

## REFERENCES

1. K. Ziegler, German Patent 487,727 (issued January 7, 1930) and Belgian Patent 527,736 (issued October 1, 1954).
2. ———, Belgian Patent 534,792 (issued May 1, 1955): also Belgian Patent 534,888 (issued May 1, 1955): also Belgian Patent 540,459 (issued February 9, 1956).
3. ———, E. Holzkamp, H. Breil and H. Martin, Angew.Chem., 67, 541(1955).
4. M. E. P. Friedrich and C. S. Marvel, J.Am.Chem.Soc., 52, 376, (1930).
5. K. Ziegler, F. Dersch, H. Wollthan, Justus Liebigs Ann.Chem., 511, 13, (1934).
6. L. M. Ellis, US. Pat. 2,2112,155(issued August 20,1940), E.I. Du Pont de Nemour & Company.
7. W. E. Hanford, J. R. Roland and H. S. Young, US. Pat.2,377,779 (issued June 5,1945), E.I. DuPont de Nemour & Company.
8. K. Ziegler and H. G. Gellert, Justus Liebigs Ann.Chem., 567, 195 (1950).
9. ———, Angew.Chem., 64,323,(1952).
10. ———, Brennst-Chem., 35, 321(1954), Belgian Patent 527,736 (issued October 1,1954).
11. E. Holzkamp, Thesis, Technische Hochschule, Aachen(May 21,1954),
12. K. Ziegler, Metallorganische verbindungen vom Standpunkte der Makromolekularen Synthese, in"International Symposium on Macromolecular Chemistry Proc."Prague,1957,Pergamon Press, 1957, pp. 295-306.
13. G. Natta, Science,147, 261(1965).
14. G. Natta, P. Pino, M. Farina, Cinetica della polimerizzazione dell'etilene catalizzata da composti alluminio-alchilici in International Symposium of Macromolecular Chemistry, Milan, 1954, Supplement A of La Ricerca Scientifica 25, 1955, p.120-133.
15. ———, Atti Accad. Naz.Lincei..Mem..Cl.Sci.Fis..Mat.Nat..Sez. 3a[8]4,61(1955).
16. ———, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti and G. Moraglio, J.Chem.Soc., 77, 1708(1955).
17. ———, Angew.Chem., 67, 430(1955).
18. ———, Chim.Ind.(Milan) 37, 88(1955).
19. ———, J.Polym.Sci., 16, 143(1955).
20. N. G. Gaylord and H. F. Mark, Linear and Stereoregular Addition Polymers," Wiley(Interscience), New York,1959.

21. E. J. Vanderberge, US. Pat. 3,051,690(August 28,1962),Hercules Powder Company.
22. B. Ettore and L. Luciano, Italian Patent 554,013 (January 5,1957), Montecatini.
23. G. Natta and I. Pasquon, Adv.Catal., 11, 1(1959).
24. ———, I. Pasquon and A. Zambelli, J.Am.Chem.Soc., 84, 1488(1962).
25. Hong Man Park and Wha Young Lee, " The Effect of Triethylaluminium Treatment on a Ziegler-Natta Catalyst Supported on Magnesium Chloride Prepared by a Recrystallization method, for Propylene Polymerization." Eur.Polym.J., Vol. 28, No.11, pp.1417-1422, 1992.
26. D. N. Taveira Magalhaes, O. Do Coutto Filho and F. M. B. Coutinho, "Ziegler-Natta Catalysts for Ethylene and Propylene Polymerization Supported on Adducts of Magnesium Chloride with Methyl and Ethyl Alcohols, " Eur.Polym.J. , Vol.27, No.8, pp.827-830,1991.
27. D. N. Taveira Magalhaes, O. Do Coutto Filho and F. M. B. Coutinho, "Ziegler-Natta Catalysts for Ethylene and Propylene Polymerizations Supported on the Products of Thermal Desolvation of the Adducts of Magnesium Chloride with Methyl and Ethyl Alcohols," Eur.Polym.J., Vol.27, No.10, pp.1093-1096, 1991.
28. B. V. Kokta and R. G. Raj,,"Interaction of  $\alpha$ -TiCl<sub>3</sub> with organaluminium compounds and its correlation with propylene polymerization II. Characterization by IR," Polym. Bull., 22,111-117,1989.
29. ——— and R. G. Raj, "Interaction of  $\alpha$ -TiCl<sub>3</sub> with organoaluminium compounds and its correlation with propylene polymerization I. Kinetics of Interaction." Polym. Bull., 22, 103-110, 1989.
30. S.A. Sergeev,G.D. Bukatov,E.M. Moroz ,and V.A. Zakharov, " X-ray studies of Interaction Between Magnesium Chloride and Ethyl Benzoate components of the catalyst for Propylene Polymerization," React.Kinet.Catal.Lett., Vol.21, No.3, 403-407(1982).
31. James C. W. Chien, L. Charles Dickinson,and James Vizzini , "Magnesium Chloride Supported High Mileage Catalysts for Olefin Polymerization XX. Solid State NMR," J.Polym.Sci.: Part A: Polym.Chem., Vol.28, 2321-2333 (1990).
32. ———, Jiun-Chen Wu, " Magnesium Chloride Supported High Mileage Catalysts for Olefin Polymerization.III. Electron Paramagnetic Resonance Studies." J.Polym.Sci.: Polym.Chem. Ed. ,Vol.20, 2461-12471(1982).

