

# Effect of Fatty Amine and Perfluorocarbon as Anti-Fouling Agent on the Catalyst Activity and Titanium Oxidation State in Slurry Polymerization of Ethylene

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**ABSTRACT:** In this work, the effect of two antifouling materials on the activity of catalyst used to produce polyethylene in a 1-L slurry reactor and on the titanium oxidation state of the catalyst was investigated. Armostat 300 with the formula alkyl  $C_{14}$ – $C_{18}$  bis(2-hydroxyethyl)amine is an antistatic agent that reduces static electricity of the polymer particles. It was found that within the concentration of 0.16–1.32 g/mmol Ti, Armostat 300 helps to increase the catalyst activity to 1.3–2 times. The variation of the titanium oxidation state of the catalyst in the presence of Armostat 300 at 80°C with Al/Ti molar ratio of 100 showed that Ti (III) species increased. The effect of Armostat 300 on  $T_m$ , %  $X_c$ , density, bulk density, and MFI of polymer was insignificant.

In this work, Zonyl FSN-100 with the formula  $R_f(CH_2CH_2O)_xH$ ,  $R_f = F(CF_2CF_2)_y$ ,  $y = 1$ – $9$ ,  $x = 1$ – $26$  was used as antifouling agent in copolymerization of ethylene with 1-butene. It was found that Zonyl FSN-100 at the concentration range of 5–20 ppm reduces the catalyst activity to 1.11–1.9 times. It was also shown that Ti (III) species in the presence of Zonyl FSN 100 decreased. This antifouling agent slightly decreased the properties of polymer including %  $X_c$ , density, and  $M_w$ . © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 257–260, 2006

**Key words:** fouling; Ziegler–Natta catalyst; ethylene; slurry polymerization

## INTRODUCTION

In slurry polymerization of ethylene particularly where the liquid medium is a saturated aliphatic hydrocarbon, for example hexane, a problem is the adhering of the solid particles to reactor walls. When fouling occurs, the smoothness of the wall surface of the reactor is lost and a polymer layer on the inner face of the reactor forms. Hence, the heat transfer efficiency of the reactor decreases and the temperature control of the reactor becomes more difficult.<sup>1,2</sup> Reactor fouling results in many serious problems, including poor heat transfer, poor particle morphology, and forced reactor shutdown.<sup>2,3</sup> In slurry polymerization process, the fouling phenomenon occurs, while it does not occur in the solution polymerization. The slurry process offers a number of advantages over a solution process, namely, easier removal of the reaction heat, high polymerization yield, and capability of producing very high molecular weight polymer and low investment and production cost.<sup>4</sup> In slurry polymerization of ethylene, it is useful to immobilize the catalyst on a support to control polymer morphology. One disadvantage of the supported catalyst is that it leads to the

generation of electrical charges upon the polymer particles. The deposition of solid particles on the reactor wall occurs consequently.<sup>3,5</sup> A technique used to prevent fouling is the addition of small quantities of antifouling agent to the polymerization reactor.<sup>1–3,5,6</sup> Fouling phenomenon has been observed in HDPE plants. The polymerization process consists of two series stirred tank reactor. In the first reactor, homopolymerization of ethylene occurs, while in the second reactor, copolymerization of ethylene with 1-butene occurs to modify the density of polyethylene product. For reduction of fouling, it is useful to add small amount of fatty amine Armostat 300 as antistatic agent in homopolymerization stage of ethylene.<sup>3,5</sup> It is also useful to use small amount of perfluorocarbon Zonyl FSN 100 as antistatic and surface active agent that reduces surface tension in copolymerization of ethylene.<sup>7</sup> The amount of antifouling agent to be added is small, based on the mmoles of the catalyst or based on the hexane in the polymerization system. These materials should not decrease the activity of catalyst. They should not influence the properties of polymer such as MFI,  $M_w$ ,  $T_m$ , %  $X_c$ , density, and bulk density. In this work, the effect of two antifouling agents, Armostat 300 and Zonyl FSN 100, on the catalyst activity in the reactor, polymer properties, and oxidation state of titanium of the catalyst in glass flask were investigated.

