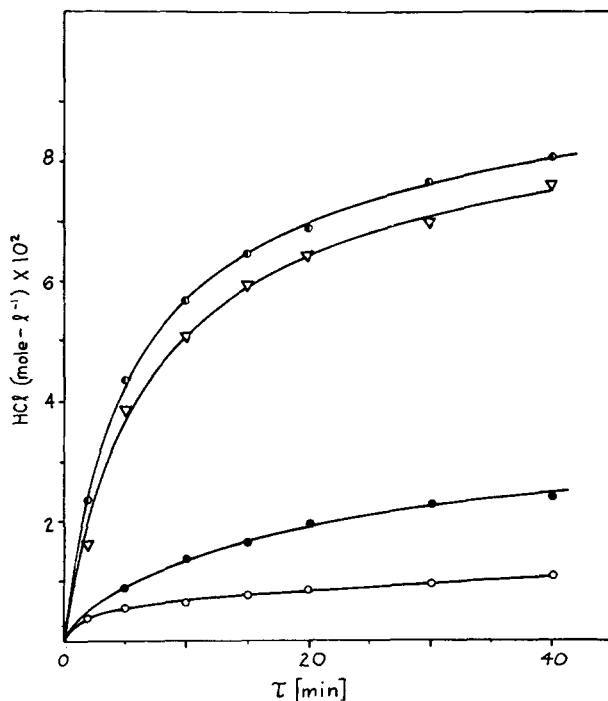
Fig. 2.   The interaction of α-TiCl₃ with antioxidants: T, 150°C; 9 liters N₂/hr; [TiCl₃]ₜₘ2/g = 0.2 mole/liter; (O) decaline; (●) 0.04 mole/liter DLTDP in decaline; (∇) 0.04 mole/liter antioxidant D in decaline; (◐) 0.04 mole/liter antioxidant B in decaline.

different antioxidants is given in Figure 2.   It can be seen that the phenolic antioxidants exhibit the highest reactivity with respect to α-TiCl₃.   In our previous paper we have shown that the IR intensity of the valency vibration of OH groups decreases simultaneously with the libration of HCl.   The decrease of optical density can be ascribed to the following reaction of OH group of an antioxidant:

$$ArOH + TiCl_3 \rightarrow HCl + ArOTiCl_2 \tag{15}$$

The reactions of substituted phenols with $TiCl_4$ follow a similar course.[24,25] HCl and titanate are also formed. Chlorotitanates of phenolic antioxidants have an intensive red-brown color and do not exhibit any stabilization effect (details will be given in the next paper).

Reactions of HCl With Antioxidants in the Polymer

Phenolic antioxidants are not resistant against HCl formed by their interaction with α-$TiCl_3$ at the temperatures of PP processing. The variations of infrared spectra of different phenolic antioxidants heated up to 300°C in an HCl atmosphere (with exclusion of oxygen) are given in
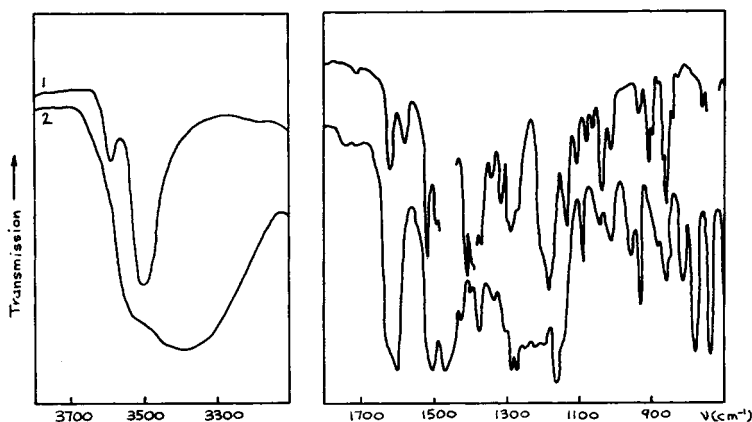
Fig. 3. Infrared spectrum of antioxidant A: (1) standard; (2) after heating at 300°C, HCl, 15 min.
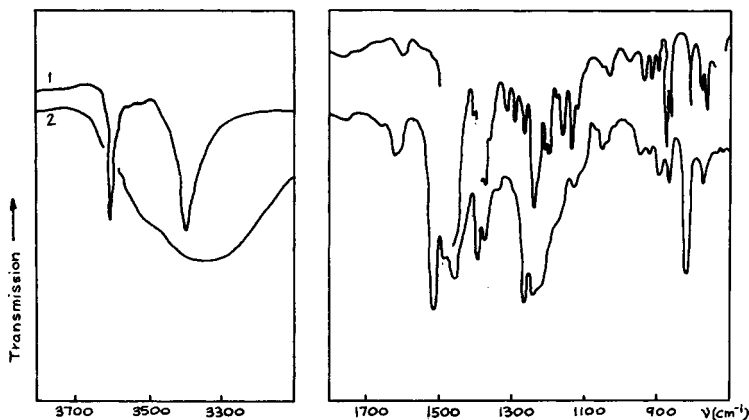
Fig. 4. Infrared spectrum of antioxidant B: (1) standard; (2) after heating at 300°C, HCl, 15 min.

