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Initial Rate and Aging Effect of Ethylene Polymerization with Ziegler-Natta Catalysts. III

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The initial rate and the aging effect of ethylene polymerization with $TiCl_4$- and $TiCl_3$-$AlEt_3$ catalyst were investigated. The initial rate, r, was expressed by the equation; $r=k_1P_E+k_2P_E^2$, where p_E is the ethylene partial pressure and where k_1 and k_2 are constants. The explanation of the equation is as follows:

$$\text{(active site)} + \text{M} \xrightarrow{k_1} \text{(polymerization site), rate, } k_1P_E$$

$$\text{(polymerization site)} + \text{M}^* \xrightarrow{k_2} \text{(propagation), rate, } k_2P_E^2$$

M shows the ethylene monomer which is liberated by the catalyst formation or which is introduced into the system. M* is the monomer which is introduced into the system. The initial rate decreased in the $TiCl_4$-$AlEt_3$ system with the aging-time interval; on the other hand, in the $TiCl_3$-$AlEt_3$ system the rate showed its maximum at about half an hour's aging. The optimum aging temperature was found to be 20°C. The decrease in the rates between the two systems may be ascribed to the reduction of the Ti atom in the initial valence state of the reaction to the lower valence.

In a preceding paper,[1] the kinetics in the stastionary state of ethylene polymerization and the effect of hydrogen on the rate in connection with the $TiCl_3$-$AlEt_3$ catalyst system were described. This paper will be concerned with the initial rate and the aging effect of ethylene polymerization by the $TiCl_4$- and $TiCl_3$-$AlEt_3$ systems. It is well known that the catalyst systems of the Ziegler-Natta type consist of the reaction products resulting from titanium halides in conjugation with alkylaluminum compounds. We have confirmed that the active sites of the catalyst result from the reaction of titanium halides ($TiCl_4$ or $TiCl_3$) and alkylaluminum, while the polymerization sites result from the addition of monomer molecules to the active sites.

When triethylaluminum as alkylaluminum is employed, the liberation of ethylene and other saturated hydrocarbons has been verified by different authors.[2-7] By the addition to the active sites of ethylene liberated in the reaction of titanium halides with triethylaluminum, some polymerization sites will be formed prior to the introduction of the ethylene monomer into the reaction system. A considerable number of active sites will also exist on the catalyst surface. If the polymerization starts at the active sites, the initial rate will be second-order with respect to the monomer concentration, but if it starts at the polymerization sites, the order will be first. This is bacause a molecule of ethylene reacts with an active site to produce a polymerization site; then another molecule affects the polymerization site and the propagation proceeds.

In order to verify this, we studied the initial rate of ethylene polymerization with the $TiCl_4$- and $TiCl_3$-$AlEt_3$ catalyst systems.

The aging effects of the catalysts on the initial rate are still controversial. Very few studies have been made of the aging effect in the $TiCl_4$- and $TiCl_3$-

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[1] T. Matsuda, T. Keii, A. Kojima and T. Ishida, *Kogyo Kagaku Zasshi*, **71**, 1124, 1128 (1968).

[2] A. Malatesta, *Can. J. Chem.*, **37**, 1176 (1959).

[3] E. J. Arlman and J. R. de Jong, *Rec. Trav. Chim. Pays-Bas*, **79**, 910, 1319 (1960).

[4] R. Havinga and Y. Y. Tan, *ibid.*, **79**, 56 (1960).

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[6] L. Rodriguez, H. Looy and J. Gabant, *J. Polym. Sci., Part A-1*, **4**, 1905, 1917 (1966).

[7] M. L. Cooper and J. B. Rose, *J. Chem. Soc.*, **1959**, 795.

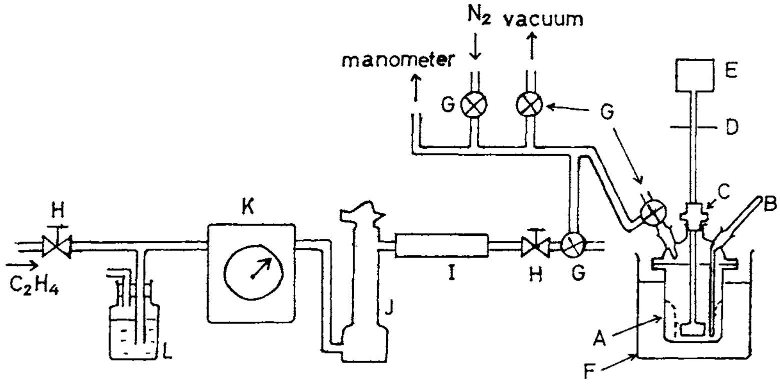

Fig. 1. Diagram of the apparatus of ethylene polymerization.
A, Reactor (esparable flask); B, Thermometer; C, Vacuum Stirrer; D, Stroboscope; E, Motor; F, Water bath; G, Valves; H, Needle valves; I, P_2O_5; J, NaOH pellet; K, Wet gas meter; L, Monostat

