1
The Invention

1.1
First Observations 1950/1953

As dramatic and exciting as the history of the development of the Ziegler catalysts may be on its own, nevertheless revisiting the events that took place around the world in the same area of research is no less fascinating. It was particularly in the United States, where, in different parts of the country, within the span of a few years, simultaneous, but independent, efforts were underway to investigate transition metal compounds as catalyst components in connection with the conversion of olefins.

Numerous litigations during the last 30 years provided an opportunity for a number of individuals, among others, those in research organizations, to disclose and provide supporting evidence for the developments taking place within their own institutes as well as to establish legal positions concerning the events that took place between 1950 and 1955. Through countless cross-examinations conducted during these litigations, the facts of the case, the historical chronology of the events, and the functions performed by individual research personalities were disclosed to the public.

In 1958, the US Patent Office declared a so-called “interference”[1] [1] between Du Pont, Standard Oil of Indiana, Phillips Petroleum, Hercules Powder and Montecatini. The issue involved was a product claim directed to the new and up to that time unknown polypropylene. The product claim to the new “solid, crystalline polypropylene” material which the Office proposed to all parties involved, read as follows:

> *“Normally solid polypropylene consisting essentially of recurring [2] polypropylene units, having a substantial crystalline polypropylene content.”*

Neither the parties nor the US Patent Office had considered including Karl Ziegler’s patent rights in this proceeding. The claim proposed by the Examiner did not

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[1] “Interference” is a procedure carried out by US-Patent law according to which the Board of Patent Appeals in the US Patent Office determines the priority of two or more timely overlapping inventions of identical or similar claim content.

Polymers, Patents, Profits. Heinz Martin

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indicate whether or not high molecular “thermoplastic” polypropylene was included. But more on this later.

US law provides that three criteria must be met when determining prior inventorship (priority), criteria which are also internationally respected:

(1) Production of a composition of matter satisfying the limitation of the Count.
(2) Recognition of the composition of matter; and
(3) Recognition of a specific practical utility for the composition.

Product yields of barely a few milligrams were not sufficient to satisfy these requirements, but not only could US inventors assert the earliest filing date of a patent application as evidence of priority, but even before that, they also could establish an earlier priority based on testimony-supported documentation (such as laboratory journal entries).

In 1971 [1], the US Patent Office found, in connection with this interference, that Montecatini was entitled to the earliest product claim directed to “polypropylene”. The losing parties appealed this decision to the competent district court. In 1980, i.e. more than 25 years after the discoveries had been made, the court [3] determined that it was neither Standard Oil nor Du Pont nor Montecatini, but Phillips Petroleum who was entitled to the benefit of priority of invention [4]. The sensational aspect of this decision will be discussed later. For now suffice it to say that the court found that Montecatini had committed fraud on the Patent Office where Phillips Petroleum was concerned and had, therefore, forfeited any right to an award of priority (see p. 31; Chapter 3, footnote 33; p. 115; p. 159; Chapter 5, footnote 1).

1.1.1
Standard Oil of Indiana

In 1950, at the “Exploratory Research Division” at Whiting, Indiana, Dr. Bernhard Evering and his research team were exploring the effects of catalysts on alkylation reactions with ethylene. A. Zletz, Carmody and E. F. Peters were the team members who worked together on this project during that time. They obtained substantially solid polymers as by-products.

The catalysts in question consisted of “reduced” molybdenum oxide on aluminum oxide carriers. One of the earliest entries in Zletz’s laboratory journal (dated July 18, 1950) also suggests that this catalyst could be used for the polymerization of propylene [5]. The reference to the polymerization of olefins, including propylene, in Mr. Zletz’s journal was initialed by J.C. Stauffer (“Senior Patent Adviser”) on July 21, 1950. Presumably this was intended to establish a date of conception and/or priority. Although Zletz described such polymerization experiments in his journal entries dated August 11, 1950 and August 31, 1950, these experiments never became the subject matter of a patent application.

During his experiment on September 29, 1950, Carmody isolated a propylene polymer [6]. It was fabricated into a thin, “somewhat flexible, not brittle” film. The product was also subjected to viscosity measurements and infrared spectra [7]. A later determination of crystallinity showed 38%, according to Heinen [8], and 27–30% according to Luongo [9]

That same day, Carmody conducted a further propylene polymerization experiment [10], and later on, so did Peters on April 30, 1953 (P-1) and July 17, 1953 (P-9), using similar catalysts (cobalt molybdate) [11]. When repeating this experiment in 1965, these products were characterized as 1,2-polypropylene having 77–95% crystallinity. No yields were specified.

Patent applications filed in 1951 [12, 13], naming A. Zletz as the inventor, may serve as an indication of how, in general, chemists at Standard Oil of Indiana were dealing with transition metal catalysts. In 1952, E. Field and M. Feller [14, 15], who were attached to the same research laboratories, described, from a large number of experiments using ethylene, two examples which used propylene alone (see US Patents ‘647, Example 21, and ‘453, Example 7). Whether it was a clever patent attorney who while working on the patent applications, suggested including these Examples – the 80 mg yield and/or complete lack of data on yield are less than convincing – or whether the experiment did in fact lead to the described results, will forever be shrouded in mystery. Much of the attention of numerous chemists, expert witnesses, and legal counsel was centered on these two examples during subsequent litigations. At no time did Standard Oil of Indiana either assert or designate these patent applications as priority applications [16].

Propylene polymerization experiments conducted in 1953 were included in a patent application by Zletz and Carmody (US SN 223,642), but this application was abandoned on May 20, 1954 in favor of US Application SN 462,480, filed October 15, 1954, which however, no longer contained these experiments. One can only surmise the reasons for such action: the yields [6, 10] (0.7 and/or 3.83 g) were too small, the product could not be reproduced, and had not been recognized as polypropylene. They contained a high methylene/methyl ratio (the court tolerated 1.1, but not 1.5 and higher – theoretically the ratio should be “1.0”), which led to the conclusion that these could not be polymers with a regular 1,2-propylene chain configuration. It was eventually learned that up to the year 1958, it had been impossible to determine the presence of crystalline polypropylene from infrared data alone. A retroactive interpretation of infrared spectra was, however, legally inadmissible.

Although the 1953 X-ray images of the products appeared to indicate crystalline fractions, quantitative figures were not available. In the final analysis, there was the possibility of an amorphous ethylene/propylene co-polymer content.

The documented experiments carried out by Standard Oil of Indiana in September of 1950 and between April and the end of July, 1953, were not accepted as proof of priority, “since neither the making of the product had been adequately described, nor had the product been recognized or a utility therefore been given,” as the judge later noted. It was not until approximately June 15, 1954, that Zletz realized that molybdenum oxide on aluminum oxide carriers was suitable as a catalyst for the polymerization of olefins. Dr. W. Bailey, an expert witness engaged by one party, told the court that disproportionation of propylene on molybdenum catalysts in butene and ethylene is known, so that, since ethylene polymerizes more rapidly than propylene, ethylene/propylene co-polymers must necessarily be present in the product.

Judge Wright ruled that Standard Oil was to be granted a priority date of October 15, 1954, the date that the Zletz Application Serial No. 462,480 was filed in the US Patent Office.

Due to the unsatisfactory results obtained when using the molydenum catalysts for propylene polymerization, Standard Oil of Indiana had neither developed its own commercial production, nor offered licenses, conceivably because of the unfavorable priority situation. It was not until the late 1960s and early 1970s that Standard Oil started producing polypropylene, this time, however, using Ziegler catalysts[2] (organoaluminum compounds and titanium halides). In 1972/1973, Amoco Chemical Corporation, a wholly-owned subsidiary of Standard Oil of Indiana, obtained a license for this production from Ziegler.

1.1.2
Phillips Petroleum Company

Phillips Petroleum Company, a crude oil processing company like Standard Oil of Indiana, maintained a process development section for catalytic processes in Bartlesville, Oklahoma, USA, which was a subdivision of an exploratory station for hydrocarben conversion. Dr. W.C. Lanning was the head of this operational section, while J.P. Hogan was a group leader, and R.L. Banks, G. Nowlin and E. Francis worked as research chemists. At that time, Hogan's group was focusing specifically on the conversion of gaseous olefins to liquid oligomers. They were exploring transition metal oxides, such as nickel oxide on a silica – aluminum oxide carrier, in terms of their effectiveness as catalysts.

In June 1951, the team worked with a mixture of chromium- and nickel oxide using the same carrier material. Ultimately, it was the type of catalyst which uses chromium oxide alone on the carrier material in the form of a reactor bed which, on October 9, 1951, for the first time caused the polymerization of propylene into, *inter alia*, semi-solid polypropylene [17]. E. Francis isolated 40–50 g of a polymer which G. Nowlin later fractionated, and one fraction of which he characterized as polypropylene gel, insoluble in both chloroform and benzene.

In November of 1951, when repeating the experiment under identical conditions, Hogan, Banks and Francis [18] recovered 70.5 g of a sticky polymer containing fractions which, again, were insoluble in boiling methylisobutyl ketone and n-pentane. Some of the products thus satisfied the claim that they were solid and moreover, that an infrared spectrum would show recurring polymer units (head – tail polymerization or 1,2 addition). This discovery, albeit fragmentary, was probably made between February and June of 1952. Crystallinity would be verified later by way of an infrared spectrum and X-ray analysis. In December of 1952, one of the products originally recovered in April of that year (PO-116) was determined to have a melting point of as high as 130 °C. The fact that the product was insoluble in boiling methylethylketone

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[2] G. Natta, for the first time, had defined the catalysts used by him and formed from aluminum alkyls and titanium halides as Ziegler catalysts (Lit. 165 and 166, first patent applications 1954).

led to the conclusion that it contained crystalline fractions. The measurement results obtained from an analysis of the polypropylene products recovered during the second half of 1952 [19] were set forth in a patent application filed January 27, 1953 [4]. But Phillips' assertion that they had demonstrated the utility of the polypropylene products as solid thermoplastics lacked evidentiary support, even though the usefulness of the products as wax additives had been established. The text of the patent application contained neither the word "crystalline" nor an indication that the products were useful as wax additives. Nevertheless, it was found that Phillips had documented both criteria. The mere supposition that the new material might be useful for the same purposes as polyethylene did not, however, constitute sufficient evidence. Furthermore, the melting point measurements obtained did not guarantee that the products would remain stable when subjected to molding temperatures (molded plastic). There was no indication that the products were useful as solid thermoplastics. As Judge Wright stated in 1980:

> *"The Court accordingly finds that Phillips failed to prove that its scientists knew enough about their product to conclude that it was useful as a solid plastic [20]."*

The ruling with regard to this defect would prove to be of great significance later on. To indicate the presence of crystalline fractions in the polypropylene product, the Phillips application mentioned the lack of solubility of the polymers in pentane at room temperature, a melting point range of the solid residue between 240 and 300 °F (115–149 °C), a density range between 0.90 and 0.95, an "intrinsic" viscosity between 0.2 and 1.0, and a molecular weight range of between 5000 and 20,000, including specific fractions between 200 and 50,000. According to the specification, the sticky polymer, having a molecular weight between 500 and 5000, could be separated into semi-solid, pentane-soluble fractions and solid, pentane-insoluble fractions. Examples were given only with respect to the semi-solid and/or sticky products.

Later on, that is, many years after the filing of the 1953 application, a number of experts repeated the examples presented in that application[3]. In 1980, the court [21]

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[3] In 1955 C. Capucci of Montedison, found that solid polypropylene can be produced as described. But the method of work-up differed from the disclosure of the Phillips application. Nevertheless an 'intrinsic' viscosity (I.V.) of 1.02 was measured on a sample of the product, i.e. at the upper limit of the disclosed range. Yet, this sample was not a raw product, but an insoluble fraction [22].
In 1956, H.S. Eleuterio of Du Pont, repeated examples out of the parallel Belgian Phillips patent 530,617 (equivalent to the Phillips US application 1953). He extracted the raw polymer from the catalyst, evaporated the solvent and isolated a solid product, 56% crystallinity.
In 1962 G. Trada of the Edison Company, repeated the Phillips experiments. He extracted the product with boiling xylene and after evaporating the xylene extracted the residue with pentane. The viscosity of the residual polypropylene was 1.31 and the product was 57% crystalline. After extraction with boiling heptane the viscosity of the residue was raised to 2.0 and the crystallinity remained unchanged.
Following the Phillips disclosure for the work up D. Witt of Phillips, isolated a material having a melting range of 125–130 °C and a viscosity (I.V.) of 0.73–0.95. In 1964 reproducing the procedure J.A. DeLap of Phillips, was not able to show different data.
Results from reproduction experiments were described by G. Longi of Montedison, during 1965 [23].

found that these products were not covered by Phillips' disclosure. Furthermore, it was not verified whether these products had been subjected to infrared or X-ray analysis. Longi proved that significantly higher-melting, crystalline products (melting point up to 167 °C, I.V. 1,37, crystallinity 71.5%) could be isolated. The same court further found that while the 1953 Phillips application did contain a description of the method for producing crystalline polypropylene, it failed to disclose all of the ranges of crystalline polypropylene and, therefore, was not entitled to claim the entire range. The application indicated that the described products had a molecular weight of approximately 5000–20,000. Whether products having a molecular weight of up to 50,000 were included in this range must remain doubtful. The only definite disclosure made by Phillips in its 1953 application was that a solid, at least partially crystalline material had been produced.