33. ——— and Tsule Ang, "Magnesium Chloride Supported High Mileage Catalysts for Olefin (Decene-1) Polymerization. XIV. Propagation and Chain Transfer." J. Polym. Sci.: Part A: Polym. Chem., Vol. 25, 919-934(1987).
34. ———, Jiun-Chen Wu and Chi-i Kuo, "Magnesium Chloride Supported High Mileage Catalysts for Olefin Polymerization. V. BET, Porosimetry and X-ray Diffraction Studies," J. Polym. Sci.: Polym. Chem. Ed., Vol. 21, 737-750(1983).
35. ——— and Youliang Hu, "Superactive and Stereospecific Catalysts. III. Definitive Identification and Active Sites by Electron Paramagnetic Resonance," J. Polym. Sci.: Part A: Polym. Chem., Vol. 27, 897-813(1989).
36. L.V. Gaponik et al., "Higher Aluminum Trialkyls and Magnesium Aluminum Alkyls as Components of Ziegler-Natta Catalysts," J. Applied Polym. Sci., Vol. 38, 1975-1985(1989).
37. Maria Carmela Sacchi, Chengji Shan et al., "Stereochemical Investigation of the Initiation Step in  $MgCl_2$ -Supported Ziegler-Natta Catalysts. The Lewis Base Activation Effect." Macromolecules, 23, 383-386, 1990.
38. Jin San Yoon and Young-Tae Jeung, "Studies on the catalyst modification in propylene polymerization using ethylene-propylene copolymerization," Polym. Bull., 22, 233-238(1989).
39. James C. W. Chien, Youliang Hu and James C. Vizzini, "Superactive and Stereospecific Catalysts. IV. Influence of Structure of Esters on  $MgCl_2$  Supported Olefin Polymerization Catalysts," J. Polym. Sci.: Part A: Polym. Chem., Vol. 28, 273-284(1990).
40. ——— and Chi-i Kuo, "Magnesium Chloride Supported High Mileage Catalysts for Polymerization. X. Effect of Hydrogen and Catalyst Deactivation," J. Polym. Sci.: Part A: Polym. Chem. Ed., Vol. 24, 2707-2727(1986).
41. Frederick J. Karol, "Catalysis and The Polyethylene Revolution," R. B. Seymour and T. Cheng(eds.), History of Polyolefins, 193-211, 1986, D. Reidel Publishing Co., USA.
42. Norio Kashiwa, Junichi Yoshitake and Akinori Toyota, "Studies on Propylene Polymerization with a Highly Active  $MgCl_2$  supported  $TiCl_4$  catalyst system," Polym. Bull., 19, 333-338,(1988).
43. Marie Lesna and Jiri Mejzlik, "The Influence of carbon mono- and dioxide upon kinetics of ethylene polymerization Catalyzed by Ziegler-Natta Systems," Collection Czechoslov Chem. Commun., Vol. 45, 1980.