$AlEt_3$ catalyst systems.[8-11] Simon and Gyhmes[8] investigated the aging effect on the polymerization rate of ethylene in the $TiCl_4$-$AlEt_3$ catalyst system, and indicated that the effect did not appear at a particular temperature. Kodama and his coworkers[9] found that the activity of such a catalyst decreased considerably with time at 60°C, although the catalyst activity did not change much at 30°C for up to 4 hr. Hoeg and Liebman[10] studied the aging effect on the propylene polymerization, using $TiCl_3$ and Al(iso-Bu)$_3$, and found that these catalysts were thermally unstable. Schnecko and his co-workers[11] examined the difference in the aging effect by monomers upon the ethylene, propylene, and butene-1 polymerization rates by the $TiCl_3$-$AlEt_3$ and $TiCl_3$-$AlEt_2Cl$ systems. Thus, the different aging effects reported by various authors may be ascribed to the formation of lower valence states of titanium, which presumably are less stable and less efficient as catalysts, or to the coagulation of catalyst particles, whereby the available surface is decreased.

We examined the time and temperature effect of aging on the initial rate and attempted to analyze the valence state of titanium in the course of aging, which presumably causes the rate decrease.

Experimental

Reagents. The titanium tetrachloride was purified by distillating it several times with Cu powder until the distillate lacked color and by then diluting it to 10 wt% solution with *n*-heptane. The δ-Type of titanium trichloride supplied by the Toho Titanium Co. was used without any purification. The triethylaluminum was employed as 10 wt% *n*-heptane solution given by the Mitsubishi petrochemical Co. The toluene was purified by rectification in the presence of metallic sodium. The ethylene and nitrogen were dried under NaOH pellets and P_2O_5.

Polymerization Apparatus and Technique. The apparatus is shown in Fig. 1. Polymerization was carried out in a 500-m*l* separable flask provided with three depressed sides. Agitation was kept at 1000 rpm

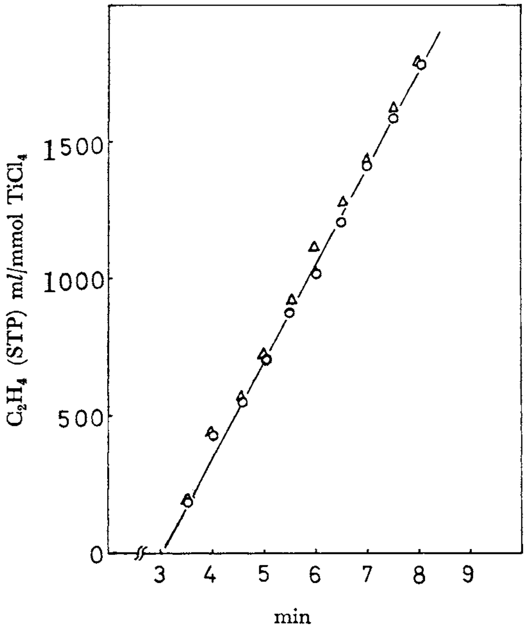

Fig. 2. The effect of nitrogen on the rate of ethylene consumption.
○, Without nitrogen; △, In addition of nitrogen P_E=40 cmHg; Polymerization temperature 20°C

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8) A. Simon and G. Gyhmes, *J. Polym. Sci.*, **53**, 327 (1961).

9) S. Kodama, T. Kagiya, S. Machi, T. Shimizu, S. Yuasa and K. Fukui, *J. Appl. Polym. Sci.*, **3**, 20 (1960).

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11) H. Schnecko, M. Reinmöller, W. Lintz, K. Weirauch and W. Kern, *Makromol. Chem.*, **84**, 156 (1959).