1.1.3
Du Pont

1.1.3.1 From the Beginning up to the Patent Application

According to statements made by Du Pont, it was in late January and February of 1954 when a group of chemists at the "Petrochemical Department" started a systematic search for suitable polymerization catalysts for the co-polymerization of norbornene and ethylene. At that time, the fundamental discovery which formed the basis for the development of the Ziegler catalysts for the polymerization of ethylene into solid, plastic-like polyethylene at the Max-Planck-Institute for Coal Research at Mülheim was 2–3 months old. Patent applications [24] directed thereto had been filed in the German Patent Office, and Montecatini, Farbwerke Hoechst, and Ruhrchemie AG [25] had been advised by Ziegler, through confidential communications, of the composition of the best-performing catalysts known at that time.

Whether and to what extent the Du Pont research group led by W.F. Gresham (Research Director), Anderson, Robinson, Merckling and Truett had knowledge of the work being carried out at the Max-Planck-Institute at Mülheim, could not be conclusively be established.

However, a memorandum [26] from the Du Pont Patent Department, dated August 4, 1954, mentioned that Gresham knew that Ziegler had developed a new polyethylene product, and that he had an idea about the composition of the Ziegler catalyst. In August of 1954, Du Pont filed patent applications in the US Patent Office disclosing and claiming the production of high molecular weight, solid polyethylene [27, 28] as well as polypropylene [29].

The initial experiments conducted at the Du Pont laboratory were based on the use of catalysts according to Max Fischer [30][4]. Upon repeating the Fischer experi-

[4] Max Fischer (BASF, Ludwigshafen) varied the efficiency of aluminum trichloride as a Friedel-Crafts-catalyst for the production of lubricating oils from ethylene, by addition of titanium tetrachloride and a small amount of aluminum powder. In addition to viscous oils solid ethylene polymers were also formed. It was known that aluminum powder can reduce the titanium in titanium tetrachloride. That was the basis on which the Du Pont team developed the working hypothesis that the formation of solid high MW polymers required that the titanium in the catalyst must be in a lower valence and later, that the valence must be below 3. Titanium dichloride by itself polymerizes ethylene into solid high MW polymers as shown, but titanium trichloride is ineffective.

ments using ethylene, the only products initially recovered were oils, and Truett, one of the researchers, characterized the Fischer reaction as “capricious” [31], because he was unable to determine the external conditions that would account for the formation of either nothing but oils, or actual solid polymers, as were subsequently found. Meanwhile the research group had expanded to more than a dozen chemists. A working hypothesis had been established according to which it was a transition metal halide alone, in reduced form [32], that would have to be responsible for the catalytic activity. The reducing agents employed were metals (aluminum or magnesium), but also – it was April, 1954 by now – Grignard-compounds [33]. No conclusion was reached as to the usefulness of aluminum alkyls or alkyl aluminum chlorides.

At that time, Ziegler had already entered into a number of option and/or license agreements [34], and there were test facilities from which polyethylene samples were distributed to interested parties and the curious. It was not difficult to analyze such samples for ash residues and to conclude that they contained at least aluminum and titanium. It was not until the early summer of 1954 that Gresham initiated the use of organoaluminum compounds. The suggestion had been made by a chemist by the name of Hyson [35], who, even though he had not been previously involved with this project, was still knowledgeable and experienced in working with Ziegler’s aluminum alkyls. At the end of July, 1954, Hyson conducted experiments with ethylene, during which equimolecular amounts of aluminum trimethyl and titanium tetrachloride under extreme pressures (up to 1000 atmospheres) and temperatures (100–200 °C) were found to be effective as catalyst components. Later on, however, Hyson switched from pure aluminum alkyls to lithium aluminum tetraalkyls, since he considered the short-chained aluminum alkyls in particular, to be too dangerous to use due to their inflammability when exposed to air. Hyson also suggested that propylene as well as olefins in general could be used for polymerization [36].

Subsequent developments are described in the specifications of the patent applications filed between August 16 and 19, 1954 which claimed the production of catalysts for the polymerization of ethylene [27, 28]; the August 19, 1954 application claimed, *inter alia*, the production of polypropylene. [29]. The former suggested Grignard-compounds, lithium aluminum tetraalkyls and aluminum trimethyl as reducing agents for titanium tetrachloride, while the latter contained examples showing the use of lithium aluminum tetraalkyls or Grignard-compounds as the reducing component. None of these applications names Hyson as an inventor. The use of phenyl magnesium bromide and titanium tetrachloride as a catalyst mixture is described in an initial experiment of May 21, 1954, all further experiments are dated in August, a detail of vital significance for DuPont from the standpoint of patent rights.

1.3.1.2 **Only a Scant Experimental “Polypropylene”**

During the period from April through August of 1954, Stamatoff and Baxter conducted a series of experiments at DuPont using different catalysts for both ethylene and propylene. A large number of these experiments yielded either no polymer at all or liquid polymers (oils) only. In some cases, where minute quantities of solid polymer were formed, the products were never analyzed. On May 21, 1954, Baxter [37] had converted propylene with the aid of a mixture of Grignard-compounds and titanium tetrachloride, but the yield, 0.5 g of a powder, was not conclusive. Even though a film was formed from this product, which was characterized as "tough and elastic" – infrared spectra indicated absorption at 8.69 ìm (internal methyl group) – no quantities were specified for this methyl content, nor was crystallinity mentioned – thus, the analysis provided no conclusive results.

In 1980, within the context of the above-described litigation between Standard Oil of Indiana, Phillips Petroleum Co., Du Pont and Montecatini, Judge C.M. Wright [38] affirmed a 1971 decision of the Board of Patent Interferences [39] (the board of appeals for interference proceedings] which held that the earliest priority established by Du Pont with respect to the production of solid, crystalline polypropylene was August 19, 1954 [29]. Du Pont's assertion that they were entitled to the earlier priority of the May experiment was rejected by the judge, since the experimenters had not only failed to recognize, in a legal sense, the polypropylene product as such, but had also neglected to show any utility, as required by the rules. The judge stated: "It is clear that the infrared spectrum of the product of the May experiment, fabricated by Mr. Beck (Du Pont), showed no indication that the product had any polypropylene crystallinity whatsoever."

In August of 1954, Baxter obtained a larger yield of polypropylene when using a catalyst combination of titanium tetrachloride and lithium aluminum tetrahexyl. An X-ray analysis of these products now showed a crystalline content of 15–10%, but even these values were not submitted to the Du Pont Patent Department in August (see p. 223).

No later than 1955, it had become obvious to Du Pont that its own position, in particular with respect to polypropylene was poor as compared to all of its competitors. But it took the individuals involved another 25 years before they would become aware of this (see above). Any yields and insights obtained from these experiments were too slight for Du Pont to expect an award of priority. Du Pont has never seriously considered the commercial production of polypropylene.

1.2
Max-Planck-Institute, Mülheim on the Ruhr

1.2.1
K. Ziegler, H. Breil, E. Holzkamp and H. Martin

While the three above-mentioned companies and their research teams working in the polymer field had obtained the described results independently from one another, the development at the Italian chemical company Montecatini is inseparably entwined with the developments at the Max-Planck-Insitute for Coal Research. In other words, the initial impulse for all of the activities taking place at Montecatini with respect to "polyolefins" was provided by the Institute at Mülheim on the Ruhr, as will be documented hereinafter (see p. 29).

Giulio Natta, Director of the Instituto Di Chimica Industriale Del Politecnico in Milan, a research institute subsidized by Montecatini within the framework of a contractual association[5)], was training a number of young chemists for Montecatini among others. Early on, he had pointed out to Montecatini that the research carried out at the Max-Planck-Institute for Coal Research at Mülheim might be of potential importance for Montecatini. According to his own statements, Natta had closely followed Ziegler's publications and lectures since at least 1952. At that time, Ziegler and his co-workers were exploring the so-called growth reaction[6)] of ethylene on aluminum triethyl and the selective dimerization of higher alpha-olefins on organoaluminum compounds. Obviously of particular interest was the dimerization of propylene to 2-methylpentene-1 as well as the dimerization of butene to 2-ethylhexene-1. In January of 1953, Montecatini and Ziegler entered into an "agreement" [34], granting Montecatini an exclusive license for Italy under certain patent rights [40] concerning

> *"the conversion of olefins with the use of organometallic catalysts."*

The license also included any

> *"ancillary processes, a well as all other future processes which would be developed in the field of olefin conversion with the use of organometallic compounds as catalysts."*

The definition of the subject matter under contract was so comprehensive that, 1 year later, it prompted a debate as to whether the "Ziegler catalysts" (organometallic mixed catalysts) discovered during the second half of 1953 would fall under this definition [41].

The agreement furthermore provided that any subsequent inventions made by Montecatini in the contract field should be offered to Ziegler, and that Montecatini would retain the right to grant licenses in other countries for any of its own inventions falling under the above definition [41]. The down payment of 600,000 Deutsch Marks was attractive to Ziegler, especially because the existing "know-how" for conversion to industrial-scale production was by no means complete. Only a small experimental pilot plant was available.

Ziegler's Italian patent rights at that time covered, *inter alia*, the "polymerization of ethylene" [40]. But it should be mentioned here that while the products in question were, at best, wax-like in character, they consisted primarily of hydrocarbon oils (see "Growth reaction", this chapter, footnote 6). The aluminum trialkyl catalysts used were free from transition metal compounds.

In the Spring of 1953, in line with the agreement, Montecatini sent two chemists, Paolo Chini and Roberto Magri, as well as an engineer, Giovanni Crespi, to Mülheim

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[5)] G. Natta assigned patent rights to Montecatini. The chemists whom he trained were partly employees of Montecatini.

[6)] Growth reaction: the stepwise addition of ethylene molecules to aluminum triethyl leads to the formation of a longer hydrocarbon chain i.e. the chain grows. Contrary to this result a replacement reaction was defined if the chain was removed from the aluminum. This could occur after one, two or several steps of growth, according to specific conditions.

with the aim of familiarizing themselves with the licensed subject matter and to learn the process production and method of use of aluminum alkyls. The three guests arrived at Mülheim to start their visit on February 24, 1953 [42] at a point in time when a number of interesting observations were being made at the Max-Planck-Institute for Coal Research during work with aluminum alkyls.

While investigating specific growth reactions on ethylene, E. Holzkamp, a doctoral student with K. Ziegler, had noticed an important development which deviated from the usual test results: instead of a chain-building reaction, he observed a displacement reaction, which for the most part produced butene, the dimer of ethylene, a portion of which, was again dimerized. The search for the cause of this reaction, as is generally known pointed to traces of nickel metal from the chromium – nickel – steel of the autoclave acting as a co-catalyst. By adding finely dispersed nickel, the addition reaction could be curtailed. However, the exploration of the use of other transition metals and their effect was considered too ambitious an undertaking for a doctoral thesis.

A young undergraduate, H. Breil, was then assigned to the task of preparing suitable transition metal compounds and, in collaboration with E. Holzkamp, investigating their action as so-called displacement catalysts.

Although the Italian guests worked inside the Max-Planck-Institute, they were being introduced to the organic chemistry of aluminum in a different area of the building, away from the Holzkamp/Breil laboratory. At that time, the Institute was also accommodating another guest, Dr. A. Glasebrook of the US-based Hercules Powder Co. Following an invitation by Ziegler, Dr. Glasebrook had been assigned by his company to become acquainted with organoaluminum chemistry in order to see whether its use on an industrial scale would be of sufficient interest, given his company's field of interests. Among other places, Dr. Glasbrook also worked at the Holzkamp laboratory. Every day, all of the guests, the three Italian gentlemen and A. Glasebrook, had lunch together at a nearby restaurant and exchanged information.

1.2.2
Experiments between May and December, 1953

In May of 1953, E. Holzkamp conducted two back-to-back experiments, in both cases using a combination of chromium acetylacetonate and aluminum triethyl as the catalyst mixture, the intent being of course, to test the effect of the chromium compound in place of nickel, as a displacement co-catalyst on ethylene [43, 44]. In the first instance, he recovered "approximately 30 g of a mostly higher molecular weight product, about 30% of which was non-melting," while the second experiment yielded a "residue of 16 g of a non-melting product." The only variation in the two experiments was the degree of ethylene pressure being applied.