Figures 3, 4, 5, and 6.   A broad absorption band in the region of 3200–3600 cm^{-1} which corresponds to the valency vibration of associated OH groups appeared in all spectra.   The extent of association of alkylated phenols depends on the substitution in the neighborhood of OH groups.   Substit-
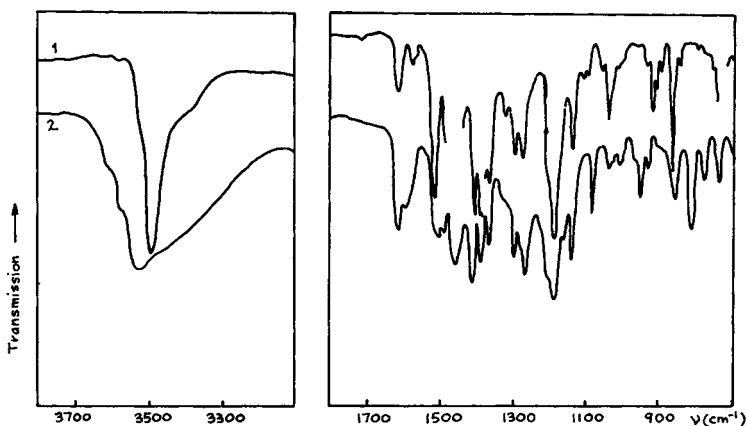
Fig. 5.   Infrared spectrum of antioxidant C: (1) standard;   (2) After heating at 300°C, HCl, 15 min.
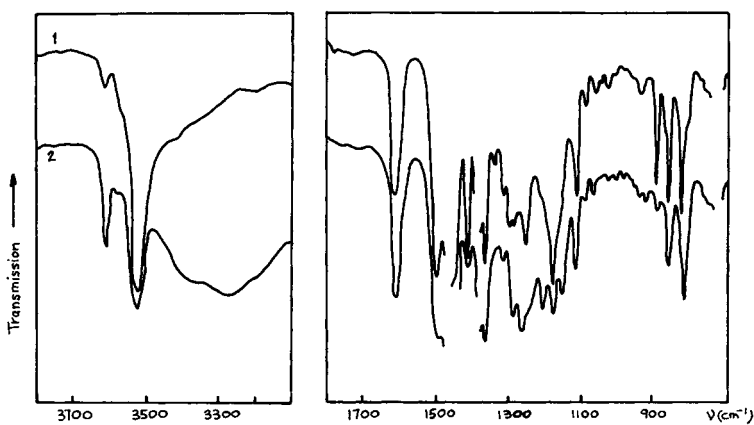
Fig. 6.   Infrared spectrum of antioxidant D.   (1) standard;   (2) after heating at 300°C, HCl, 15 min.