44. Lixin Sun, Zejian Lu, Yun Lu and Shangun Lin, "Copolymerization of Ethylene and Butadiene with Supported Titanium Catalyst," J. Polym. Sci.: Part B: Polym. Physics, Vol. 26, 2487-2500 (1986).
45. P. J. Tait, "Kinetic Studies on Ziegler-Natta Polymerization- An Interpretation of Results," Studies in Surf. Sci. and Catalysis. (Tominaga Keii, ed.), Catalytic Polymerization of Olefins, No. 25, pp. 305-322, Kodansha Ltd., Japan, 1986.
46. A. Munoz-Escalona, J. G. Hernandez and J. A. Gallardo, "Design of Supported Ziegler-Natta Catalysts Using SiO<sub>2</sub> as Carrier," Studies in Surf. Sci. and Catalysis. (Tominaga Keii, ed.), Catalytic Polymerization of Olefins, No. 25, pp. 305-322, Kodansha Ltd., Japan, 1986.
47. John Boor, Jr., "Ziegler-Natta Catalysts and Polymerization", Academic Press, USA, pp. 33-67.
48. K. Ziegler, E. Holzkamp, H. Breil and H. Martin, Angew. Chem., 67 (541), 1955.
49. S. E. Wilson, W. L. Callender, "Stereochemical Control in Ziegler-Natta Catalyst," Advances in Polyolefins (Raymond B. Seymour and Tai Chang, editor), Vol. 1, pp. 171-178, Plenum Press, New York, 1987.
50. K. Soga, M. Terano and S. Zkeda, Polym. Bull., 1, 849, (1979).
51. Frederick J. Karol, "Studies with High Activity Catalysts for Olefin Polymerization," Cat. Rev.-Sci. Eng., 26(3&4), 557-595, 1984.
52. U. Giannini, Makromol. Chem. Suppl., 5, 216-229, 1981.
53. A. Greco, G. Perego, M. Cesari and S. Cesca, J. Appl. Polym. Sci., 23, 1319-1332, 1979.
54. ———, J. Appl. Polym. Sci., 23, 1333-1344, 1979.
55. P. D. Gavens, M. Bottril, J. W. Kelland and J. McMeeking, "Ziegler-Natta Catalysis," Comprehensive Organometallic Chemistry (Geoffrey Wilkinson, editor), Vol. 2, pp. 476-545, Pergamon Press, 1982.
56. K. Ziegler, Br. Patent 799,823 (1954).
57. A. Gilchrist, J. Polym. Sci. (B), 34, 49, 1959.
58. P. Pat and H. J. Sinn, Angew. Chem., 70, 496, 1958.
59. J. Boor, J. Polym. Sci. (C), 1, 257, 1963.
60. C. D. Nenitzescu, C. Huch and A. Huch, Angew. Chem., 68, 438, 1956.
61. E. J. Arlman and P. Cossee, J. Catal., 3, 89-90, 1964.
62. L. A. M. Rodriguez and H. M. van Looy, J. Polym. Sci. (A-1), 4, 1966.
63. K. L. Ivin, J. J. Rooney and C. D. Stewart, J. Chem. Soc., Chem. Comm., 603, 1978.