Around the same time, and taking into account the nickel co-catalysis reaction previously observed, H. Martin, a postdoctoral assistant with Ziegler, was testing the theory that, if the reaction vessel being used was completely free of any potential traces of nickel, the growth reaction of ethylene on aluminum triethyl should proceed wholly unencumbered, all the way to yielding true polyethylene. This required a simultaneous, step-by-step reduction in the amount of aluminum triethyl employed, so as to allow the chains forming on the aluminum to develop with a high excess of ethylene [45]. To that end, an anodized aluminum vessel was fitted into the pressure reactor, into which aluminum triethyl and ethylene were introduced at a 1 : 280 ratio, a temperature of 55 °C and a pressure of 150 bars, and brought to reaction in hexane as the reaction medium. The reaction continued for 20 h, yielding a high fraction of solid paraffin products [46].

In a letter dated the end of July 1953 [47], K. Ziegler reported to Montecatini (R. Orsoni) on the status of the developments, stating *inter alia*:

> *"For approximately the past 2 to 3 months, the entire realm of polymerization problems has, again, been intensively addressed by Dr. Martin and others. I believe that here, too, we are on the threshold of new developments and insights."*

In September, 1953, the research endeavors yielded products with melting points between 80 and 100 °C [48].The molecular weights of these products, however, failed to rise above 10,000 [49]. Parallel thereto, there was an increase in the olefin content of the products, which indicated that the displacement reaction was still taking place even under these conditions7).

During the process of systematically exploring any available transition metal compounds, Breil also used titanium tetrachloride together with aluminum triethyl as a catalyst mixture under ethylene pressure. He made the following entry in his laboratory journal [50]: "Yield 3.5 g of butene ... additionally, a high polymer residue, black (titanium), rubber-like mass." It was noteworthy that despite a lowering of the exterior heating, the reaction mixture heated up by itself within a few minutes and maintained this elevated temperature level for several hours. Upon review, it can merely be said that apparently, a repetition of the experiment had neither been planned nor was it executed at the time, possibly because the results had been unsatisfactory and did not comply with the aim of titanium displacement catalysis.

This assessment of the situation was later confirmed by Karl Ziegler during a deposition conducted in 1967 [52] in connection with a patent litigation involving Ziegler, Du Pont, and Natta, and/or in 1969 [53] between Montecatini, Dart Industries Inc., Chevron Chemical Co. and Enjay Chemical Co., Humble Oil and Refining Co. and Avisun Corporation regarding the subject of polypropylene. The person asking the question, Mr. Irons, US patent attorney for Montecatini, was actually inquiring as to whether an experiment using titanium tetrachloride had been conducted prior to August 1954 (he presumably meant in connection with polypropylene). Ziegler corrected him by saying that, in his opinion, Irons obviously meant 1953, and denied that any experiment had been conducted prior to August 1953 during which the formation of polyethylene had been observed. Mr. Irons con-

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7) Almost 40 years later H. Martin and coworker [51] found in connection with other activities that pure aluminum triethyl and also other aluminum trialkyls converts ethylene into high molecular weight solid polyethylene if the temperature is lowered to room temperature. The reaction is then very slow, but the displacement reaction is suppressed.

Fig. 1.2 Erhard Holzkamp, Heinz Breil and Heinz Martin

firmed this view [54] saying that by the end of July 1953, “you had not yet made a high molecular weight solid polyethylene.”

After the August 1953 vacation period, the repetition of an experiment using chromium acetylacetonate together with aluminum triethyl and ethylene [55] was being reported. Breil recovered small amounts of “soft paraffins”, and when using molybdenum acetylacetonate, found “paraffins of medium consistency plus a minor quantity of butene” [56]. At the beginning of October, the influence of vanadium acetylacetonate was being investigated, whereby some polymers (paraffins) were recovered along with butene [57–59]. Manganese acetylacetonate catalyzes the formation of butene [60], as does platinum acetylacetonate [61].

On October 26, 1953 [62], Breil used zirconium acetylacetonate together with aluminum triethyl and ethylene. Of the converted ethylene 90% now consisted of solid products: 38 g of “hard paraffin, polyethylene”. The triumph was complete. The product was pressed into an initial sheet (100–300 atmospheres, 130–150 °C Fp). On November 13, 1953 [63], Breil repeated this experiment, this time however, in the presence of hexane as the reaction medium. While, from a later viewpoint, this proved to be trivial, at the time it represented a significant variation of the process. The surface availability of the heterogeneous catalyst was being enhanced. Up to that time, reactions involving organoaluminum compounds had been carried out practically free of solvents. The yield of solid, finely powdered polyethylene, was tripled and stressed bands were tested for tensile strength (30 kg/mm^2). An infrared spectrum failed to indicate the presence of methyl groups. Three days later [64], propylene was used for the first time in place of ethylene with the same catalyst. “No solid, but only liquid products, dimerisate” were obtained. Thus, the concept of polymerizing propylene in place of ethylene existed on paper, but could not be reproduced in practice [65].

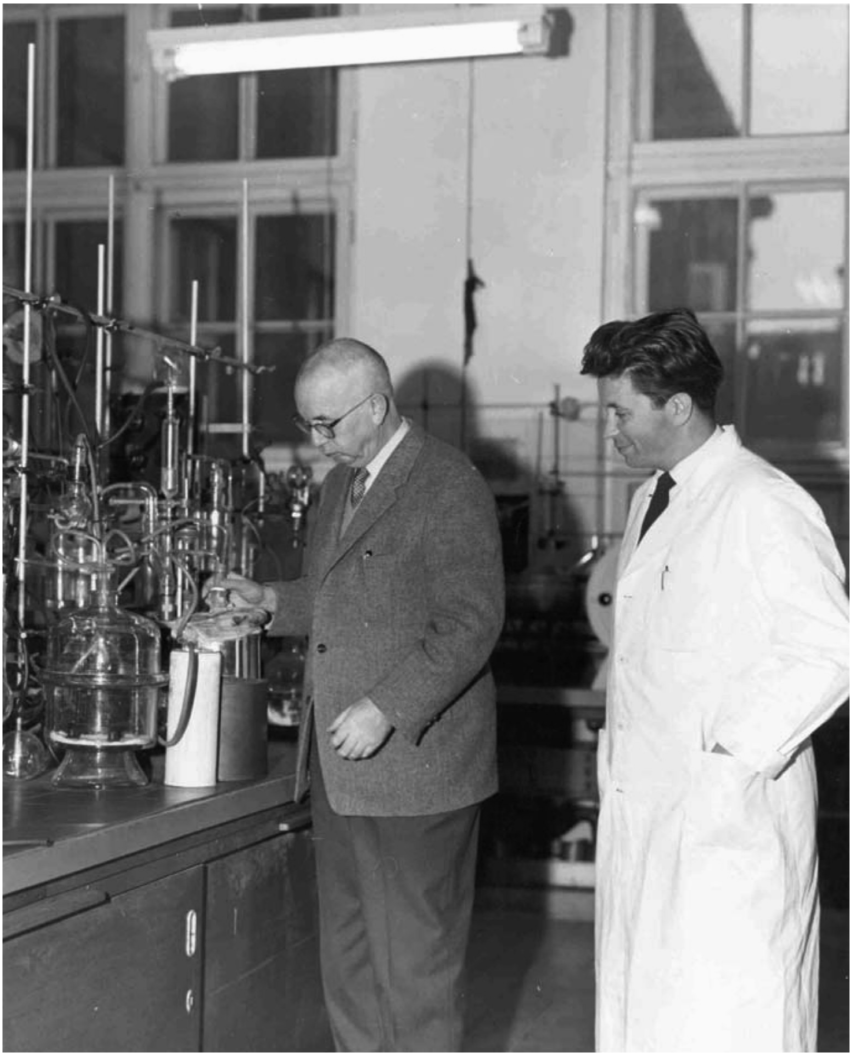

Fig. 1.3 Karl Ziegler and Heinz Martin at work in the laboratory

During the months of May through December, 1953, the three Italian visitors, and/or one of them[8], maintained written contact with their, and/or his, supervisors, Orsoni and Ballabio, both engineers at Montecatini in Milan. The Max-Planck-Institute and Ziegler had no knowledge of these reports, but they were uncovered during the course of subsequent litigations. While the letters written between May and July,

[8] In August G. Natta had suggested, that after the summer vacation, only one chemist, R. Magri, should return to Mülheim [82].

1953 [66-80] dealt with the dimerization of olefins, as covered by the agreement, including dimerization with added colloidal nickel, as well as the production of the starting materials (06/17/1953, page 3 “Ziegler Processes” [72]), Magri, in a letter dated 11/15/1953 [81], reported to Milan that he had learned from certain co-workers of Karl Ziegler – no names were mentioned – that during the course of investigating the influence of different “metals” on the reaction of aluminum triethyl and ethylene, a “high polymer of the polythene type had been obtained.”

He had afterwards seen the product for himself and described its properties as “true and genuine polythene.” He also conveyed some further information he had received at the Institute, according to which one of the polyethylene samples had purportedly resulted from an experiment conducted with aluminum triethyl in the presence of traces of zirconium at 100 bar and 100 °C.

On November 16, 1953 [83], K. Ziegler filed, in the German Patent Office in Munich, a patent application, which he himself had drafted, entitled “Process of the Polymerization of Ethylene” and was granted a priority date of November 17, 1953. The application claimed “a process for the production of a high molecular weight polyethylene useful as a plastic”, using “mixtures of aluminum trialkyls with salts of the metals titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten as polymerization catalysts” and specifying “ethylene at pressures of more than 10 atmospheres and temperatures above 50 °C as process characteristics.” The claim was limited to the production of polyethylene. At the time, no practical results had as yet been obtained with the use of propylene and higher olefins towards the formation of solid polymers.

On November 27, 1953 [84], encouraged by the activity of the zirconium acetylacetonate in connection with ethylene polymerization, Breil experimented with a mixture of aluminum triethyl and titanium tetrachloride in the presence of hexane as the reaction medium. The polymerization reaction proceeded at a rate of 90 % conversion of the starting ethylene. As compared to zirconium acetylacetonate, this experiment, conducted at only slightly elevated temperatures and an ethylene pressure of 55 atmospheres, was highly exothermic in nature, and the resulting product was black.

Around the same time, H. Martin sought to produce larger amounts of polyethylene by using the zirconium acetylacetonate/aluminum triethyl mixture [85] as well as the titanium tetrachloride and aluminum triethyl combination [86]. Not only did the result, 200 and/or 900 g of polyethylene, confirm past findings, but it also clearly demonstrated that, for the first time, the catalysts were so highly active that polymerization of ethylene at room temperature and normal pressure now appeared possible. After a few days, ethylene polymerization in a three-necked flask and later in a 5-l jar [87] was being undertaken as a standard experiment. The number of guests being taken by surprise by these amazingly simple procedures increased rapidly, and the news spread quickly and uncontrollably out of the Institute. Any disclosure regarding the composition of the catalysts was, however, scrupulously avoided. On December 12, 1953, Ziegler filed an addition application [88] in the German Patent Office, which, again, he had drafted himself. This time, the claims were directed to a method using an ethylene pressure of 1 atmosphere and lower temperatures above – 20 °C. The Patent Office accorded the application a filing date of December 15, 1953.

Further results then followed in quick seccession. Martin was successful in polymerizing ethylene with ethyl aluminum chlorides, particularly diethyl aluminum chloride, but also ethyl aluminum sesquichloride and ethyl aluminum dichloride in place of aluminum triethyl as a component of the catalyst, thus broadening the range of available catalysts [89–94]. This was a significant achievement, since dialkyl aluminum chloride compounds alone were not suitable for the growth reactions[9] with ethylene [95]. At the same time, Breil gained his first insight into the reaction products resulting from a conversion of titanium tetrachloride with aluminum triethyl, i.e. the catalyst components [96–98].

In mid-December 1953, Breil attempted to repeat the propylene polymerization process [99]. In preparing the catalyst mixture, he replaced aluminum triethyl with aluminum trioctyl and zirconium acetylacetonate with titanium tetrachloride. Of all the experiments from the early days in the historical development of the Ziegler catalysts, it was this one that was to be minutely scrutinized, commented on and crticized by experts, chemists and lawyers for the next 25 years. This experiment elicited the entire spectrum of judgments and opinions, some in written form, from "fall out" to "polypropylene must have been present".

There was no doubt that the product was characterized as "polyethylene, sticky" and furthermore that propylene was initially pressed onto the catalyst mixture. The absence of a reaction, recognizable by a fall in pressure and/or rise in temperature, caused Breil, after "blowing off" a portion of the original propylene, to test the efficiency of the catalyst by adding more pressurized ethylene. Even then, "there was only a minor pressure drop after shaking." A weight balance of recovered "polyethylene" on the one hand and the amount of ethylene and propylene introduced on the other should have led to the conclusion that propylene had been polymerized to a solid product, which must have been present either as a mixture of pure polypropylene and pure polyethylene or as a co-polymer [100]. At the time, however, no one sought further clarification of the result. The intention was rather to fully and completely devote all available time to the development of the catalysts and their effect on ethylene. Fourteen years later (in 1967), H. Martin repeated the first part of this experiment – catalyst mixture and propylene [101]. With spontaneous heating, the experiment produced more than 90% solid, high molecular weight polypropylene.