uents in α-position hinder sterically the formation of associates and narrow absorption bands corresponding to the valency vibrations of monomeric or dimeric OH groups are observed.   The formation of associated OH groups of those phenolic antioxidants which were heated in the presence of HCl gives the evidence that substituents in the neighborhood of OH groups were

split off as a result of degradative reactions. Similarly, the variation of the spectra in the region of 870–770 cm^{-1} can be attributed (out-of-plane deformation vibration of C—H bond) to changes in substitution of the aromatic nucleus.

Tables I and II summarize the results of paper chromatography analysis and molecular weights of degraded antioxidants and also the antioxidant efficiencies expressed as induction periods. The tables show that degrada-

TABLE I

Phenolic antioxidant	Temperature of interaction, °C	N₂		HCl		I.P.,[a] standard, min
		Mol wt	I.P.,[a] min	Mol wt	I.P.,[a] min	
Antioxidant A	250	—	—	—	—	260
	300	340	240	180	60	
Antioxidant B	250	316	—	306	—	160
	300	301	150	187	40	
Antioxidant C	250	370	—	241	—	210
	300	370	180	179	45	
Antioxidant D	250	330	—	302	—	230
	300	319	200	242	55	
2-tert.Butyl-5-methylphenol	—	—	—	—	—	50

[a] Induction period, measured at 180°C. Polypropylene was stabilized with synergic system of antioxidants: 0.3 p. DLTDP + 0.1 p. phenolic antioxidant.

tion of antioxidants involves not only splitting off of aromatic nuclei but also dealkylation of substituted phenols. The antioxidants degraded in this way exhibit only a very low stabilization efficiency compared to un-reacted antioxidants. Besides the products mentioned, intensively brown-colored compounds (not identified) were also formed during the degradation.

The decomposition of DLTDP in HCl atmosphere occurs at about 350°C.

Effect of HCl Acceptors (Labile Cl) on Thermooxidative Stability of PP

HCl acceptors remove HCl or react with Ti—Cl bonds (e.g., epoxides)[26] and thereby improve the thermooxidative stability of PP containing small amounts of titanium as a polymerization catalyst residue. The effect of those compounds on the induction period of oxidation of PP and on the color of PP is given in Table III. The effect of some complexing agents is also shown for comparison. The function of an acceptor becomes evident if we compare the effect of zinc diethyldithiocarbamate with that of tetra-ethylthiuramdisulfide which has a similar chemical structure but does not

exhibit induction periods and polymer decoloration characteristic of zinc diethyldithiocarbamate.

DISCUSSION

The above results show that thermal reactions of antioxidants (especially phenolics) with residues from titanium compounds strongly influence the thermooxidative stability of PP. Those reactions occur during initial

TABLE II

| Standard	S₁		S₂		S₃	
	Degrad. antioxidant R_F	Standard R_F	Degrad. antioxidant R_F	Standard R_F	Degrad. antioxidant R_F	Standard R_F
Antioxidant A[a]						
m-Cresol	0.19	0.18	0.09	0.09	0.04	0.04
—	0.34	—	0.17	—	0.08	—
2-tert.-Butyl-5-methyl-phenol	0.72	0.73	0.55	0.56	0.33	0.33
Antioxidant B						
p-Cresol	0.22	0.22	0.09	0.09	0.05	0.05
2,4-Di-methyl-phenol	0.35	0.36	0.18	0.17	0.11	0.11
—	0.48	—	0.31	—	0.18	—
—	0.66	—	0.46	—	0.25	—
2-tert.-butyl-4-methyl-phenol	0.74	0.75	0.56	0.56	0.34	0.34
Antioxidant C						
m-Cresol	0.18	0.18	0.08	0.08	0.04	0.04
—	0.80	—	0.18	—	0.06	—
2-tert.-butyl-5-methyl-phenol	0.69	0.70	0.56	0.56	0.34	0.35

Chromatographic systems: S₁, 25% dimethylformamide (in benzene), diisopropyl-ether-heptane (1:2); S₂, 25% dimethylformamide, hexane; S₃, 50% dimethylform-amide, hexane.