64. J. D. Fellman, G. A. Rupprechet and R. R. Schrock, J.Am.Chem.Soc., 101,5099,1979.
65. L. L. Bohm, Polymer. 19, 545, 1978.
66. Herman F. Mark, " Encyclopedia of Polymer Science & Engineering," John Wiley & Son, USA, 1986.
67. Suwaree Suphchochai, " Ethylene Polymerization by Modified Ziegler-Natta Catalyst," Master Thesis, Polymer Technology, 1990.
68. ASTM Committee, "Dilute Solution Viscometry of Ethylene Polymer," American Standard Testing of Material Institute, Philadelphia, (ASTM D3593-77)1958.
69. ASTM Committee, " Measurement of Density of Plastics by the Density-Gradient Technique," American Standard Testing of Material Institute, Philadelphia, (ASTM D1505-57T)1958.
70. S. Floyd, G. E. Mann and W. H. Ray, " Heat and Mass transfer Limitation and Catalyst Deactivation Effects in Olefin Polymerization for Gas Phase and Slurry Reactors " Catalytic Polymerization of Olefin Tominaga Keii and Kazuo Soga, editor), Vol. 25, 324-339, Kodancha, Tokyo, 1986.
71. J. C. W. Chien. J.Polym.Sci.. Part A, 425, 1963.
72. P. J. T. Tait, "Kinetics Studies on Ziegler-Natta Polymerization - An Interpretation of Results," Catalytic Polymerization of Olefin (Tominaga Keii and Kazuo Soga, editor), Vol.25, 305-322, Kodancha, Tokyo, 1986.
73. G. Boocock and R. N. Haward, Soc.Chem.Ind.(London). No.20, 3, 1966.
74. E. J. Arlman, J.R. de Jung, J. Beintema, and L. L. van Reijan, Rec. Trav. Chem... 80, 1129, 1960.
75. P. J. T. Tait and I. A. Jaber, " Studies on the Polymerization of Propylene Using Highly Active Magnesium Chloride Supported Ziegler-Natta Catalysts: Effects of Alkyl Concentration on the Polymerization Rate and on the Active Center Concentration, " Catalytic Olefin Polymerization (Tominaga Keii and Kazuo Soga, editor), Vol.56, 11-28, Kodancha, Tokyo, 1990.
76. Tominaga Keii, "Mechanistic Studies on Ziegler-Natta Catalysis - A methodological reconsideration". Catalytic Polymerization of Olefin (Tominaga Keii and Kazuo Soga, editor), Vol.25, 1-29, Kodancha, Tokyo, 1986.
77. Dong-Ho Lee and Young-Tae Jeong, " Propene Polymerization with  $Mg(OEt)_2$  - supported  $TiCl_4$  catalyst - 4.Effects of Hydrogen, " Eur.Polym.J., Vol.29, 883-888, 1991.

78. Fred W. Billmeyer, Jr., "Textbook of Polymer Science," 86-95, John Wiley & Sons Inc., Singapore, 1984.
79. Il Kim, Jae Ha Kim and Seong Ihl Woo, "Kinetic Study of Ethylene Polymerization by Highly Active Silica Supported  $TiCl_4/MgCl_2$  Catalyst," J. of Applied Polym. Sci., 39, 837-854, 1990.
80. George Odian, "Principles of Polymerization," 309-320, McGraw-Hill Inc., USA, 1970.
81. Tetsuo Hayashi, Yoshio Inoue and Riichiro Chojo, "Chain-End Structures in Polymerization Prepared with  $\alpha-TiCl_3 / Et_2AlCl$  Catalytic System in the Presence of Hydrogen," Macromolecules, 21, 2675-2684, 1988.
82. Jame C. W. Chien and Chi-i Kuo, "Magnesium Chloride Supported High-Mileage Catalysts for Olefin Polymerization. X. Effect of Hydrogen and Catalytic Site Deactivation," J. Polym. Sci.: Part A: Polym. Chem. Ed., 24, 2707-2727, 1986.
83. P. Cossee, "Ziegler-Natta Catalysis I. Mechanism of Polymerization of  $\alpha$ -olefin with Ziegler-Natta Catalysts," J. of Catal., 3, 80-88, 1964.
84. E. J. Arlman, "Ziegler-Natta Catalysis II. Surface Structure of Layer-Lattice Transition Metal Chloride," J. of Catal., 3, 89-98, 1964.
85. E. J. Arlman and P. Cossee, "Ziegler-Natta Catalysis III. Stereospecific Polymerization of Propene with the Catalyst System  $TiCl_3-AlEt_3$ ," J. of Catal., 3, 99-104, 1964.
86. S. Fuji, "Ethylene Polymerization with the Catalysts of One and Two Component Systems Based on Titanium Trichloride Complex," Coordination Polymerization, 135-153, Academic Press Inc., New York, 1975.
87. V. A. Zahkarov, G. A. Bukatov and Y. I. Yeranakov, Makromol. Chem., 176, 1959-1963, 1975.
88. A. C. Balazs and K. H. Johnson, J. Chem. Phys., 77, 3148-3154, 1982.
89. H. Schnecko, M. Reinmoller, K. Weirauch, V. Bednjagin and W. Hern, Makromol. Chem., 73, 154, 1964.
90. Bruce C. Gate, Jame R. Katzer and G. C. A. Schuit, Chemistry of Catalytic Processes, 151, McGraw-Hill Book Co., USA, 1963.
91. J. C. W. Chien, J. Polym. Sci.: Part A, 425, 1963.
92. Piotr Sobota, "The Role of  $MgCl_2$  as supporter of the New Generation of Olefin Polymerization Catalysts," Polym.-Plast. Technol. Eng., 28(5&6), 493-510, 1989.