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TABLE I  
Physical Data of the Catalyst

Bulk density (g/cm <sup>3</sup> )	Density (g/cm <sup>3</sup> )	Particle size			Specific surface: BET (m <sup>2</sup> /g)
		Median value $d_0$ ( $\mu\text{m}$ )	Standard deviation (s)	Pore radius $r_p$ ( $\text{\AA}$ )	
0.58	1.32	30	0.315	39.7	149.0694

## EXPERIMENTAL

### Materials

Polymerization grade of ethylene, nitrogen, and hydrogen of extra pure grade (99.999%) were further purified with molecular sieve. *n*-Hexane from a HDPE plant was obtained, fractionally distilled, and further dried over sodium metal and molecular sieve. Aluminum triethyl was supplied by Schering AG (Berlin, Germany) and was used as received.  $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ , 85%  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  for titration, and *N,N*-diphenylbenzidine and sodium diphenyl amine sulfonate as indicators were supplied by Merck (Dormstadt, Germany). The catalyst used in the present investigation was the reaction product of  $\text{Mg}(\text{OC}_2\text{H}_5)_2$  with  $\text{TiCl}_4$ . The molar ratio of the elements in the catalyst was Ti : Mg : Cl = 0.135 : 1 : 2.3. The physical data of the catalyst is given in Table I.<sup>8</sup>

Fatty amine, Armostat 300, with the formula alkyl  $\text{C}_{14}\text{-C}_{18}$  bis(2-hydroxyethyl)amine and perfluorocarbon, Zonyl FSN 100, with the formula  $\text{R}_f(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$ ,  $\text{R}_f = \text{F}(\text{CF}_2\text{CF}_2)_y$ ,  $y = 1\text{-}9$ ,  $x = 1\text{-}26$  were supplied by Akzo Nobel Chemicals (Amersfoort, the Netherlands) and Dupont (Luxemburg), respectively.

### Polymerization

A 1-L stainless steel reactor was filled with 400 mL hexane and equipped with jacket and a stirrer. To purify the reactor, before each polymerization experiment, it was flushed with nitrogen at about 2 bar gauge pressure and then evacuated. This procedure was repeated at least 15 times. Then the reactor was purged with ethylene. Solution (1–8 mL) containing 5–40 mg of antistatic agent (Armostat 300) in hexane or 0.5–2 mL solution containing 1.65–6.6 mg perfluorocarbon (Zonyl FSN 100) in toluene, 3 mmole  $\text{AlEt}_3$  as cocatalyst and 0.3 mmole catalyst, were introduced to the reactor at 80°C. Al/Ti was equal to 100. Hydrogen as chain transfer agent (partial pressure = 4 bar) and 4 g 1-butene as modifier of density in copolymerization were charged to the reactor. Finally, the reactor was charged with ethylene to 8 bar gauge pressure. At the end of 1 h, the ethylene flow was stopped and the reactor mixture was cooled to room temperature. After evaporation of *n*-hexane and drying, 61.6–122.5 g of polyethylene powder was obtained.

### Determination of titanium oxidation state of the catalyst

The oxidation states of Ti were determined by redox titration of the catalyst.<sup>9–11</sup> Because the catalyst was air-sensitive, a glass flask equipped with magnetic stirrer and heater was used. The glass flask was under nitrogen purge continuously. The catalyst (about 0.03 mmole Ti), triethylaluminum, and Armostat 300 or Zonyl FSN 100 were added under inert atmosphere to 40 mL of hexane. The catalyst was activated at 80°C by using Al/Ti molar ratio equal to 100 in the presence of 0.16–1.32 g of Armostat 300/mmol Ti or 5–20 ppm of Zonyl FSN 100 based on the amount of hexane used in the polymerization reactor. Then the mixture was stirred for 10 min. The activated catalyst in the presence of Armostat 300 or Zonyl FSN 100 was analyzed to determine the Ti (IV), Ti (III), Ti (II) by the method suggested by Chien.<sup>11</sup> Two redox titrations were carried out.

#### Titration A

$\text{NH}_4\text{Fe}(\text{SO}_4)_2$  (0.1N) was added to activated catalyst mixture until a Fe/Ti molar ratio equal to 3 was reached.<sup>9</sup> All the titanium of the catalyst reduced by cocatalyst and antifouling was oxidized to Ti (IV) by Fe (III). To the stirred mixture, 10 mL of 85%  $\text{H}_3\text{PO}_4$  was added to improve the end point of titration. Two milliliters of *N,N*-diphenylbenzidine was added as indicator and the formed Fe (II) was titrated with 0.02N  $\text{K}_2\text{Cr}_2\text{O}_7$  solutions. At the end point of titration by  $\text{K}_2\text{Cr}_2\text{O}_7$ , the color changed sharply from white to violet. The following relation exists:  $\text{K}_2\text{Cr}_2\text{O}_7$  equivalents  $A = n_{\text{equiv}}\text{Ti}(\text{III}) + 2 n_{\text{equiv}}\text{Ti}(\text{II})$ .