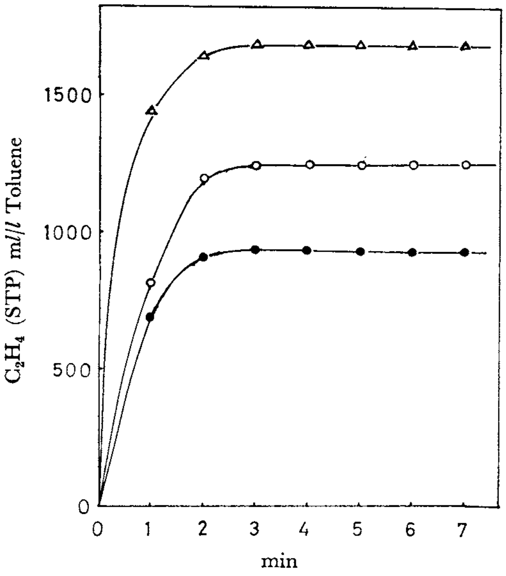

Fig. 3. The dissolution rate of ethylene in toluene. ● $P_E=15$ cmHg at 40°C, ○ $P_E=15$ cmHg at 0°C, △ $P_E=74$ cmHg at 20°C

sufficient to obtain non-diffusion controlled conditions regarding the polymerization rate.

In a 500-m*l* flask replaced with nitrogen, 200 m*l* of toluene and the required amounts of $TiCl_4$ or $TiCl_3$ and $AlEt_3$ were in this order intorduced by syringes under a nitrogen atmosphere. Stirring at a constant speed was accomplished, and the flask was immersed in a water bath which was adjusted to keep the fluctuation of the temperature within 0.1°C.

The rather excessive mole ratio of $AlEt_3$ to titanium halides was chosen so that the $AlEt_3$ reacted enough with titanium halides and so that the rate of polymerization was independent of the $AlEt_3$ concentration;[12] *i.e.*, the Al/Ti ratio in the catalyst system was chosen to be 4, while the concentration of titanium halides was 1 mmol.

After the evacuation of the reaction apparatus, ethylene was fed through a needle valve; the time of polymerization was recorded immediately. The rate of ethylene consumption in polymerization was measured by a wet-flow meter.

Analysis of Titanium. The valence state of titanium was analysed by the method described by Martin and Stedefeder.[13] In a three-necked, 300-m*l* flask equipped with a stirrer and containing a catalyst solution, 30 m*l* of alcohol and 10 m*l* of 2 N HCl solution, both of which had already been cooled, are added under nitrogen at —50——70°C; the solution is then titrated with a 0.1 M $FeCl_3$ solution, using methyleneblue as the indicator. No effect of nitrogen on the rate of ethylene consumption was observed, as is shown in Fig. 2. Even at the low partial pressure of ethylene of 10 cmHg, with or without nitrogen, and even on the introduction of nitrogen during polymerization, the rate of ethylene consumption did not alter. Therefore, all the polymerizations at low ethylene partial pressures were carried out with the addition of nitrogen, keeping the total reaction pressure at the atmospheric level.

As may be shown in Fig. 3, ethylene, when dissovled, reaches the saturated state within a few minutes after the introduction of ethylene at rather high partial pressures, but at pressures of ethylene lower than 10 cmHg, satulation was reached after at least 10 min. During this interval, the polymerization and the dissolution of ethylene will take place at the same time; therefore, we chose the polymerization at ethylene partial pressures higher than 10 cmHg. Meaningful flowmeter readings began only after 3 min due to the filling-up of the reaction flask.

Results and Discussion

Initial Rate of Polymerization. The ethylene consumption *versus* the time had a linear relationship for about 10 min. Some representative results are shown in Figs. 4 and 5. The initial rate of polymerization, *r*, was defined in terms of the decline of the straight lines dotted for an interval from 3 min to 10 min. About the relation of initial rates to the partial pressure of ethylene, P_E, we found that r/P_E was proportional to P_E (Figs. 6 and 7). Therefore, *r* is expressed by the following equation:

$$r = k_1P_E + k_2P_E^2 \qquad (1)$$

In this equation k_1 and k_2 are constants. The values of the constants, k_1 and k_2 are shown in Table 1; the activation energies calculated using

