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POLYOLEFINS 11
Processes, Products, Processing

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FEBRUARY 14–15, 1978
GALLERIA PLAZA HOTEL
HOUSTON, TEXAS

SOCIETY OF PLASTICS ENGINEERS, INC. • **SOUTH TEXAS SECTION**

POLYOLEFINS II
Processes, Products, Processing

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POLYOLEFIN PATENTS 1977

Marion Johnson PE

Prepared for Society of Plastics Engineers Regional Technical Meeting, Polyolefins, February 14, 15, 1978, Houston, Texas.

Slide 1 The first topic for the morning is Polyolefin Patents. The subject is much too broad for twenty minutes, so I shall merely hit the high spots as I see them, and leave a few minutes at the end for questions.

What is a Patent?

A patent is a grant, by the U. S. Government, to an individual inventor or group of inventors, of "the right to exclude others from making, using, or selling the invention" (1) for a period of seventeen years. A patent application is filed, researched, reviewed, and compared, until the originality of the invention is determined by a board of patent examiners, who may then grant a patent on the application. The seventeen year "right to exclude" commences when the patent is issued, usually one or more years after the invention is made. A patent may be sold, assigned, or licensed by the inventor, as a regular article of commerce having value. Most companies bind their technical employees in technology assignment agreements in which the employee agrees to assign to the employer any patents which may result from his work in the employers' business. Thus, in my later discussion, I may refer to a Phillips patent, meaning a patent which has been assigned to Phillips by the inventor.

Why get a Patent?

Polymerization process patents are sought for many reasons, but the primary one is the protection afforded to cover research expenses.

The protection is often a mixed bag, however, because the application for patent requires revelation of trade secrets; the patent file is opened after the patent is granted.

Who uses Patents?

Patents are used by researchers, such as the writer, to gain insight into the direction of research by a particular company in a particular field of technology. Use of patent literature is an open and honest way of obtaining industrial intelligence, and often enables a business operation to assesss its own competitive situation in comparison with other businesses in the same field of endeavor. Most businesses actively avoid any hint of patent infringement, and thus use the patent literature to aid in the direction of research into areas of endeavor not covered by patents held by another firm. Patent literature may be helpful in choosing a process to license when a business desires to enter a new field without developing its own technology in the field. Occasionally, there is a head to head confrontation over technology and patents, such as in polypropylene now, but that is not usual. As an example, new entrants into high density polyethylene have traditionally chosen between licenses of Phillips, or Ziegler- Natta, technology. The polyolefin technology universe is rapidly expanding right now, and the trend is now clearly toward researching for ways around patents, while at the same time finding new innovations to eliminate costly processing steps.

Before I start the technical discussion, I want to mention a good article in the November 7, 1977, issue of Chemical Engineering, entitled "Hints on Reading Patents" (2). I should also mention that here in

Houston, we have all the Patent Gazettes (abstracts), from the beginning, in the Houston Public Library, and microfilm copies of all U.S. Patents since 1967 at Rice University Library. Rice also, being an official depository, has automated search capability, which enables them to list all patents issued in a particular classification. These libraries are very good.

So here we go into technology. For those of you who are not polymer process oriented, I will spend a few minutes on the three major processes now in use, and then get into innovations which I see as being significant improvements in cost or quality of product. The three are:

High Pressure Process

Low Pressure Solution and Slurry

Low Pressure Vapor Phase

Slide 2 Of the processes, the oldest and best known is the high pressure process for making low density polyethylene. Simplified, the process is comprised of:

a compression step - ethylene, or mixtures of ethylene and co-monomers, such as propylene, vinyl acetate, acrylic acid, etc. are compressed to pressures in the range of 2000-5000 ATU.

a polymerization step - in the presence of free oxygen, or oxygen releasing catalysts, the monomers polymerize to about 20% solids, in single-pass tubular reactors as shown, or in stirred autoclave reactors.

a degassing step - the monomer/polymer mixture is vented down to around 100 ATU, the polymer separated, and further processed in degassing extruders.

a compounding step - raw polymer is mixed with additives and modifiers, in hot melt compounders, to make a variety of products.

The technology practiced in the process is basically forty years old. Recent innovations have been mainly new catalysts, new co-monomers, and new mechanical gadgets to reduce operating cost. The cost to produce polyethylene by this method is relatively high, compared to the newer low pressure processes, but the products produced have had properties which, until recently, could not be matched by products from the low pressure processes.