[a] GL chromatographic analysis: 96% isobutene in gaseous phase.

thermal processing of PP (granulation) and even in an inert atmosphere. The mechanism of this interaction can be depicted as:

$$\begin{array}{c} \diagdown \\ Ti{-}Cl \\ \diagup \end{array} \xrightarrow{\text{AOH}} \begin{array}{c} \diagdown \\ Ti{-}OA \\ \diagup \end{array} \quad \begin{array}{l} \text{1. degradation of anti-} \\ \text{oxidant skeleton} \end{array}$$

$$+ $$

$$HCl \xrightarrow{\text{AOH}}$$

$$\text{2. dealkylation} \qquad (16)$$

Because of the heterogeneous nature of the catalyst residue (titanium component), the conversion of antioxidant to titanate will depend on sur-

TABLE III

Acceptor HCl or complexing agents[a]	I.P.,[b] min. 180°C	Polymer color[d]
Polypropylene standard	250	5
Polypropylene without antioxidants	20	1
Stearate Zn	340	2
Phenoxipropenoxide	570	2
Butoxipropenoxide	430	2
Di-n-butyltin-di-2-ethylhexyl-maleinate)	530	2
Di-n-octyltindilaurate-laura	480	2
ZnO	600	1
Phenylethyldithio-carbamate Zn	520	2
Diethyldithiocarba-mate Zn	450	2
Tetraethylthiuram-disulfide	230	5
Tartaric acid	180 / 220[c]	7
Citric acid	200 / 240[c]	6
Acetylacetone	230 / 260[c]	5
γ-Butyrolactone	230[c] / 170	5
Tetraethyloxamide	120 / 180[c]	6

[a] Concentration in polymer, 0.2%.

[b] The content of titanium in polymer was 0.012%. Polypropylene was stabilized with synergic system of antioxidants: 0.3 p. DLTDP + 0.1 p. antioxidant A.

[c] Impregnated from solutions.

[d] Reflected light (%): 1, 60–50; 2, 50–45; 3, 45–40; 4, 40–35; 5, 35–30; 6, 30–25; 7, 20–25.

face area and on steric conditions on the titanate surface. Therefore it can be assumed that only some Ti—Cl bonds react with antioxidants. Liberated HCl, because of its mobility in the polymer melt, comes into contact

with antioxidants and catalyzes degradation and dealkylation reactions. The products of those reactions indicate that the reaction is the Friedel-Crafts dealkylation and dearylation catalyzed by aprotic acids with the formation of σ-complex:

$$\text{alkene} + HCl$$
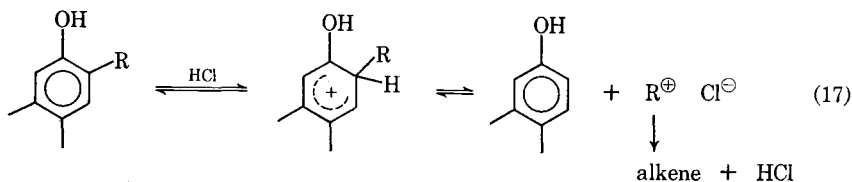
Ziegler-Natta catalysts and their oxidation products belong to the class of Lewis' acids and therefore it can be expected that, in addition to formation of titanates, dealkylation and dearylation reactions of phenolic antioxidants also occur on the surface of the catalyst residues.

If the concentrations of titanium compounds in the polymer are low (<0.05%) and if the molar ratio TiCl/AOH $\ll$ 1, the effect of HCl as a dealkylation (dearylation) catalyst (or cocatalyst) predominates over the effect caused by the formation of titanates. In this way we can explain a favorable effect of HCl acceptors on the thermooxidative stability and color of PP.

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