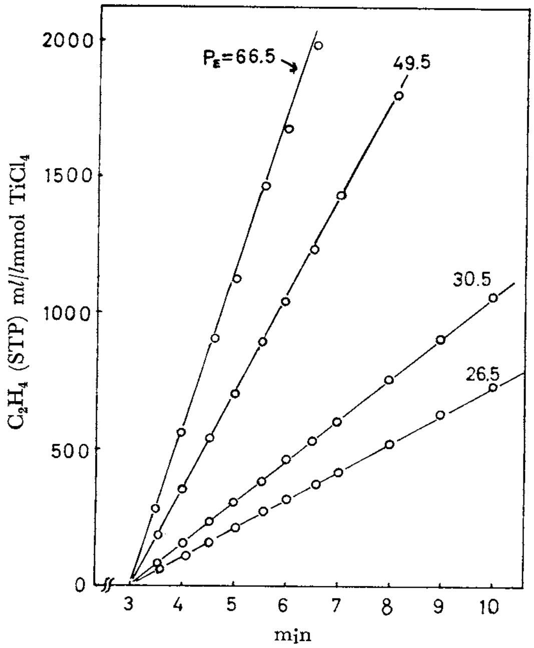

Fig. 4. The amount of ethylene consumed *vs.* time at $TiCl_4$-$AlEt_3$.
Polymerization temperature 20°C

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[12] T. Keii, T. Takagi, M. Taira, K. Soga, N. Saiki and Y. Murayama, *Shokubai*, **5**, 243 (1963).

[13] H. Martin and J. Stedfeder, *Ann.*, **618**, 17 (1958).

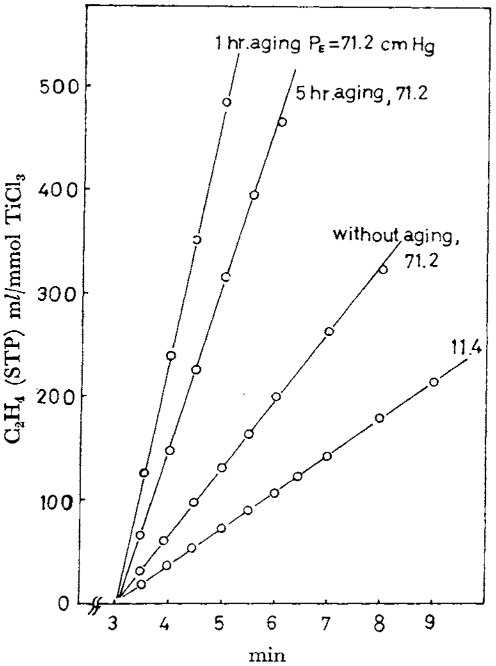

Fig. 5. The amount of ethylene consumed *vs.* time at $TiCl_3$-$AlEt_3$.
Polymerization temperature 20°C

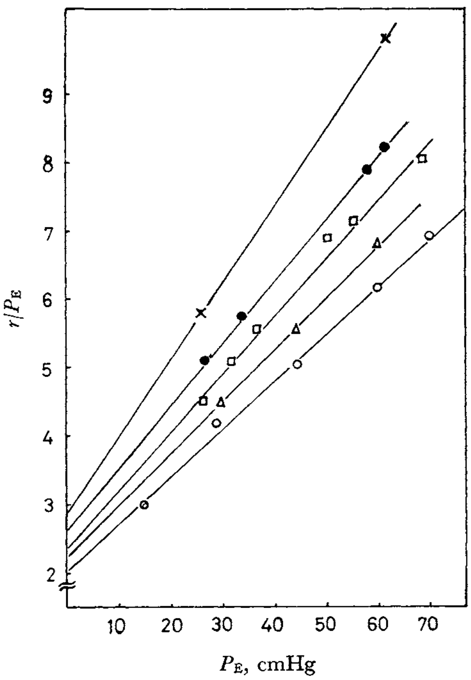

Fig. 6. The relationship between *r* and P_E at $TiCl_4$-$AlEt_3$.
Unit of ordinate; C_2H_4(STP) ml/mmol $TiCl_4$·min
○ 6°C, △ 12.5°C, □ 20°C, ● 30°C, × 43.5°C