Slide 3 The low pressure polyolefin processes, in use today, are of two basic types, each capable of producing a variety of polyolefins, principally polyethylene and polypropylene. The Rexene polypropylene process depicted on the slide, is close enough for description of both polyethylene and propylene slurry processes. Simplified, the process consists of:

a catalyst preparation step - solid or liquid catalysts are prepared under anhydrous conditions for introduction into the process. The solid catalysts are: for example,

chrome-silica
nickel-molybdena

The liquid catalysts are: for example,

aluminum alkyl - organo titanium

a reaction step - mixtures of catalysts, olefins, and diluents, are reacted at temperatures gennerally less than 100°C, at pressures generally less than 50 ATU, to form polymer slurry, of around 20%

solids.

a recovery step - concentrated polymer slurry is removed from the reactor, stripped of diluent, washed to remove residual catalyst, and washed to remove undesirable polymer fractions, such as low-molecular weight, or atactic (non-crystalline) polymer.

a compounding step - polymer powder, after washing, is mixed with additives, modifiers, and hot compounded into finished grades of products.

Slide 4 The second low pressure polyolefin process practiced today is the vapor phase process, in commercial use by Union Carbide, Naptha-chemie, and B.A.S.F. The processes can be basically represented by the Carbide patent drawing (5). The process includes:

a catalyst preparation step - liquid or solid catalysts are prepared in anhydrous conditions for introduction into the process.

a reaction step - olefins and catalyst are injected into a fluid bed reactor, where they react to form fluidized granules of polyolefin powder, at temperatures generally less than 100°C, and pressures generally less than 50 ATU.

an auxiliary cooling system - olefins are recycled through a cooling loop to remove heat of polymerization, before being returned to the fluid bed.

a product recovery step - polymer powders are removed from the fluidized bed by a pressure locking device, and then treated to remove unreacted olefins, undesirable polymer fractions, and residual catalyst.

a compounding step - polymer granules may be sold to customers as produced, or after hot melt compounding with additives.

Since there is a lot of excitement about the Carbide process for vapor phase polymerization of low and high density polyethylene, this process will be discussed first.

Research in polymerization of olefins has taken two generally different directions, parallel in their effect in the industry. The polymerization has often produced :

a fraction of low molecular weight or non-crystalline product

a fraction of residue containing residual catalyst.

The search to eliminate these expensive by-products has resulted in development of catalysts :

to produce more stereospecific polymers

to produce more total polymer per unit of catalyst.

The developments have resulted in catalysts capable of polymerizing olefins under conditions in which the polymers were hard, and non-tacky, despite varying degrees of crystallinity and various levels of molecular weight. The new catalysts, thus, made vapor phase polymerization possible.

The Union Carbide process was fairly completely described in the Johnson patent (5), of 1972. The process configuration, some operating conditions, and a catalyst configuration were revealed in sixty one examples and twenty nine claims. The patent teaches the

Slide 5 use of substitute bis(cyclopentadienyl)chromium II, as shown, with substituted silates, as shown, impregnated onto silica support, activated by calcining, and fed into the reactor. Reactions were reported to be all at less than 100°C, and less than 50 Psig, yielding polymer products generally fitting properties of high density polyethylene. The patent claims polymer yield of 800,000 per unit catalyst. The silane treatment of the catalyst enables incorporation of comonomers into the polymer structure for physical property modification.

Slde 5 The second Johnson patent (6), in 1972, discloses the utility of hindered chromate esters , such as the di-2-alkyl bornyl chromate ester, to spread the chrome onto the support, and discloses the after treatment of catalyst with alkylaluminum, alkylboron, or aluminum alkoxides to produce broad molecular weight distribution. Reactions were at less than 100°C, and less than 100 psi.

The Union Carbide process for producing low density polyethylene by vapor phase polymerization was unveiled in the Levine patent (7), in March 1977. The process depends upon a catalyst which will allow incorporation of sufficient quantities of 1-olefin comonomers to achieve significant levels of branching without the production of undesirable levels of hexane extractable low molecular weight polymer.

Slide 7 Old data by Marks (8), on Phillips product, correlated the quantities of methyl branches (from propylene), or ethyl branches (from butene), required to reduce crystallinity by 20%.