#### Titration B

The same amounts of reactants were dissolved in 30 mL of 10%  $\text{H}_2\text{SO}_4$ . Ti (II) species in the catalyst were oxidized by the protons. Two milliliter of indicator solution sodium diphenylamine sulfonate in  $\text{H}_2\text{O}$  was added and titrated directly by  $\text{K}_2\text{Cr}_2\text{O}_7$ . The end point was observed by a sharp color change from purple to green. The following relation exists:  $\text{K}_2\text{Cr}_2\text{O}_7$  equivalents  $B = n_{\text{equiv}}\text{Ti}(\text{III}) + n_{\text{equiv}}\text{Ti}(\text{II})$ .

**TABLE II**  
Effect of Fatty Amine (Armostat 300) on the Catalyst Activity and Properties of Polymer in Homopolymerization of Ethylene (Al/Ti = 100, Temp. = 80°C, P<sub>total</sub> = 8 bar)

g Fatty amine/ mmol of Ti	Polymer (g)	Activity (kg PE/g Ti hr)	MFI	M <sub>w</sub>	T <sub>m</sub> (°C)	X <sub>c</sub> (%)	Density (g/cm <sup>3</sup> )	Bulk density
0	61.6	42.86	0.55	87,423	135.09	62.34	0.9540	0.336
0.165	111.5	77.6	0.51	88,034	134.6	68.53	0.9583	0.335
0.33	122.5	85.53	0.41	90,331	134.94	66.64	0.9561	0.334
0.66	87	60.5	0.6	78,051	134.62	66.81	0.9557	0.316
1.32	81	56.36	0.275	93,424	135.22	66.17	0.9552	0.304

The amount of the three titration species present in the activated catalyst can be calculated as follow: Ti (II) = A - B, Ti (III) = 2B - A, Ti (IV) = [ΣTi<sup>n+</sup>] - B

### Characterization

The heat of fusion ( $\Delta H_f$ ) and melting temperature ( $T_m$ ) were determined by Mettler Toledo 820-E DSC-4 systems. The sample was first heated to 160°C at 10°C/min, kept at 160°C for 2 min, cooled to 30°C at 10°C/min and finally the DSC scan was recorded at 10°C/min. From  $\Delta H_f$ , % crystallinity was calculated:

$$\%X_c = \Delta H_f \times 100 / 293.6 \quad (1)$$

Melt flow index (MFI) was measured with a Ceast system in 190°C and by a 2.16 kg load (ASTM method D-1238-95). Bulk density was measured by ASTM method D-1895. Intrinsic viscosity [ $\eta$ ] of polymer dissolved in decalin was measured at 135°C by an ubelohde viscometer. The molecular weight was calculated by Mark-Houink equation:<sup>12</sup>

$$[\eta] = 6.77 \times 10^{-4} M_v^{0.67} \quad (2)$$

## RESULTS AND DISCUSSION

Fatty amine, Armostat 300, as antistatic agent is an electron donor. The contact between the antistatic agent, the catalyst, and the cocatalyst is preferred to occur in the presence of hydrocarbon liquid.

It has been found that the antistatic agent is dispersed uniformly not only at the surface of polymer particles but also inside them.<sup>5,13</sup> Polymerization tests were carried out at various antifouling agent concentrations. Table II shows the effect of the Armostat 300 on the activity of Ziegler-Natta catalyst and properties of the polymer. The differences among the MFI values and among the  $M_w$  values are not significant. Therefore, the effect of Armostat 300 on the MFI and  $M_w$  may be ignored. It is seen that Armostat 300 has not significant effect on  $T_m$ , %  $X_c$ , and density. A maximum activity is observed at 0.33 g of Armostat 300/mmol Ti concentration and after that activity de-

creases with increasing fatty amine concentration. It is clear that the activity of the catalyst is strongly related to the antifouling agent (Armostat 300) concentration. Table III shows the titanium oxidation states in the presence of Armostat 300 and triethylaluminium at 80°C in the glass flask after 10 min. The catalyst was activated with triethylaluminium and the reaction was completed after 5 min.<sup>14</sup> It was observed that the Ti (III) species in the catalyst increased with increasing Armostat 300 concentration. The polymerization of ethylene is catalyzed by both Ti (II) and Ti (III) species, but Ti (III) is more active than Ti (II). It was found that there is a relationship between the degrees of titanium reduction and the catalytic activity in ethylene polymerization. Therefore, the increase of Ti (III) species increased the activity.