93. L. L. Murrel, "Immobilization of Transition Metals: Complex Catalysts on Inorganic Supports," Advanced Material in Catalysis, (Jame J. Burton and Robert L. Garten, editors), 236-266, Academic Press, USA, 1977.
94. R. H. Griffith, "The Geometric Factor in Catalysis", Advances in Catalysis and Related Subjects, Vol.1, 91-103, Academic Press, USA, 1948.
95. Alan H. Cowley, Mike C. Cushner, Raymond E. Davis and Paul E. Riley "Crystal and Molecular Structure of the 1:2 Aluminium Trichloride complex  $AlEt_3 \cdot 2THF$ ," Inorg. Chem., 20, 1179-1181, 1981.
96. John Boor, "Ziegler-Natta Catalysts and Polymerizations", Academic Press, USA, 111-130, 1979.
97. Frederick J. Karol, "Coordinated Anionic Polymerization and Polymerization Mechanisms," ACS Symposium series, No. 285, 69-94, 1985.
98. A. Langner, "Electron Spin Resonance Study of Radical Formation in cis-Poly(phenylacetylene)/Ferric Acetylacetonate-Triethylaluminum (PPa/Fe-Al). 1. Procedure of Line-Shape and Saturation Analysis," Macromolecules, 23, 2198-2202, 1990.
99. A. Langner, "Electron Spin Resonance Study of Radical Formation in cis-Poly(phenylacetylene)/Ferric Acetylacetonate-Triethylaluminum(PPa/Fe-Al). 2. Result and Interpretation of Result," Macromolecules, 23, 2203-2210, 1990.
100. A. G. Oblad, G. A. Mills and Heinz Heinemann, "Polymerization of Olefins (To Liquid Polymers), Catalysis (Paul H. Emmett, editor), 341-406, Reinhold Publishing Corp., USA, 1985.
101. A. Munoz-Escalona, J. G. Hernandez and J. A. Gallardo, "Catalytic Activity and Control of the Nascent Morphology of Polyethylenes Obtained with First and Second Generation of Ziegler-Natta Catalysts," J. of Applied Polym. Sci., Vol.29, 1187-1202(1984).
102. A. Munoz-Escalona, J. G. Hernandez, J. A. Gallardo and A. Sustic, "Particle Control of Supported Ziegler-Natta Catalysts", Advance in Polyolefins, 179-202, Plenum Press, New York, 1984.
103. Robert T. Morrison and Robert N. Boyd, Organic Chemistry, 409-460, Printice Hall of India Private Ltd., 2ed., New Delhi, 1971.
104. J. Brandrup and E.M. Immergut, Polymer Handbook, John Wiley & Sons Inc., 1975, USA.
105. Norbert Platzler, "Commodity and Engineering Plastics," USA, John Wiley & Son, 1981

106. D. Campbell and J. R. White, " Polymer Characterization : Physical Techniques,"  
Chapman and Hall Ltd., USA.1989.
107. L.S. Bark and N.S. Allen, " Analysis of Polymer System," Applied Science Publishers  
Ltd., UK.,1982.
108. Mark G. Styring and Archie E. Hamielec, " Determination of Molecular Weight  
Distribution by Gel Permeation chromatography ," Determination of  
Molecular Weight.( Antony R. Cooper ,editor) John Wiley & Sons Inc.,  
USA.,1987.



**VITA****Mr. Satit Phiyanalimat****Degree of Master of Engineering (Petrochemical Technology)****Thesis Topic:** Ethylene Polymerization on High Activity  
Ziegler-Natta Supported Catalyst**Major Field:** Petrochemical Technology**Biography:****Personal data:** He was born in Sukhothai on September 12, 1967.**Education :** He received B.Sc.(Chemistry) from Chiang Mai University in 1989. And he had carried out the special problem about Voltammetric Determination of Lead in Soil. Afterwards, he had received UDC scholarship from Chiang Mai University to study at Chulalongkorn University majoring in Petrochemical Technology. He had finished M.Eng.(Petrochemical Technology) in 1993.**Professional Experience:**Chemist trainee at Colgate-Palmolive (Thailand) Co.Ltd., during summer season 1988.