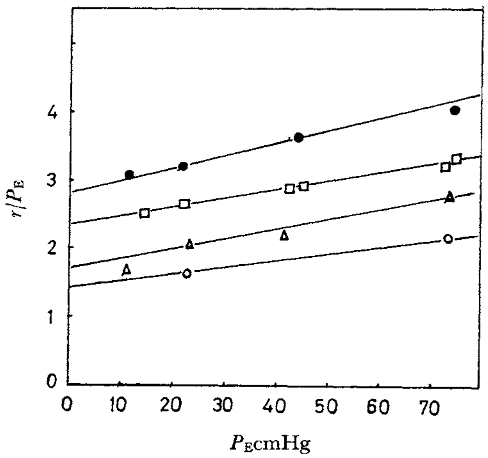

Fig. 7. The relationship between *r* and P_E at $TiCl_3$-$AlEt_3$.
Unit of ordinate; C_2H_4 (STP) ml/mmol $TiCl_3$·min
○ 6°C, △ 10°C, □ 20°C, ● 30°C

k_1 and k_2 are listed in the last column of the table. The first term, k_1P_E, refers to the initial rate starting from the polymerization sites resulting in a catalyst complex formation, while the second term, k_2P_E, refers to the rate starting from the polymerization sites built up by the reaction of the active sites and ethylene molecules introduced.

The activation energies in the $TiCl_3$-$AlEt_3$ system are larger than those in the $TiCl_4$-$AlEt_3$ system. Consequently, the polymerization sites in the two catalyst systems will be different. The difference in the activation energies calculated by k_1 and k_2 will be the energy required for the formation of the active sites.

Schindler[14] described the rate equation in ethylene polymerization by the $TiCl_4$-$Al(iso\text{-}Bu)_2$ system as:

$$R_p = \frac{KP_E^2}{1+K'P_E} \tag{2}$$

Table 1. The rate constants and activation energies of ethylene polymerization

Temperature °C	$TiCl_4$-$AlEt_3$		$TiCl_3$-$AlEt_3$	
	k_1	k_2	k_1	k_2
2	—	—	1.50	1.00×10^{-2}
6	2.10	6.65×10^{-2}	—	—
10	—	—	1.75	1.60
12.5	2.40	7.67	—	—
20	2.50	8.67	2.40	1.63
30	2.65	9.67	2.75	2.67
43.5	2.90	11.0	—	—
A.E.*	1.0	3.5	2.6	5.7

* Activation energy (kcal/mol)

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[14] A. Schindler, *J. Polym. Sci., Part C*, **4**, 81 (1963).

Here R_p is the rate of the polymerization, and K and K' are constants. The equation expresses the second-order kinetics with respect to the ethylene partial pressure as long as the pressure remains low enough in order to make $K'P_E$ small compared to unity. The values of k_1 in Eq. (1) are not as small as the k_2 values, which can be neglected, as may be seen in Table 1.

At a low pressure the rate will be first-order with respect to P_E, judging from our data. Keii and his co-workers[15] reported that the rate of the initial state in propylene polymerization was second-order with respect to the propylene partial pressure. In this case, the rate starting from the polymerization sites which were already formed during the catalyst complex formation will be neglected in the propylene polymerization; *i. e.*, the first term in Eq. (1) will be neglected in comparison with the second term. Consequently, the polymerization sites constructed in the reaction of the active sites with the propylene monomers introduced will be more active than the other polymerization sites already present as a result of the catalyst formation. Though the activation energies almost agree with those obtained by Fukui, Kagiya and their co-workers,[16] the energies seem to be rather small in comparison with those reported by other authors.[17-18] Our lower values are difficult to ascribe to the diffusion control of ethylene into the solvent, so it seems that our values are attributable to the ethylene polymerization in the initial stage.

Aging Effect

The relation of the aging time to the initial rate in the $TiCl_4$ and $TiCl_3$-$AlEt_3$ systems at 20°C is shown in Fig. 8. The initial rate decreases with the aging interval in the $TiCl_4$-$AlEt_3$ system, and in the $TiCl_3$-$AlEt_3$ system the rate attains its maximum value after about half an hour of aging. The maximum in $TiCl_3$-$AlEt_3$ may be due to an increase in the concentration of the active sites, followed by an increase in the effective surface area by the collapse of $TiCl_3$ particles. On the other hand, the decrease in r may be ascribed to the

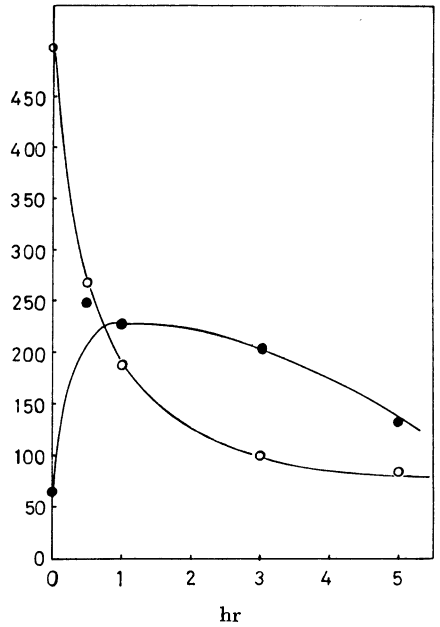

Fig. 8. The relationship between r and aging time. Aging temperature, 20°C
Unit of ordinate; C_2H_4 (STP) ml/mmol $TiCl_4$- or $TiCl_3$·min
○ $TiCl_4$-$AlEt_3$, ● $TiCl_3$-$AlEt_3$