1.2.2.1 **Montecatini Points to the Contractual Rights and Obligations**

Inspired by Mr. Magri's reports and his visit in late-November 1953 [102], Mr. Orsoni [103] inquired whether the production of "high molecular weight ethylene polymers" would be covered by the scope of the January 1953 contract, based on the state of the discovery and crucial finding. As bait and in order to attain the information on the catalysts quickly, he mentioned the possibility of pushing for the development of the "polymerization of ethylene ... on a major industrial scale in Italy".

Shortly before Christmas 1953, R. Magri, the last remaining guest from Italy, approached Ziegler and asked for a definite declaration regarding the nature of the new catalysts and to have them incorporated into the existing contract with Monte-

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[9] See p. 9 + 10

catini. Ziegler put him off, but handed him the two patent applications [83, 88] that he had meanwhile filed, with a request to pass them on to Mr. Orsoni. In his letter of January 6, 1954 [104] to Mr. Orsoni – receipt of which was acknowledged by Orsoni in his response dated January 25, 1954 [105] – Ziegler intimated that "an extensive field ... had been opened up." In the same letter, Orsoni invited Ziegler to visit him in Milan. For the first time, it appeared that Ziegler himself must have had scruples and doubts regarding his own conduct, because in the last paragraph, he suggested:

> *"I trust that you and I are in complete agreement that any further development of this group of new catalysts should remain, for the time being, exclusively in our hands."*

and

> *"Surely you will appreciate that it is very important to us that we ourselves initially exploit our new discoveries for maximum benefit. Actually, my request to you that the completely undisturbed progression of this work be left exclusively to us for the time being, should be self-evident within the framework of a partnership such as it exists between you and us."*

Would Ziegler have been in breach of the agreement, if he had delayed passing on the most recent results for 6 months? Secure ownership of the new discoveries and the inherent unique chance of being in possession of a guaranteed commercially viable product and working with this monopoly was certainly the pivotal motivation for seeking out a strong industrial partner even at this early stage.

1.2.3
Experiments from December 1953 through April 1954

Not only did Martin's December experiments aim to produce the optimum activation of ethylene with the aid of ethyl aluminum chloride compounds and titanium tetrachloride at normal pressure and low temperatures, leading to greater diversity within the catalysis field, but this class of catalysts also became extremely important particularly in the commercial production of polypropylene that was to follow later. The diethylaluminum chloride/titanium tetrachloride catalyst system was then used to verify the formation of ethylene/propylene co-polymers [106], to successfully test the polymerization medium – higher molecular weight saturated hydrocarbons [107] – and the co-polymerization of ethylene with dienes [108] and, for the first time, to convert butadiene[10] into a polymer with the aid of the aluminum trialkyl/titanium tetrachloride catalyst combination, even though the latter results were less favorable than those obtained with ethylene [109].

The same polymerization activity was observed when the chlorine in the diethylaluminum chloride was replaced with alkoxy groups [110, 111], such as methoxyl, and the compound employed in combination with titanium tetrachloride. Catalysts

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[10] See p. 74

formed on this basis would rise to prominence as so-called "high speed" catalysts 30 years later when they were used in the polymerization of propylene (see p. 226).

During the reaction of diethylaluminum chloride and titanium tetrachloride, a fine, brown-colored powder deposits in the reaction vessel, which, on its own, is virtually inactive with respect to ethylene, but in combination with fresh diethylaluminum chloride constitutes an extremely effective catalyst combination useful for converting ethylene to solid high molecular weight polymers [112, 113]. This powder was determined to be titanium trichloride[11), to which poorly adsorbed aluminum compound was still attached. A further reduction of the titanium does not take place under these conditions. This finding, of course, begged the question whether the purple, commercially available variety of titanium trichloride was also effective. Indeed, in combination with diethyl aluminum chloride [114] as well as aluminum triethyl [115], it was capable of converting ethylene to solid high molecular weight polymers, albeit at a slower rate than had been previously observed.

A similar result was obtained when titanium trichloride was replaced with titanium dichloride; thus, aluminum triethyl or diethyl aluminum chloride in combination with titanium dichloride led to the formation of active polymerization catalysts [119].Violet titanium trichloride and black titanium dichloride were highly crystalline starting products.

At that time, Breil discovered that the product consisting of titanium tetrachloride and aluminum triethyl would have to be a partially hydrocarbon-soluble, black-colored, low-valence titanium halide compound. The composition led him to conclude that the product could not be a uniform compound, but that the titanium, in large part, was present in divalent form. The insoluble moiety alone was effective as a catalyst for the polymerization of ethylene [120], which, as already mentioned, was not true for titanium trichloride (see also Chapter 5, footnote 45).

Breil was furthermore able to show that effective catalyst mixtures could also be obtained, on the one hand, by replacing the aluminum trialkyls with metal alkyls such as magnesium dimethyl [121], Grignard compounds [122] as well as zinc diethyl [123], sodium phenyl [124] and lithium butyl [125] and also, as was to be expected, sodium aluminum tetramethyl and sodium aluminum tetraethyl [126], but also, unexpectedly, lithium hydride [127] and lithium aluminum tetrahydride [128]. On the other hand, titanium tetrachloride could be replaced with compounds of transition metals from subgroups IV, V and VI of the Periodic Table, particularly the halides, in addition to nickel chloride [129], iron chloride [130, 131], and manganese chloride [132]; the latter three, however, were effective only if combined with diethylaluminum chloride, (reduction not to titanium metal) but did not work in combination with pure metal alkyls (displacement catalyst in the dimerization of ethylene). Tungsten hexachloride [133], molybdenum pentachloride [134] and chromium trichloride [135], on the other hand, could be activated only when combined with alu-

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11) Amorphous (β)-titanium trichloride is an unstable modification or a mixture of various modifications. The "brown" powder described was indentified by X-ray analysis as partly crystalline [116]. The powder as well as β-titanium trichloride is transformed into the stable violet, pure crystalline α-titanium trichloride by longer tempering. Only about 4 mole% of the brown titanium trichloride [117] (measured surface 240 m^2/g) is available for adsorption with diethyl aluminum chloride[118].

minum trialkyls for the conversion of ethylene to high molecular weight polymers. However, only part of these experiments were included as examples in subsequent patent applications, a disadvantage which would hamper further patent claim delineation.

1.2.4
Letter from Ziegler to his Patent Attorney von Kreisler

On January 7, 1954, Ziegler asked Dr. A. von Kreisler [95] to represent him as his patent attorney before the German Patent Office and sent him copies of the patent applications, drafted by himself, which had been filed in November and December of 1953. When explaining the situation, he pointed out that "the recent newly discovered catalytic processes no longer have any immediate connection to our earlier reaction processes." By this statement he meant that the previously studied catalytic effects were limited to "genuine aluminum trialkyls", whereas the finding that alkylaluminum chlorides with titanium tetrachloride were also useful as effective catalysts was a "complete novelty." From this he concluded that the "real catalysts were ... most likely organometallic compounds of the added heavy metals with unusually low valancies." This was a newly gained insight into polymer chemistry. Accordingly, he asked von Kreisler to prepare a further patent application directed to the use of alkyl aluminum halides and those of the general formula R_2AlX.

In this context, he mentioned later on in the same letter a prior patent application by BASF, Ludwigshafen [136] (actually, it was a patent), the disclosure of which led him to arrive at a serious conclusion:

> *"The object of this application is undoubtedly a forerunner of our new processes. Except the inventors failed to recognize what they had in hand. For the polymerization of ethylene, they used a mixture of aluminum chloride, metallic aluminum, titanium tetrachloride, and, besides oily products (see p. 2, line 85), obtained perhaps a 40% yield of a polyethylene material which had characteristics similar to our own products. The inventors added the aluminum powder to bind hydrochloric acid (p. 1, line 20, and p. 2, lines 1–2). Actually, however, a combination of aluminum metal, aluminum chloride and ethylene at higher temperatures regularly leads to the formation of genuine organoaluminum compounds; this result has even found its way into the literature. The true mechanism of the process according to the BASF patent, thus, consists in the primary formation of a small amount of ethyl aluminum sesquichloride from aluminum chloride, aluminum metal + ethylene (the reaction does not completely tally, and a whole line of dehydrogenation by-products are also formed), and these genuine organoaluminum compounds, in combination with the titanium tetrachloride, then lead to the solid polyethylene, the same as we have obtained at the Institute. The inventors, of course, failed to see this connection."*

In the course of subsequent adversary proceedings, especially in the United States, this letter was disclosed to opposing counsel and, thus, moved into the public domain. As was to be expected, the opponents used Ziegler's letter as an admission that the Ziegler catalysts were covered by this BASF patent and, therefore, were no longer patentable.

As late as mid-1955, when assessing the same BASF patent in his doctoral thesis [137], Breil wrote that the "white powder" as described in the patent, "obviously, is a polyethylene of the same type as my polyethylenes." And regarding the catalysts he went on to say:

> *"It seems obvious to me that in experiments of this type, a catalyst of the type of my catalysts would be formed. The inventor of the patent failed, however, to recognize the essential nature of his process. The polymerization catalyst is formed either by Al, $AlCl_3$ and ethylene combining to primarily form organoaluminum compounds (see C. Hall, A.W. Nash, J. Inst. Petrol, Technol. 23, 679* **1937** and 24, 471 **1938**), *which react with titanium tetrachloride, or the metallic aluminum directly reduces the titanium tetrachloride."*

Neither of these statements was supported by any experimental data. It was not until 1958, and continuing intermittently through 1992, in between long intervals, that experiments were conducted at the Max-Planck-Institute at Mülheim under scientifically exact standards, to test the mode of action of the catalyst described by Max Fischer in the BASF patent. Not only were the above-described first impressions found in need of extensive revision, but, based on these experiments, it was also subsequently possible to identify the intermediate compounds and end-products of the Max-Fischer-catalyst [138–140]. But more on this later.

Back to mid-January 1954: von Kreisler filed the next two patent applications in the German Patent Office, the first of which was directed to the use of, among other compounds, alkyl aluminum halides in combination with transition metal compounds [141], and in the second application the aluminum compounds were replaced by magnesium alkyls [142].

1.3
Montecatini, Milano/G. Natta and Co-workers

1.3.1
The First Experiments with Ziegler catalysts

Based on the disclosure of the first two patent applications which had been divulged to Montecatini/Natta between late December and early January 1954, as well as three additional Ziegler patent applications [143], Ziegler's work was being discussed by Natta and his co-workers during January and February [144]. Magri translated the first two patent applications together with Chini and Crespi. Copies of these documents were made available to Dr. Varda, the Head of Montecatini's Patent Department, and engineer Orsoni [145], who was in charge of the Technical Development Section. On February 9, 1954, Chini began to repeat certain of the experiments described by Ziegler, starting with Example 2 in combination with Example 4 from Ziegler's second patent application [88, 146, 147]. He polymerized ethylene with a catalyst mixture of aluminum triethyl and titanium tetrachloride at atmospheric pressure, resulting in solid, crystalline, high molecular weight polymers. He was struck by the great ease of the polymerization process. While the results of these reproduced experiments had been discussed at the time with both Natta and Orsoni, no such discussions took place with Ziegler or his co-workers.

At that time, P. Pino and G. Mazzanti also worked under Natta. Pino supervised and conceived parts of the experimentation program, and Chini, Mazzanti, Longi, Angelini and Giachetti were Pino's co-workers [148].

On March 8 and 9, 1954, while passing through on his way to Southern Italy, where he planned to spend his vacation, Ziegler accepted an invitation from Montecatini to stop in Milan, and he met Natta and Orsoni. At the hosts' request, the discussion was recorded [149] and signed in the form of a contractual arrangement entitled "Cooperation between Professor Ziegler and Montecatini", that is, the content was legally acknowledged. The Memorandum, dated March 9, 1954, regulated the division of labor regarding future developments as between Ziegler's Institute, on the one hand, and Natta/Montecatini on the other.

Ziegler:

> *"b) Exploration of new mixed catalysts for the polymerization of olefins (particularly ethylene) based on the principles of production of the mixed catalysts described in the prior Ziegler polyethylene applications."*
> *Natta:*
> *"a) Production of branched-chain polymers resulting from the action of aluminum alkyl contacts … on substances containing interchangeable active groups."*
> *"b) Kinetic study of the chain elongation reaction of ethylene … and"*
> *"c) X-ray analysis of the structures of the polyethylene materials obtained from various different production methods."*
> *Further assignments were to be carried out at Montecatini's Ferrara plant:*
> *"d) Production of high molecular weight polyethylene on a technical scale, …"*
> *"f) Production of alpha-butene …"*
> *"g) Technological running comparison of the end polymers."*

The last paragraph of the Memorandum explicitly provided for Ziegler that

> *"any investigations involving the new catalysts and regarding the manipulation of the polyethylene molecular weight should initially be handled exclusively by him and his organization."*

Ziegler additionally told his contract partners of the successful co-polymerization of ethylene and propylene [150].