For 0.165–0.33 g of Armostat/mmol Ti concentration the bulk density was not changed significantly compared with the case of no antifouling addition. But it decreased with increasing Armostat 300 concentration from 0.33 to 1.32 g of Armostat 300/mmol Ti. Therefore with increasing Armostat 300 concentration, the morphology is gradually transferred into more open structure and poor replication of the shape of the catalyst particles.<sup>15-17</sup>

The effect of perfluorocarbon, Zonyl FSN 100, on the activity of catalyst and properties of polymer is shown in Table IV. Zonyl FSN 100 is a surface active compound containing one perfluorocarbon group and more hydrophilic groups that disperses the polymer or copolymer of ethylene in hexane to reduce fouling of the reactor with adherent polymer particles. Zonyl

**TABLE III**  
Titanium Oxidation State in Glass Flask  
(Al/Ti = 100, Temp. = 80°C)

g Armostat 300/mmol Ti	Ti(II) (%)	Ti(III) (%)	Ti(IV) (%)
0	53.33	33.33	13.33
0.16	43.2	43.47	13.33
0.33	36.5	50.17	13.33
0.66	48	38.67	13.33
1.32	50.5	37.17	13.33

**TABLE IV**  
**Effect of Zonyl FSN 100 on the Catalyst Activity and Properties of Polymer in Copolymerization of Ethylene (Al/Ti = 100, Temp. = 80°C, P<sub>total</sub> = 8 bar, 1-butene = 4 g)**

g Zonyl FSN 100/g diluent (ppm)	Polymer (g)	Activity (kg PE/ g Ti hr)	MFI	$M_w$	$T_m$ (°C)	$X_c$ (%)	Density (g/cm <sup>3</sup> )	Bulk density
0	87	60.5	1.36	59,900	128.83	57	0.943	0.332
5	78	52.28	1.5	57,300	129.28	55	0.941	0.309
10	55	38.27	1.7	52,700	128.22	53	0.940	0.309
20	46	32.0	2.0	49,000	127.92	50.7	0.938	0.329

FSN 100 is insufficiently soluble in hexane, it is soluble in polar hydrocarbon solvent for example toluene. It is seen that as the concentration of Zonyl FSN 100 increases, the activity decreases. Zonyl FSN 100 as surface active agent is adsorbed on the surface of the solid catalyst. The catalyst and the antifouling agent form a kind of catalyst complex. This appears to make better the affinity between the catalyst and the solvent.<sup>1</sup> Therefore, the affinity between reactor wall and the catalyst would be weakened, but the complex formation between catalyst and Zonyl FSN 100 poisons the active site of Ziegler–Natta catalyst.<sup>2</sup>

It is shown in Table IV that with increasing Zonyl FSN 100 concentration, molecular weight ( $M_w$ ) of polymer slightly decreases and MFI slightly increases. These differences may not be significant.

With increasing Zonyl FSN 100 concentration, crystallinity of polymer slightly decreases, and density of polymer decreases too. The scattering of  $T_m$  values and small difference among them show that the variation of Zonyl FSN 100 concentration does not affect  $T_m$ .

Table V shows the variation of the titanium oxidation states in the presence of Zonyl FSN 100. Zonyl FSN 100 decreased the Ti (III) concentration. Therefore, the activity of catalyst in the polymerization reactor decreased.

## CONCLUSIONS

It was observed that fatty amine antifouling agent, Armostat 300, has positive effect on the catalyst activ-

ity and it was shown that it is a promoter. It was found that within the concentration of 0.16–1.32 g/mmol Ti, Armostat 300 helps to increase the catalyst activity to 1.3–2 times in the polymerization reactor. It was shown that Ti (III) species in the glass flask increased. The effect of Armostat 300 on  $T_m$ , %  $X_c$ , density, and MFI of polymer is insignificant. Another antifouling agent is Zonyl FSN 100 that was used as surface active agent in copolymerization of ethylene with 1-butene. It was found that zonyl FSN-100 at the concentration range of 5–20 ppm reduces the catalyst activity to 1.11–1.9 times and Ti (III) species in the glass flask decreased. This antifouling agent slightly decreased the properties of polymer including %  $X_c$ , density, and  $M_w$ .

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**TABLE V**  
**Titanium Oxidation State in Glass Flask (Al/Ti = 100, Temp. = 80°C)**

ppm Zonyl FSN 100 g/g diluent	Ti(II) (%)	Ti(III) (%)	Ti(IV) (%)
0	53.33	33.33	13.33
5	59.4	27.27	13.33
10	64	22.67	13.33
20	68.5	18.17	13.33