According to the Levine patent (7), a microspheroidal catalyst support (Grace 952) is impregnated with an aqueous solution of chromium dioxide; drained and reslurried in isopentane; treated with tetraisopropyl titanate while in isopentane slurry; allowed to dry by evaporation of isopentane; mixed with diammonium hexafluoro silicon, and then activated in the absence of air at varying temperatures up to 800°F. The patent then reports fluid bed trials to polymerize ethylene with 1-butene comonomer to produce a variety of low density (0.91-0.94) polyolefins at reasonable yields of up to 15,000 per unit catalyst, with hexane solubles being typically less than 5%. Ash content of the polymer varied a lot, but averaged around 100 ppm.

Union Carbide has not revealed (or I have not found) important technology relating to the gadgetry for introducing the solid catalyst into the system, for removal of polymer from the system, or for system scavenging of catalyst poisons to make the catalyst system described as productive as reported. B.A.S.F. and Naphthachemie are reportedly using facilities which are similar to the Union Carbide process, and I will make brief mention of them in the following patent review.

Lists of U. S. Patents, applying to polyolefin process, have been prepared for the period of 1977 until this writing (mid December) In general summary, we find:

in the supported catalysts for olefin polymerization the most desirable factors are -

- very large surface area per unit weight of carrier
- fine interstitial membranes between carrier pores
- thorough dispersion of promoter onto carrier
- use of combinations of activators for specific properties

in the unsupported catalysts for olefin polymerization the most desirable factors are

- very pure materials
- use of combinations of activators
- more or less precipitate to achieve stereoregularity
- ease of removal of spent catalyst

Each attribute has been addressed in various ways, and the tables list patents with comments.

Note the chrome patents where titanium or some other metal has cropped up. Phillips has even precipitated titanium into its support gel structure.

Note the predominance of large molecules used in impregnating metals onto catalyst supports. Efficiency.

Note the use of non-metal deposits to impart specific properties in resins produced by supported catalysts. Branching and molecular weight distribution.

Note the inclusion of magnesium and calcium into supported Ziegler systems. Better stereospecificity and easier removal.

Note increasing use of O^- containing compounds in soluble Ziegler systems.

I want to call particular attention to the Naphthachemie patent (9), in which the two components of the Ziegler-Natta system are added to the reactor independently and separately, and reactors are in series. I would speculate that this technique would improve process control and probably improve stereoregularity and molecular weight control.

Now, I will entertain questions and comments, cautioning you first that I am weak on the Ziegler Natta System. I think, "They have finally reduced this SCIENCE to an ART." (10) I have read many, but not all of the patents cited in the tables.

TABLE I

Polymer Process

4,058,654	Bulk Polymerization	Sutter (Bayer)	15 November 1977
4,058,652	Auto Refrigeration	Smith (Exxon)	15 November 1977
4,048,417	Heat Treat Reactor Walls	Noel (Solvay)	13 September 1977
4,048,412	Fluid Bed Process	Caumartin (Naphthachemie)	13 September 1977
4,039,472	Increase Particle Size	Huff (Amoco)	2 August 1977
4,035,560	Fluid Bed Process	Caumartin (Naphthachemis)	12 July 1977
4,012,573	Process Cooling Cycle	Trieschmann (B.A.S.F.)	15 March 1977
4,007,321	Loop Concentrator	Scholz (B.A.S.F.)	8 February 1977

TABLE II

Catalyst Supports

4,056,669	Catalyst Support	Ballard (I.C.I.)	1 November 1977
4,053,565	Silica Xerogel	Krekeler (Nat. Petrochem.)	11 October 1977
4,053,435	Rigid Anhydrous	Lynch (Gulf)	11 October 1977
4,048,414	Gel Preparation and Dope	Frelingsdorf (B.A.S.F.)	13 September 1977
4,042,770	Gel Preparation and Dope	Bachh (B.A.S.F.)	16 August 1977
4,042,769	Rigid Anyhdrous	Lynch (Gulf)	16 August 1977
4,036,933	Silica Xerogel	Lauffer (Duetsch-Gold)	19 July 1977
4,037,042	Spray Dry Hydrogel	Mueller-Tamm (B.A.S.F.)	19 July 1977
4,009,327	Lithium Hydrogel	Witt (Phillips)	22 February 1977
4,001,196	Titanium Containing Support	Witt (Phillips)	4 January 1977