Two days after the meeting, on March 11, 1954, Natta instructed his co-worker, Chini, to use propylene while otherwise using the exact same parameters as employed in previous catalyst preparation. The propylene was added to the Ziegler catalyst initially at room temperature and atmospheric pressure [151], and later at elevated pressure. Chini recovered 3.5 g of solid polypropylene. The internal designation, according to a statement by Corradini, was a "Ziegler–Chini" product [152][12]. The following day, a shaped piece of the polypropylene thus obtained was stretched up to 500%, and an X-ray image revealed the typical characteristics of a crystalline polymer [153]. The raw product was then fractionated by solvent extraction and the insoluble fraction presumed to be crystalline. Pino instructed Mazzanti to work together with Chini on the experiments [154]. On March 15, Mazzanti and Chini together made a second attempt [155] at polymerizing propylene and performed a third test on March 24, 1954 [156], again based on Ziegler's first patent application. In the latter experiment, propylene pressure was applied from the very outset. The details of this test were recorded in Chini's laboratory journal, but not in that of Mazzanti. Further experiments were conducted on March 26, April 5, and May 26, 1954 [157, 158].

As early as March, Natta compiled all the data thus far available on propylene polymerization as well as the findings previously obtained regarding ethylene polymerization and forwarded them to the Patent Department at Montecatini [159].

The sequence of events which shaped the early history is described here in such detail, because it was the very results obtained from Chini's initial experiments which formed the basis for Natta/Montecatini's assertion that they were the first to "independently" produce high molecular weight polypropylene. All of the involved individuals at Milan were well aware that they had deliberately breached the agreement made with Ziegler and that Montecatini [160] "invade(d) a sphere of polymerization with our tests which Ziegler had explicitly reserved for himself when giving us advance notice of the discovery of his co-catalyst." and that Ziegler

> *"might one day request the restitution of the invention on the strength of illegal derivation."*

and furthermore, that the possibility of polymerizing propylene would not have existed without the detailed information supplied by Ziegler [161].

Chini:

> *"I expressed in my opinion, which is an opinion that Professor Ziegler should have been so mentioned in the patent."*
>
> *"I believed that if we did not have the information about the polyethylene preparation we would not have been able to prepare the polypropylene."*

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[12] Corradini had prepared the X-ray images.

1.3.2
Natta, Orsoni and DeVarda's Visit to Ziegler at Mülheim on May 19, 1954

The preparation, execution and results obtained from the experimental program implemented by Natta and his co-workers at Milan–as is evident from the sequence of events – were neither disclosed to either Ziegler or his co-workers nor discussed with them. Up to the end of July/beginning of August, 1954, Ziegler had no inkling of what had meanwhile occurred there. Even when Natta, Orsoni and DeVarda came to Mülheim on May 19, 1954 [162] to visit Ziegler [162], nothing was said to Ziegler on that subject. This was with full intent on Montecatini's part.[13] As had become apparent during an earlier internal discussion at Montecatini, the individuals involved wanted to avoid triggering a confrontation with Ziegler based on a patent application, filed solely in Montecatini's name and directed to the production of polypropylene, without knowing whether Ziegler had already previously polymerized propylene. They decided to find out during this visit to Ziegler [163]:

> *"... it would have been quite a complicated matter if by filing our patent we would have found that Ziegler had made ahead of us the polypropylene -the invention of polypropylen. Now, these doubts were clarified in May 19th (1954) when we went to Mülheim and Ziegler volunteered the information not only that he had tried to polymerize propylene, but that he had not succeeded, and therefore he thought it would not work. I mean the catalyst he had employed or had used would not."*

Further a notice by DeVarda [162]:

> *"He [Ziegler] did say "it does not go. It does not run. It does not succeed.' ...*
> *... words he [Ziegler] used and I remember them absolutely exactly "Polypropylene does not work.'"*

According to his recollection [164], Ziegler's response to a casual question as to whether he had also polymerized propylene was:

> *"No, not up to now, but we have successfully co-polymerized ethylene and already successfully co-polymerized ethylene and propylene."*

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13) In a later deposition (for this reason the court had moved to Milan in 1969) G. Natta was asked why he did not inform Ziegler about his experimental results: "I did not tell him because I had to take patents first."
In March 1970 G. Natta was deposed again as a witness. He presumed to declare that his question was whether or not somebody should try to polymerize propylene, Ziegler's reaction was: "Propylene could not polymerized." "If I have not been able to succeed, nobody would succeed." [147]
The Nobel-price laudatio for G. Natta does not mention Natta as the inventor of polypropylene, but indicates that Natta found that certain types of Ziegler catalysts led to stereoregular macromolecules, a diplomatic détour of the conflict between Ziegler and Natta.

The visitors from Italy believed that Ziegler's attitude justified their conclusion that to file a patent application quickly claiming the polymerization of propylene with the use of a Ziegler catalyst was entirely within the bounds of legal propriety [162]. This Montecatini application [165] was accepted by the Italian Patent Office in Rome on June 8, 1954. It was directed not only to the method of production [166] – the polymerization of propylene using Ziegler catalysts: $TiCl_4$ and $AlEt_3$ – but also to the high molecular weight polypropylene products, the structure of which was determined, *inter alia*, by X-ray structural analysis. G. Natta was named as the sole inventor. The first four examples of this patent application corresponded to the above-described experiments of March 15 and 26, April, and May 4 and 26, 1954. The first Chini experiment was not included in the application, nor was Chini later named as a co-inventor [161].

On July 27, 1954, a second application [167] was filed, claiming enhancement of the regular structure of the solid, crystalline polypropylene due to the presence of asymmetrical carbon atoms, and similar polymers from olefins with four or more carbon atoms. The catalysts disclosed in the specification were, again, Ziegler catalysts. Initially, no inventors were indicated, but the applicant subsequently named G. Natta, P. Pino and G. Mazzanti. The propylene polymers, as described in both of these applications, were of the same kind [168], and even the product obtained from Chini's first experiment was encompassed by the claim of the first application [169].

As it turned out later (see p. 118), Montecatini's inconsistency in naming the inventors, on the one hand, and its assertion, on the other hand, that the polypropylene products according to both applications were similar and also corresponded to the product obtained from Chini's first experiment, would prove disastrous from a standpoint of patent law. The issue of what Pino and Mazzanti had contributed to the invention was never fully resolved.

It should be reiterated here that neither had Ziegler been informed nor his consent been requested in regard to the filing of these applications. Ziegler first learned of the fact that Natta's team had polymerized propylene from Orsoni's letter [170] of July 30, 1954, which stated:

> *"During our meeting on May 20 at Mülheim, you declared that propylene and styrene did not lend themselves to the formation of superpolymers. This assessment took us somewhat by surprise, since even then we were convinced that we had been successful in producing at least the superpolymer of propylene."*

A few days later Natta also contacted Ziegler [171], just after the latter had sent to Milan on July 21, 1954 [172]both an initial sample of the high molecular weight, solid polypropylene produced at Mülheim (see p. 30 "July 1954, Polypropylene") and a pressed sheet made of polypropylene. In his accompanying letter, Ziegler intimated that a systematic testing program focusing on the polymerization of alpha-olefins, styrene, methyl styrene, butadiene as well as the halogenated ethylenes and possible mixed polymerizations had been set up.

Through X-ray analysis, Natta observed that these polypropylene products manifested a 45 % crystalline content:

> *"We had already obtained similar products last March."*

Natta further reported that other polyolefins, such as poly-alpha-butene and polystyrene, exhibited similar structures as the polypropylene.

Later on, Montecatini's US patent attorney, Harry Toulmin, writes [173]:

> *"An issue that I have long feared might be raised in connection with the question of what Professor Natta contributed over Dr. Ziegler and therefore whether Professor Natta was a genuine inventor has now been precipitated by the attached editorial."*
> *"Therefore, Natta, using the exact catalyst of Ziegler produced polypropylene in his early work. It was not until later that he began to be selective in his selection of the catalyst."*
> *"Dr. Orsoni, in one of his communications, indicated that he thought, as we understood him, that you could avoid this situation because of the selection by Natta of a special catalyst, but unfortunately, in the early invention, which was fundamental, Professor Natta used the exact catalyst of Ziegler, and it was not until later that Natta began his selectivity."*

1.4
K. Ziegler and Co-workers

1.4.1
H. Martin: Experiments May–July 6, 1954; H. Breil: Masters Thesis

The main focus which gave direction to the series of experiments conducted at Mülheim between May and mid-July 1954 was established by the fact that upon determining the molecular weight of the polyethylenes produced, very high values (several hundred thousands up to several millions) had been ascertained. Processing on conventional extruders was not possible. The solution to the problem presented itself in the finding that the molar ratio of the components employed in the preparation of the catalyst appeared to be crucial in determining the chain length of the polyethylene produced. This finding was confirmed and re-confirmed through a large number of experiments, whereby products with molecular weights between 20,000 and about 1 million could be easily synthesized [174]. Relatively short-chained products were more easily moldable than products with molecular weights in the several hundred thousands range. Highly crystalline polyethylene products with molecular weights between 50,000 and 80,000 could then be processed in standardized machines by established methods and formed into fibers, injection molding and sheet products.

By varying the catalyst composition, not only could the chain length be controlled, but the activity (conversion of gram ethylene/gram catalyst) was also affected. With a decrease in the amount of organoaluminum compound per titanium component used, conversion increased dramatically.

All in all, this fruitful period not only opened up new possibilities for the practical application of low pressure polyethylene, which could now be produced with extreme ease, but for the first time it also became apparent that the catalysts, depending on the method used for their production, showed great selectivity in their effect.

On June 28, 1954, H. Breil presented his Masters Thesis [175] "On Organometallic Mixed Catalysts" to Bonn University. It contained a description of his previous experiments, provided a summary of the effectiveness of the catalysts being explored, and supplied indications which helped clarify the reaction mechanism of the new polymerization catalysts:

> *"4. We were able to establish that the polymerization of ethylene to produce high molecular weight 'polyethylene' involves an entirely new reaction mechanism, and that the organoaluminum compounds represent merely auxiliary components useful in the production of the catalyst."*
>
> *"8. It is now conceivable that the new polymerization catalysts contain low-valent metal compounds of the heavy metals, the valencies of which are, in part, saturated by organic radicals."*

1.4.2

H. Martin, July 1954: Polypropylene

During the second week in July, Martin co-polymerized [176] ethylene and propylene by contacting the monomers with an aluminum trialkyl/titanium tetrachloride catalyst in hydrogenated diesel oil, thus reducing to one-sixth the amount of aluminum in relation to the amount of titanium, as compared to the January 7, 1954 [106] experiment. On July 13, 1954 [177], the turbulent polymerization that occurred upon introducing ethylene into the propylene-saturated reaction mixture, persuaded him to use propylene alone at a low pressure of between 6 and 12 bars under otherwise identical conditions. The reaction product obtained was a thick, black sludge. Of solid polypropylene 160 g was recovered. It was obvious that the raw product contained low molecular weight fractions. At a temperature of 135 °C, it was at least possible to draw filaments from the opaque molten mass.

The components of the catalyst were similar to those employed by Breil in December of 1953 [99]. Prior to the actual polymerization, the components reacted with each other for 2 h at room temperature in a solution and/or suspension medium of hydrogenated diesel oil. The amount of organoaluminum compound relative to the titanium tetrachloride was reduced to one-fifth and the propylene subsequently pressed on had a high degree of purity. (Contact with organoaluminum compound had rendered the propylene free from traces of oxygen and moisture). The polymerization reaction then took place in the presence of additional hydrocarbon diluting agents. Whether the relatively minor differences outlined with regard to the reaction procedure were responsible for the clearly positive results now obtained could not be determined with certainty.

When the experiment was repeated using aluminum triethyl as the aluminum component, the polypropylene yield was more than doubled [178], and with the use of diethylaluminum chloride almost tripled [179]. In the same manner, n-butene [180] and styrene [181] were converted to solid polymers.

The new findings constituted the basis of a further patent application [182], which was filed in the German Patent Office on August 3, 1954. Since the German Patent Law, at the time, did not provide for product protection, the new polypropylene was described in the specification only, without being included in the claims, on the one hand in terms of its characteristics:

> *"colorless, solid, plastic polypropylene, capable of being formed into transparent sheets and plates at temperatures above 140°C"*

and, on the other hand, in terms of the "fingerprint" of the infrared spectrum. The spectrum left no doubt that the product had a high crystalline content. Accordingly, the claims of this patent application were directed to a process for the polymerization and co-polymerization of olefins.

1.5
1952–1954 Polypropylene (Review)

1.5.1
Appraising the Historical Course of the Invention from a Year-2000 Vantage Point

The second half of the 20th century witnessed an incredible stimulation not only in polymer chemistry, but in particular in the chemistry of heterogeneous and homogeneous catalysis as a result of the inventions of Ziegler and his co-workers (Ziegler catalysts and their application). The hallmark of the enormously vast number of publications, biographies, and issued patents generated during that period is infinite their variety.