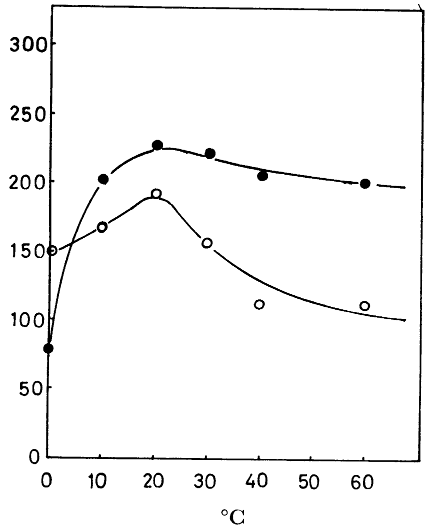

Fig. 9. The relationship between r and aging temperature.
Aging interval: an hour
Unit of ordinate: same as in Fig. 8
○ $TiCl_4$-$AlEt_3$, ● $TiCl_3$-$AlEt_3$

TABLE 2. ANALYTICAL RESULTS ON TITANIUM VALENCES

Aging time (hr)	0	3	5	Catalyst system
Ti^{2+} (%)	23	0	0	$TiCl_4$-$AlEt_3$
Ti^{3+} (%)	77	0	0	

Aging time (hr)	0	0.75	4.5	
Ti^{2+} (%)	32	36	94.5	$TiCl_3$-$AlEt_3$
Ti^{3+} (%)	63.4	40	0	

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[15] T. Keii, K. Soga and N. Saiki, Preprint for the International Symposium on Makromolecular Chemistry (Prague, 1965), p. 190.

[16] K. Fukuki, T. Kagiya, S. Machi, T. Shimizu and S. Yuasa, This Bulletin, **35**, 303, 396 (1962).

[17] M. N. Berger and M. B. Grieveson, *Makromol. Chem.*, **83**, 80 (1965).

[18] H. Schnecko, M. Reinmöller, K. Weirauch, V. Bednjagin and W. Kern, *ibid.*, **73**, 154 (1964).

reduction of titanium to the state of the lower valences of titanium in the $TiCl_4$- and $TiCl_3$-$AlEt_3$ systems.

The results of the analysis are shown in Table 2. The titanium ion is reduced to the lower valence state with the aging time. Especially, $TiCl_4$ is more easily reduced than $TiCl_3$. After an aging time of more than 3 hr, $TiCl_4$ is almost completely reduced, but the activity of ethylene polymerization remains. Some of the Ti^{3+} or Ti^{4+} remains, for the active sites of polymerization will be titanium ions with the valences higher than two.[19-21] Even if the active species are di- or tri-valent titanium, they may be changed through oxidation or disproportionation to mono- or tetra-valent titanium by the hydrochloric acid added in analysis.

The decrease in the initial rate with the aging time may be ascribed to reduction into the lower-valence state of titanium. The fact that the sum of the Ti^{2+} and the Ti^{3+} present in the $TiCl_3$-$AlEt_3$ system is not 100 per cent may come from the titanium of the valence state lower than two, or tetravalent titanium may be present. The relation between the initial rate and the aging temperature after an hour's aging is shown in Fig. 9. The optimum aging temperature is found to be 20°C. The initial rate in $TiCl_3$-$AlEt_3$ was not much affected by the temperature, but in $TiCl_4$-$AlEt_3$ it was affected remarkably. The decrease in the rate caused by the aging temperature may also be ascribed to the reduction of the titanium atoms.

A more accurate determination of the cause of the aging effect will have to await another analytical method, because not all the valence states of titanium can be detected by the method of Martin and Stedefeder.[13] We are still in the process of developing a better analytical method to detect all the valence states of titanium.

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20) C. J. Brnning, W. R. Wszolek and F. X. Weber, *J. Polym. Sci., Part A-1*, **6**, 755 (1968).

21) A. Schindler, *Makromol. Chem.*, **118**, 1 (1968).