On December 10, 1963, His Majesty, the King of Sweden presented Karl Ziegler with the Nobel Prize for Chemistry [183], which he shared with Giulio Natta. In his Presentation Speech, Professor A. Fredga [184], Member of the Nobel Committee for Chemistry of The Royal Swedish Academy of Sciences, states, *inter alia*:

> *"However, Professor Ziegler has found entirely new methods of polymerization........ The combination of aluminum compounds with other metallic compounds gives Ziegler catalysts. These can be used to control polymerizations and to obtain molecular chains of the required length. However, many systematic experiments – and indeed some accidental findings - were necessary to reach this stage. Ziegler catalysts, now widely used, have simplified and rationalized polymerization processes, and have given us new and better synthetic materials.*
> *Your excellent work on organometallic compounds has unexpectedly led to new polymerization reactions and thus paved the way for new and highly useful industrial processes."*

The added remark "and indeed some accidental findings" calls for an explanation. During the past 40 years, the media in particular, have classified the invention of the Ziegler catalysts as a so-called "chance invention". This characterization was to convey to the layman that by no means did the researchers work towards the invention in a goal-oriented manner, but rather that they had accidentally stumbled across the results obtained while exploring a side-road. It was, however, easy to see that the goal of adding ethylene to the Al-C bond with any desired chain length had existed from the start, and since this was continually borne in mind by the researchers, a solution had been pursued in a methodical manner. Moreover, finding a solution was possible only for researchers who were dealing with the production and properties of metal alkyls. These two prerequisites imposed such narrow limitations on both the number of individuals and the location that the word "chance" could only have meaning if within these groupings, the interaction between metal alkyls and transition metal compounds was discovered. Admittedly, the point in time when this was made possible was propitious, since observations had been documented worldwide, even though coming from a different direction and were rather weak in their effect. After all, the discoveries made by Ziegler and his co-workers in this connection occurred within only a few short months and/or days as similar or identical results became available at Du Pont.

Professor Natta's contribution was acknowledged by Mr. Fredga, when he stated, *inter alia*:

> *"The individual molecules strung together to form polymers are often so built that the resulting chain exhibits small side groups or side-chains at certain points, generally one at every other carbon atom. But the picture is more complicated, since these side groups can be oriented either to the left or to the right. When their orientations are randomly distributed, the chain has a spatially irregular configuration. However, Professor Natta has found that certain types of Ziegler catalysts lead to stereoregular macromolecules, i.e. macromolecules with a spatially uniform structure. In such chains, all the side groups point to the right or to the left, these chains being called isotactic. How is this achieved when the microstructure of the catalyst is probably highly irregular? The secret is that the molecular environment of the metal atom, at which new units are stuck on to the chain as mentioned before, is so shaped that it permits only a definite orientation of the side groups.*
>
> *Isotactic polymers show very interesting characteritics. Thus, while ordinary hydrocarbon chains are zigzag-shaped, isotactic chains form helices with the side groups pointing outwards. Such polymers give rise to novel synthetic products such as fabrics which are light and strong at the same time, and ropes which float on the water, to mention only two examples.*
>
> *Nature synthesizes many stereoregular polymers, for example cellulose and rubber. This ability has so far been thought to be a*

KUNGLIGA SVENSKA
VETENSKAPSAKADEMIEN
HAR VID SIN SAMMANKOMST DEN 5 NOVEMBER 1963
I ENLIGHET MED FÖRESKRIFTERNA I DET AV
ALFRED
NOBEL

DEN 27 NOVEMBER 1895 UPPRÄTTADE TESTAMENTET BESLUTAT ATT DELA DET PRIS SOM DETTA ÅR BORTGIVES ÅT DEN SOM GJORT DEN VIKTIGASTE KEMISKA UPPTÄCKT ELLER FÖRBÄTTRING LIKA MELLAN

KARL ZIEGLER

OCH GIULIO NATTA FÖR DERAS UPPTÄCKTER INOM HÖGPOLYMERERNAS KEMI OCH TEKNOLOGI

STOCKHOLM DEN 10 DECEMBER 1963

Ragnar Granit

Fig. 1.4 The King of Sweden, Gustav VI. Adolf, presenting the Nobel Prize for Chemistry to Karl Ziegler on December 10, 1963; the Certificate is shown below

> *monopoly of Nature operating with biocatalysts known as enzymes. But now Professor Natta has broken this monopoly. Towards the end of his life, Alfred Nobel was thinking of the manufacture of artificial rubber. Since then, many rubber-like materials have been produced, but only the use of Ziegler catalysts enables us to synthesize a substance that is identical with natural rubber.*
>
> *You have succeeded in preparing by a new method macromolecules having a spatially regular structure.'*

The last three paragraphs will be discussed in greater detail at a later point. Such attributions as are made are only in part backed up by the historical events surrounding the invention. For now, suffice it to say that the initial polypropylene polymers produced by Natta on the one hand, and Martin on the other, were structurally practically identical. The infrared spectrum showed that both products were crystalline in nature. But it was Natta who had specifically recognized that the structure of these polymers was of regular character. Later on, through the development of crystalline $TiCl_3$ preparations, he and others were able to gradually increase the crystalline content of the polymers, a further indication of the highly selective mode of action of certain Ziegler catalysts (see p. 25).

Any appraisal and evaluation of an invention must take into account whatever patents, priorities and infringement actions are associated with it, because – as has been shown – verifiable facts, relevant documents and legal arguments in support of factual findings are often more illuminating in terms of the course and historical analysis of such inventions than are the occasional opinions espoused by some scientists.

Thirty years after the invention, Judge C.M. Wright of the US District Court at Wilmington, Delaware, after having inspected reams of evidentiary material, paid tribute to the invention itself [185]:

> *"Through application of Ziegler's discovery (catalyst), Natta at Montecatini, Martin at the Max-Planck-Institute, and subsequently, many others were able to produce crystalline polypropylene on a commercial scale."*

Two years later, on the issue of priority by Ziegler and his co-workers with respect to the process for the production of polypropylene, the US Court of Appeals for the Federal Circuit in Washington, D.C., held that [186]:

> *"It was Ziegler and his named coinventors who invented those catalysts and told Natta about them. It is here immaterial who was the first to use those catalysts to polymerize polypropylene."*

The Judges wanted to make it clear, that the infringer had literally used a patented Ziegler catalyst to polymerize propylene. Who was the first to use the catalyst for the polymerization of propylene was immaterial in this context. This, however, presupposed that both parties had demonstrated that propylene could be polymerized. More on this later.

Fig. 1.5 Giulio Natta

Aside from Natta himself (in his initial patent applications), both Professor Fredga, Stockholm, and the quoted judges in their decisions spoke of Ziegler catalysts, particularly in connection with the production of polypropylene and/or polyolefins, rather than referring to them as Ziegler–Natta catalysts, as was erroneously done later by a number of writers [187]. The scientific world had ignored the accurate terminology, and had done so for various reasons which will be discussed at an appropriate point.

The battle for priority rights is waged more often than not on a less than highly moral or ethical level, especially where international scientific information is communicated on a confidential basis, and is not treated as such. Depending on the commercial significance of the invention, a controversy may ensue, as it did in the present case, that would last over a whole generation.

The fact that Natta shed light on the crystalline structure and chain configuration of stereoregular polypropylene products with the aid of X-ray crystallography did not change the properties of the polymers, but it was definitely a scientifically important, and brilliant finding[14]. The subsequent illustration of the regular construction

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[14] Prior to this time C. Schildknecht, had for the first time, reported on the stereoisomer structures in crystalline polyvinylisobutylether [188]. Highlighting this publication P.J. Flory discussed the possibility of crystallinity because of the stereoregularity in polymers [189]. In 1953 J.D. Watson and F.H. Crick presented the double helix structure of DNA [190].

of the molecules with the aid of a helix structure was certainly of gradual importance in terms of the utility of the materials. The dependent invention of polypropylene at Milan and the independent invention at Mülheim can be explained only with the understanding that the teams at both locales started out with knowledge of the Ziegler catalysts. Giulio Natta and his co-workers had received prior information on the catalysts from Ziegler and his co-workers. Natta had reported his findings to Ziegler after the results on polypropylene had become available at the Max-Planck-Institute.

Martin had the benefit of two experiences, first his participation in the development of the Ziegler catalysts, and second the negative results obtained by Karl Ziegler and his co-workers in connection with their initial attempts to recover solid polypropylene. In the final analysis, any discussion about the fact that these negative results caused Ziegler to believe that high molecular weight polypropylene could not be produced in this manner would be irrelevant.

Neither statement made outside of court nor anything gleaned from actual court testimony proved helpful in arriving at a decision. Only the presentation of verifiable facts was sufficient to determine the issue of priority. Montecatini itself was well aware of this situation. G. Natta could not be acknowledged as an inventor of polypropylene without “derivation” being mentioned. It is this factual situation that the answer to the question of who invented polypropylene must ultimately be reduced to.

A memorandum [191] prepared in 1989 by attorney Sprung, knowledgeable with respect to the legal and particularly the patent position[15) involved, finally summarizes the situation. This memorandum was the basis for a number of important, profitable ramifications for Studiengesellschaft and the Max-Planck-Institute. Part of this has already previously been addressed.

Aside from the patent law aspect, which may be illustrated, through numerous oppositions and heated court battles, by way of this intermediate conclusion, the economic side of the picture also deserves consideration. Up to this day, polypropylene is produced on an industrial scale exclusively with the use of Ziegler catalysts. Even though, as time has passed, the catalysts have undergone some improvements and, based on the events described above appear under different names, nevertheless, the nature of the processes involved has remained the same: the combining of a transition metal component, particularly a titanium chloride-containing component, with an alkyl aluminum-containing species is as essential now as it was then.

Eight years earlier, in 1980/81, the controversy centering on the question of who was the first to actually make the “polypropylene” product irrespective of the method of its production, had been resolved by the highest patent appeal court in the United

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[15) Dr. Martin, in his experiments done in July of 1954, produced such solid, flexible polypropylene, and this experiment appears to represent the first independent invention of the solid, flexible polypropylene. From a scientific and practical standpoint, while Natta et al. may have run an experiment in Italy and obtained the solid, flexible polypropylene shortly prior to Dr Martin’s experiment, the Natta work was not independent, as it was based on and depended on information obtained from a team working at the Max-Planck-Institute under Professor Ziegler, of which Dr. Martin was a member.

States. Ziegler/Martin were not involved in these proceedings(16). Each of the litigants – Standard Oil of Indiana, Du Pont, Montecatini and Phillips Petroleum – had an opportunity to document its story, its argumentation, and its contribution towards the genesis of the invention, and thus its claim of priority.

All relevant and, in the court's view, crucial documents were taken into consideration [3]. These have also been addressed and/or cross-referenced in the outline of the early history. The outcome is being anticipated here to assist the reader at this juncture to properly integrate and appreciate any relevant connections and adversary proceedings involved.

The court accepted the evidence as showing that, among the litigating parties, it was Phillips Petroleum and/or the inventors J.P. Hogan and R.L. Banks, who were entitled to the benefit of the January 27, 1953 priority for solid, crystalline polypropylene and, thus, that they had recognized the new substance ahead of any of the other parties involved. However, not only did this particular polypropylene have other characteristics which rendered it unsuitable for commercial exploitation, but it was also produced with catalysts not suitable for use from a technical standpoint. The court expressly stated that Phillips' documentary evidence did not mention use as a thermoplastic material, but that only the application as a wax was described in certain relevant documents. The material(17) was brittle, but partially crystalline.

While W.N. Baxter, at Du Pont, had produced polypropylene with characteristics comparable to the products according to Hogan and Banks prior to August 19, 1954, i.e. prior to Ziegler/Martin, they had not recognized the product as such and had also failed to show utility. These same findings were applied to A. Zletz, of Standard Oil of Indiana, with a date of October 15, 1954. Natta and his co-workers, at Montecatini/ Montedison, were denied priority (see p. 2), i.e. Natta's claim to the invention of "polypropylene" was rejected. The priority date of Ziegler's patent application was August 3, 1954, prior to Baxter and Zletz, but clearly after Hogan and Banks.

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16) The conflict had started at an early stage in 1957, at a point in time when Ziegler was not ready to engage in substantial financial efforts. The priority patent application for polypropylene filed by Ziegler contained a product claim covering solid polypropylene. At least during the late 1980s a decision was made regarding this issue (see Section 5.9)

17) Memo A. Sprung, Lit 191: The product produced by Hogan and Banks was a brittle material, having no real commercial value or interest. Hogan and Banks' earlier work entitled Phillips to a broad patent claim covering solid polypropylene with a substantial crystalline portion.

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1 494 Fed. Supplement, p. 374, 1981: Interference 89 634: Decision Board of Patent Interferences Nov. 29, 1971; Montecatini Edison, US P 3,715,344 (SN 514 099), G. Natta, P. Pino, G. Mazzanti, priority June 08, 1954/July 27, 1954, issued Feb. 06,1973.

2 In the structure of the polymer chain uniform repeating propylene-sequences (head – tail polymerization or 1,2-addition).

3 494 Fed. Supplement, p. 370–461, 1981:
Civil Action No. 4319, District Court of Delaware – Decision Jan. 11, 1980 Standard Oil of Indiana, Phillips Petroleum Co., E.I. Du Pont de Nemour & Co. vs. Montecatini S. p.A. et al, confirmed by the Court of Appeal, 3rd Circuit, 1981.

4 Phillips Petroleum Company, USA, US P 4,376,851 (SN 558,530, Jan. 11, 1956, Continuation-in-part of SN 333,576, Jan. 27, 1953, abandoned, and SN 476,306, Dec. 20, 1954, abandoned), J.P. Hogan, R.L. Banks, priority Jan. 27, 1953.

5 494 Fed. Supplement, p. 398, 1981: Civil Action No. 4319, District Court of Delaware, Decision Jan. 11, 1980, Standard Oil of Indiana, Phillips Petroleum Co., E.I. Du Pont de Nemour & Co. vs. Montecatini S. p.A. et al, confirmed by the Court of Appeal, 3rd Circuit, 1981. Molybdenum oxide was reduced with hydrogen, 850 °F (455 °C) at 400 psi pressure, adding xylene the polymerization was tried (propylene pressure 420 psi (ca. 30 atm), temperature 302 °F (160 °C).

6 494 Fed. Supplement, p. 398, 1981: Civil Action No. 4319, District Court of Delaware, Decision Jan. 11, 1980. Exp. Nr. EP-34 with the same catalyst von A. Zletz, 0.7 g solid polymers , 0.1 g of that insoluble in xylene, from Carmody described as ‘rubbery, non-tacky‘.

7 494 Fed. Supplement, p. 400, 1981: Civil Action No. 4319, District Court of Delaware, Decision Jan. 11, 1980. IR- (micron 8.63, 9.07, 10.05, 10.29, 11.12, 11.85, 12.35) (Affidavit G. Natta of Sep.13, 1956, unknown to the parties, IR of crystalline polypropylene: micron 10.02, 10.28, 11.89, as well as strong bands at 9.05, 11.12, 12.39).

8 W. Heinen, **1959**, *J. Polymer Sci.*, 38, 545 ratio of 1171 cm^{-1} to 846 cm^{-1}. (micron 8,84/11,82).

9 J.P. Luongo, **1960**, *J. Appl. Pol. Sci.* III/9, 302,
Fig. 1 ratio of 974 cm^{-1} to 995 cm^{-1}. (micron 10.26/10.05).

10 494 Fed. Supplement, p. 398, 1981: Civil Action No. 4319, District Court of Delaware, Decision Jan. 11, 1980. EP-35, with the same catalyst, yield 3.83 g.

11 494 Fed. Supplement, p. 399, 1981: Civil Action No. 4319, District Court of Delaware - Decision Jan. 11, 1980. Reduction at 805 °F (429 °C), pressure 200 and 500 psi, polymerization at propylene pressure of 160 psi, room temperature, 27 days (experiment P-1) and 3000–600 psi, temperature 205–260 °F (91–127 °C) in xylene (experiment P-9); yield 7 g resp. 4.6 g in xylene-insoluble products. In product exp. P-1 and P-9 crystallinity, IR absorption (Apr. 30, 1953) 10.03 and 11.85 resp. 10.03 and 10.27 (Luongo).

12 Standard Oil of Indiana, USA, US P 2,692,257 (SN 223,641), A. Zletz, priority Apr. 28, 1951 – “Ethylene Polymerization ....”.

13 Standard Oil of Indiana, USA, US P 2,780,617 (SN 288,501), A. Zletz, priority Apr. 28, 1951 – Ethylene polymerization with conditioned molybdenum catalyst.

14 Standard Oil of Indiana, USA, US P 2,691,647, (SN 324,610), E. Field and M. Feller, priority Dec. 06, 1952 – “Conversion of ethylene and/or propylene to solid polymers ...”.

15 Standard Oil of Indiana, USA, US P 2,731,453 (SN 324,608), E. Field and M. Feller, priority Dec. 06, 1952 – “Conversion of ethylene and propylene to solid polymers ...”.

16 Repetition of experiments von Field and Feller:
1. Declaration Martin, Nov. 19, 1987
Field and Feller, US P 2,691,647, Ex. 21.
Cobaltmolybdate US P 2,393,288 (p. 2, right col., line 3–22), no solid polypropylene.
2. Declaration Martin, Dec. 22, 1988
Field and Feller US P 2,731,453, Ex. 7 (col. 13, line 71–75, – col. 14, line 1–7): (see chapter V, [284]).
1. Catalyst US P 2,393,288, A.C. Byrns (p. 2, left col., line 62–75 and right col., line 1–2 and 25–59) formed from cobaltnitrate and ammoniummolybdate, 9 weight.-% MoO3.
2. Catalyst US P 2,320,147, E.I. Layng (p. 2, left col., line 54–73) MoO3 on Al_2O3, 10 weight-% MoO3.
According to description Ex. 7, US P 2,731,453 no solid polymer in the first case and 16 mg of a rubbery solid polymer was isolated. CH2/CH3 > 4 : 1, IR-Spectrum: no crystallinity, atactic polymers, melting range 119–130 °C.
3. Declaration Martin, March 01, 1989
US P 2,731,453 and 2,691,647 Field et al.
This declaration was related to the decision in Civil Action 4319, District Court of Delaware. There the two patent rights were not considered because Standard Oil of Indiana did not use the filing dates for a claim of priority.
Also G. Natta tried to repeat Field and Feller. In a declaration, dated Sep.13, 1956, Natta confirmed no solid propylene only hydrocarbon oils were formed repeating Ex. 21, using five different catalysts. Changing the preparation of the catalyst, not described in the 647 patent Natta received 0.055 g of a waxy polymer product, melting point 135 °C, molecular weight 13,000. The product was totally soluble in boiling heptane, CH2/CH3 = 2 : 1.0.

17 494 Fed. Supplement, p. 411, 1981: Civil Action No. 4319, District Court of Delaware, Decision Jan. 11, 1980. E. Francis: Exp. Nr. 4721–16 (Okt. 9, 1951) 5.5 h at 88 °C and nearly 40 bar pressure, isopentane as solvent.

18 494 Fed. Supplement, p. 411, 1981: Civil Action No. 4319, District Court of Delaware, Decision Jan. 11, 1980. Hogan, Banks and Francis: Exp. 4721–26, Nov.19, 1951, silica-aluminum oxide-carrier, containing 4 weight-% chromium oxide, was heated and activated at 390 °C. Activation means that by treating the catalyst granules with dry air 38 h, 82 °C, 35 bar.

19 494 Fed. Supplement, p. 412, 1981: Civil Action No. 4319, District Court of Delaware, Decision Jan. 11, 1980. Exp. 4958–13, -15, -18; Feb. 1952, 15 h at 90–100 °C, 30 bar propylene pressure. The product PO-133, melting point 113 °C, IR-Absorption at 10.03 and 10.27 or 11.85 micron. From the fact that the material was insoluble in pentane and the possibility to conduct measurements of viscosity i.e. the solubility in any solvent it was concluded that the product was not cross-linked but crystalline.

20 494 Fed. Supplement, p. 418, 1981: Civil Action No. 4319, District Court of Delaware, Decision Jan. 11, 1980.

21 494 Fed. Supplement, p. 429 ff, 1981: Civil Action No. 4319, District Court of Delaware, Decision Jan. 11, 1980.

22 After treating the raw product with toluene or benzene the concentrated solution was placed in a cool mixture of acetone and methanol. The precipitated product was filtered and stepwise extracted with hot acetone, ether and boiling heptane. The residue was analyzed as described above.

23 494 Fed. Supplement, p. 429, 1981: Civil Action No. 4319, District Court of Delaware, Decision Jan. 11, 1980. Catalyst on carrier (87.3 % silicon oxide, 12.4 % aluminum). The carrier was impregnated with chromium nitrate, activated at 480–500 °C with dry air. It contained 2.77 % chromium, polymerizations: in heptane at 88–90 °C, pressure 20–32 bar, 2 h. Polypropylene-product was sepa-

rated from the catalyst by xylene at 120 or 130 °C and precipitated with acetone/methanol. The product was insoluble in heptane I.V. 5.70, melting point 167 °C.

24 Karl Ziegler, German P 973 626, K. Ziegler, H. Breil, E. Holzkamp, H. Martin, priority Nov.17, 1953 – Process for the production of high molecular poylethylenes.

25 Ziegler to Orsoni, Montecatini, Jan. 06, 1954 -
Farbwerke Höchst AG, Horn, Scherer: Notice (Memo) visit at MPI Nov. 25, 1953 – Ruhrchemie AG: Program for discussion with Prof. Ziegler March 02, 1954.

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27 E.I. Du Pont, de Nemours and Co, USA, US P 2,905,645 (SN 450 243), Anderson et al, priority Aug.16.1954 – Polymerization catalysts.

28 E.I. Du Pont, de Nemours and Co, USA, US P 3,541,074 (SN 450 244), Anderson et al, priority Aug.16.1954 – Olefin polymerization catalysts comprising divalent titanium and process for polymerization of ethylene therewith.

29 E.I. Du Pont, de Nemours and Co, USA, US P 4,371,680 (SN 451 064), W.N. Baxter, N.G. Merckling, I.M. Robinson, G.S. Stamatoff, priority Aug.19, 1954 – Polymer Composition.

30 Badische Anilin and Soda-Fabrik, German P 874 215, M. Fischer, priority Dec.18, 1943 – Process for the production of solid polymers from ethylene or ethylene-rich gases.

31 US District Court of Delaware, Civil Action 3952, Studiengesellschaft Kohle mbH vs. Dart Industries, Plaintiff's Post-Trial Brief, Mid 1982, p. 38.

32 549 Fed. Supplement, p. 734: Studiengesellschaft Kohle mbH vs. Dart, C.A. 3952 – Decision Okt. 05, 1982.
Lab journal Anderson, Du Pont, Feb. 11.1954.

33 549 Fed. Supplement, p. 734: Studiengesellschaft Kohle mbH vs. Dart,
C.A. 3952 - Du Pont April 1954 'Grignard-compounds" Dart Decision Okt. 5, 1982.

34 Agreements up to Mid 1954:
Montecatini Jan. 21,1953,
Hoechst AG Nov. 1952,
Ruhrchemie Dec. 23, 1953, (draft).

35 Lab journal Hyson, Du Pont, July 29–31, 1954 – Organoaluminum-compounds and polymerization of ethylene.

36 Lab journal Hyson, Du Pont, Aug.11, 1954, Suggestion also to polymerize propylene.

37 494 Fed. Supplement, p. 390–397, 1981:
Civil Action No. 4319, District Court of Delaware, Decision Jan. 11, 1980. Du Pont Ex. HPL 4427–86, identical with 4460–41; 6 g TiCl4, 40 ml PhenylMgBr, 200 ml cyclohexane, filtered and dried. Polymerization with 3 g of this catalysts, 100 ml cyclohexane, 50 g propylene, 30 °C. 500 mg polypropylene were isolated.

38 494 Fed. Supplement, p. 370 ff, 1981: Civil Action No. 4319, District Court of Delaware, Standard Oil of Indiana, Phillips Petroleum Co., Du Pont and Montedison- Decision Jan. 11, 1980.

39 Patent Interference Nr. 89,634, Nov. 29, 1971.

40 K. Ziegler et al, Italian Patent Applications Nr. 6850 and 6851 June 21, 1951.

41 Orsoni to Magri Nov. 27, 1953.

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43 Lab journal Holzkamp, Exp. 83, May 09, 1953.

44 Lab journal Holzkamp, Exp. 84, May 12, 1953.

45 Lab journal H. Martin, Exp. 1, June/July 1953.

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55 Lab journal H. Breil, Exp. A 18, Sep. 22, 1953, p. 214–215.

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60 Lab journal H. Breil, Exp. A 29, Okt. 08, 1953, p. 237–238.

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71 Magri, Chini, Crespi to Orsoni, June 15, 1953.

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80 Magri, Chini, Crespi to Orsoni, July 19, 1953.

81 Magri to Ballabio, Nov. 15, 1953.

82 Natta to Orsoni, July 09, 1953.

83 Karl Ziegler, Z 3799 IVb/39 c (priority Nov. 17, 1953, published Okt. 04, 1956, issued as German P 973 626, Jan.16.1960) inventor: K. Ziegler, H. Breil, E. Holzkamp, H. Martin.

84 Lab journal H. Breil, Exp. A 69, Nov. 27, 1953 (p. 305–306).

85 Lab journal H. Martin, Exp. 1, Dec. 01, 1953.

86 Lab journal H. Martin, Exp. 2, Dec. 02, 1953.

87 Lab journal H. Martin, Exp. 8, Dec. 12. 1953, Weck Glaswerke GmbH, Bochum.

88 Karl Ziegler, Z 3862 IVb/39 c (priority Dec. 15, 53, published March 21, 1957, issued as German P 1 004 810, Aug. 05, 1960) inventor: K. Ziegler, H. Breil, H. Martin, E. Holzkamp.

89 Lab journal H. Martin, Exp. 11, Dec. 16/17, 1953.

90 Lab journal H. Martin, Exp. 12.

91 Lab journal H. Martin, Exp. 13, Dec. 19, 1953.

92 Lab journal H. Martin, Exp. 14.

93 Lab journal H. Martin, Exp. 15.

94 Lab journal H. Martin, Exp. 16, Jan. 04, 1954.

95 Ziegler to von Kreisler, Jan. 07, 1954.

96 Lab journal H. Breil, Exp. 41, Nov. 30, 1953 (p. 309–310).

97 Lab journal H. Breil, Exp. 42, Dec. 01, 1953 (p. 313–314).

98 Lab journal H. Breil, Exp. 45, Dec. 08, 1953 (p. 318–323).

99 Lab journal H. Breil, Exp. A 75, Dec. 16, 1953 (p. 329–330):
200 cm3 iron autoclave, 50 cm3 aluminum alkyl (average chain length C_8),
1.5 cm3 TiCl4, 68 g propene, 'At room temperature (T 20 °C, p 20 atm) during shaking no reaction and no

self heating‘. Then, the temperature from outside increased to 45 °C, next day up to 95 °C. Thereby the pressure increase to 65 atm. ‘No reaction‘ can be determined, thereafter 31 g propene released and without opening the pressure vessel (25 °C, 14 atm residual pressure) 38 g ethylene pressed into the vessel. The autoclave now contained besides 38 g ethylene 37 g residual propene. After 4 days the autoclave was opened, from which 5 g residual propene were isolated. The entrée in the lab journal ‘ 86.5% of the original C3 H6 has reacted, 100% of the C2 H4 ‘. The solid product was washed and dried: ‘51 g PE‘.

100 Studiengesellschaft Kohle mbH vs. Dart Industries, US District Court of Delaware, Civil Action 3952, Deposition Breil, Jan. 22, 1982, Düsseldorf, p. 765 ff.

101 Lab journal H. Martin/F. Fürbach, Exp. 1000, June 21, 1967.

102 A. Schoen Nov. 10, 1953, and Orsoni to Ziegler, Nov. 27, 1953.

103 Orsoni to Ziegler, Dec. 17, 1953.

104 Ziegler to Orsoni, Jan. 06, 1954.

105 Ziegler to Orsoni, Jan. 25, 1954.

106 Lab journal H. Martin, Exp. 17, Jan. 07, 1954.

107 Lab journal H. Martin, Exp. 18, Jan. 09, 1954.

108 Lab journal H. Martin, Exp. 22–24, Jan. 18–21, 1954.

109 Lab journal H. Martin, Exp. 19, Jan. 12, 1954.

110 Lab journal H. Breil, Exp. A 86, Jan. 21, 1954 (pressure experiment).

111 Lab journal H. Martin, Exp. 29, Feb. 01, 1954 (normal pressure).

112 Lab journal H. Martin, Exp. 32, Feb. 18, 1954.

113 Lab journal H. Martin, Exp. 33, Mar. 01, 1954.

114 Lab journal H. Martin, Exp. 36, Mar. 22, 1954.

115 Lab journal H. Martin, Exp. 42, Apr. 07, 1954.

116 Original X-ray Doktorthesis H. Breil, Fig. 7–10.

117 F. Böck and L. Moser **1912**, *Monatsh.* 33, 1407/29; **1913**, 34 1825.

118 K. H. Müller, Dissertation Th. Aachen 1958.

119 Lab journal H. Martin, Exp. 45, Apr. 27, 1954 and Exp. 46, Apr. 30, 1954.

120 Lab journal H. Breil, Exp. 41, Nov. 30, 1953, Exp. 45, Dec. 8, 1953 and Exp. A 70, Nov. 30, 1953.

121 Lab journal H. Breil, Exp. A 77, Jan. 05, 1954.

122 Lab journal H. Breil, Exp. A 79, Jan. 07, 1954.

123 Lab journal H. Breil, Exp. A 96, Feb. 02, 1954.

124 Lab journal H. Breil, Exp. A 99, Feb. 08, 1954.

125 Lab journal H. Breil, Exp. A 103, Feb. 18, 1954.

126 Lab journal H. Breil, Exp. 92, Jan. 27, 1954, Exp. A 106, Mar.2, 1954.

127 Lab journal H. Breil, Exp. A 113, Mar. 18, 1954.

128 Lab journal H. Breil, Exp. A 97, Feb. 04, 1954.

129 Lab journal H. Breil, Exp. A 80, Jan. 11, 1954.

130 Lab journal H. Breil, Exp. A 81, Jan. 11, 1954 (100–200 bar pressure).

131 Lab journal H. Breil, Exp. A 82, Jan. 11, 1954 (100–200 bar pressure).

132 Lab journal H. Breil, Exp. A 101, Feb. 11, 1954.

133 Lab journal H. Breil, Exp. A 90, Jan. 26, 1954.

134 Lab journal H. Breil, Exp. A 91, Jan. 26, 1954.

135 Lab journal H. Breil, Exp. A 95, Feb. 01, 1954.

136 BASF, German P 874 215, Max Fischer (priority Dec. 18, 1943, published June 19, 1952, issued Mar. 12, 1953).

137 Dissertation H. Breil, June 23, 1955.

138 A. V. Grosse, J. M. Mavity **1940**, *J. Org. Chem.* 5, 112 and H. Martin, H. Bretinger, F. Fürbach **1985**, *Angew. Chemie* 97 (4), 323–324.

139 H. Martin, H. Bretinger **1985**, *Z. Naturforsch.* 40 b, 182–186.

140 H. Martin, H. Bretinger **1990**, *Z. Naturforsch.* 46 b, 615–620.

141 Karl Ziegler, Z 3941 IVb/39 c (priority Jan. 19, 1954, published July 18, 1957, issued as German P 1 012 460, Aug. 05, 1960) inventor: K. Ziegler, H. Breil, E. Holzkamp, H. Martin.

142 Karl Ziegler, Z 3942 IVb/39 c (priority Jan. 19, 1954, published Sep. 19, 1957, issued as German P 1 016 022, Dec. 28, 1960) inventor: K. Ziegler, H. Breil, E. Holzkamp, H. Martin.

143 Ziegler to Orsoni, Montecatini, Feb. 12, 1954.

144 Deposition Chini, March 1970, p. 1193.

145 US-Interference 99 478 Ziegler/Natta, Zieglers “Main Brief”, p. 14.

146 Deposition Chini, March 1970, p. 1196.

147 Consolidated Civil Action No. 3343, March 09, 1970, Deposition of Natta, pp. 85, 86.

148 Consolidated Civil Action No. 3343, March 09, 1970, Deposition of Pino, pp. 601, 602.

149 Agreement Mar. 09, 1954.

150 US-Interference 99 478 Ziegler/Natta, Zieglers Reply Brief, p. 25, (Document ZX 137, identified as A 0059 - A 0061) Remarks of Montecatini besides the memo, dated Mar. 9, 1954, discussion: ZX 130 and ZX 116 (M 4517): Here it is stated, that after the visit of Ziegler, other olefins such as propylene and sterene were then tried.

151 Deposition Chini 1969, p. 10 ff, and 1970, p. 1221–1232, Chini lab journal p. 42: 8.4 g $TiCl_4$, 20.4 g $AlEt_3$, mol ratio 1 Ti : 4 Al, in petrol ether, propylene at first normal pressure – then up to 12 atm, 17–75 °C, 1.25 h, yield: 3.5 g solid polymeres, thereafter extracted with ether.

152 Deposition Chini 1970, p. 1230.

153 Consolidated Civil Action No. 3343, March 09, 1970, Deposition of Natta, p. 80.

154 Consolidated Civil Action No. 3343, March 09, 1970, Deposition of Mazzanti, pp. 1475, 1478.

155 Consolidated Civil Action No. 3343, March 25–26, 1970, Deposition of Mazzanti, pp. 1631–1632, 1634–1635 and 1639–1641.

156 Consolidated Civil Action No. 3343, March 16–18, 1970, Deposition of Pino, p. 631.

157 Consolidated Civil Action No. 3343, March 25–26,1970, Deposition of Mazzanti, pp. 1649, 1650.

158 Zeugenaussage Chini March 24, 1970, p. 1272–1294
2. Exp.: catalyst $TiCl_4 + AlEt_3$ 1 : 10, room temperature, and pressure. The product was extracted: 7% with acetone, 40% diethylether, 28% heptane and 25% heptane-insoluble.
3. Exp.: 50–60 °C and pressure, yield 193 g.

159 US-Interference 99 478 Ziegler/Natta, Zieglers “Main Brief”, p. 17.

160 US-Interference No. 99,478 - Ziegler's “Reply Brief”, ZX 166, p. 29 Montecatini – internal memo.

161 US-Interference No. 96,101, Deposition Chini 1969, p. 72 and 171, 1970, p. 1233.

162 US-Interference 99,478, Brief “Final Hearing”, Natta et al, p. 31 (ZX 164, p. 615, ZX 167, p. 755–756).

163 US-Interference 99,478, Brief “Final Hearing”, Natta et al, p. 32 (ZX 166).

164 Deposition Ziegler, Duisburg, Dec. 09, 1969, p. 140.

165 Italian Patent Application 24.227/54, Montecatini, filed June 08, 1954, issued as No. 535 712, Nov. 17, 1955, inventor: G. Natta.

166 Italian Patent Application 24.227/54, Montecatini, filed June 08, 1954, inventor: G. Natta, see specifically p. 2, line 6 and p. 5, claim 6.

167 Italian Patent Application 25.109/54, Montecatini, filed July 27, 1954, issued as No. 537 425, Dec. 28, 1955.

168 Consolidated Civil Action No. 3343, March 9, 1970, Deposition of Natta, p. 264.

169 Consolidated Civil Action No. 3343, March 25–26, 1970, Deposition of Mazzanti, p. 1658–1659.

170 Orsoni to Ziegler, July 30, 1954.

171 Natta to Ziegler, Aug. 04, 1954.

172 Ziegler to Orsoni, July 21, 1954.

173 Interference No. 99,478 – Ziegler's “Main Brief”, p. 19
(ZX 182; ZR. 149–50; see also ZX 183, ZR. 150–51).

174 Lab journal H. Martin, May 10 - July 06, 1954: catalyst: TiCl4 + AlR3: Exp.-Nr. 60, 62, 64, 65, 67–71, 75–77, 81, 83, 84.
Catalyst: TiCl4 + Et2 AlCl: Exp. -Nr. 55, 72, 78–80, 85, 86.

Catalyst: other metal compounds + AlR3: Exp.-Nr. 52, 56, 57, 63.

175 Diplomathesis H. Breil University Bonn, June 28, 1954, p. 24.

176 Lab journal H. Martin, Exp. 87, July 09, 1954.

177 Lab journal H. Martin, Exp. 88, July 13, 1954.

178 Lab journal H. Martin, Exp. 93, July 21, 1954.

179 Lab journal H. Martin, Exp. 101, July 30, 1954.

180 Lab journal H. Martin, Exp. 94, July 23,1954.

181 Lab journal H. Martin, Exp. 97, July 27, 1954.

182 Karl Ziegler, Z 4348 39 b 4 (priority Aug. 03, 1954, published Dec. 28, 1967, issued as German P 1 257 430, Dec. 17, 1973) inventor: K. Ziegler, H. Breil, H. Martin, E. Holzkamp.

183 Document Nobel Prize Dec. 10,1963.

184 Nobel Lectures Chemistry 1963–1970.

185 549 Federal Supplement, United States District Court, D. Delaware, Studiengesellschaft Kohle mbH vs. Dart Industries, Inc., Civ. A. No. 3952, Oct. 05, 1982, p. 740, right col.

186 726 Federal Reporter, 2 d Series, United States Court of Appeals, Federal Circuit, Studiengesellschaft Kohle mbH vs. Dart Industries, Inc., No. 83–591, Jan. 19, 1984, p. 728.

187 Polyolefins: Structure and Properties by Herman v. Boenig, 1966, p. 120.

188 C.E. Shildknecht et al. **1948**, *Ind. Eng. Chem.* 40, 2104.

189 P J. Flory **1953**, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, p. 53, 237–238.

190 J.D. Watson, F.H.C. Crick *Nature* 1953, Vol. 171, p. 737.

191 Arnold Sprung: Memo June 17, 1989 US Patent Application Serial No. 03/514,068 of June 08, 1955.