TABLE III

COMBINATION CATALYST, SUPPORTED CHROME

4,054,538	II Allyl ligands of Chrome III	Johnson (Carbide)	18 October 1977
4,053,534	Amines	Mitchell (Mobil)	11 October 1977
4,053,437	Alum, Tit, Charred Deposit	Liu (Chemplex)	11 October 1977
4,053,436	Ppt Hydrogel Presence Tit Sulfate	Hogan (Phillips)	11 October 1977
4,052,544	Aluminum Arsente Carrier	Kehl (Gulf)	4 October 1977
4,049,896	Reducing Agent	Rekers (Nat. Petrochem.)	20 September 1977
4,041,225	Ion Exchange	Pullukat (Chemplex)	9 August 1977
4,041,224	Titanium modified	Hoff (Chemplex)	9 August 1977
4,041,226	Organophosphate	Meyer (Anderson)	9 August 1977
4,035,561	Pinecol and Organochromium	Hoff (Chemplex)	12 July 1977
4,031,298	Alkylester of Titanium	Pullukat (Chemplex)	21 June 1977
4,025,707	Mixed Aluminum hydrocarbyloxide	Hogan (Phillips)	24 May 1977
4,016,343	Chromium Alkoxide	Hoff (Chemplex)	15 April 1977
4,014,816	Silane	Hogan (Phillips)	29 March 1977
4,015,059	Indenyl, Fluorenyl radicals	Karol (Carbide)	29 March 1977
4,013,822	Alkyl, Aryl, Halo Aluminum	Feichtinger (Ruhrchemie)	22 March 1977
4,011,382	Titanium, Fluoro Compounds	Levine (Carbide)	8 March 1977
4,008,359	Organophosphates	Meyer (Anderson)	15 February 1977

TABLE IV

COMBINATION CATALYSTS, SUPPORTED ZIEGLER TYPE

4,056,669	Halo, Magnesium Oxide	Berger (Solvay)	1 November 1977
4,051,307	Phosphorous modified	Caunt (I.C.I.)	27 September 1977
4,042,771	Magnesium, Halogens	Avaro (Naphthachemie)	16 August 1977
4,037,024	Carbonyl Treated Oxide	Cesca (Snam Progetti)	19 July 1977
4,029,864	Magnesium Halide	Kurz (Wacker)	14 June 1977
4,027,087	Magnesium Halide, Mag. Carbonate	Satoh (Chisso)	31 May 1977
4,027,088	Mag. Hydroxide, Organozinc, Sulfate	Kazuo (Nippon Oil)	31 May 1977
4,021,958	Mag. salt, Alum. Methoxide	Kazuo (Nippon Oil)	10 May 1977
4,021,599	Magnesium Alkanol	Kochhar (Gulf)	3 May 1977
4,016,343	Magnesium Alkoxide	Kochhar (Gulf)	5 April, 1977
4,006,101	Mag. Silicon, Halo Alkoxy Cmpd.	Kazuo (Nippon Oil)	1 February 1977
4,004,071	Magnesium Complex with Titanium	Alchimi (Asahi)	18 Uanuary 1977

TABLE V

ZIEGLER CATALYST, MODIFIED

4,053,697	Ether modified	Asado (Sumitomo)	11 October 1977
4,048,415	Ether, Amine, Phosphate	Matuzo (Mitsui)	15 September 1977
4,032,703	Cyclic Alumino Alkylamino Hydrides	Cucinella (Snam Progetti)	28 June 1977
4,028,481	Oxyether, Carboxylic Ester	Shiomura (Mitsui)	6 August 1977
4,027,089	Magnesium Aluminum Complex with Silane	Ashima (Asahi)	31 May 1977
4,015,060	Aminoxide	Karoyann (Amoco)	29 March 1977
4,008,177	Cyclopolyenes	Rust (Hoechst)	15 February 1977
4,008,358	Tit/Van Alcoholate	Abe (Mitsubishi)	15 February 1977
4,007,132	Ether modified	Rust (Hoechst)	15 February 1977
4,007,133	Ether modified	Rust (Hoechst)	15 February 1977
4,004,071	Mag, Alum, Complex with Titanium	Ashima (Asahi)	18 January 1977

TABLE VI

OTHER CATALYSTS

4,029,866	Cationic Polymerization	Kennedy (Exxon)	14 June 1977

TABLE VII

POLYMER RECOVERY

4,051,313	Mag. Halide Removal with Organic Alcohol	Luchiani (Montiedison)	27 Septmber 1977
4,029,877	Trace Water and O_2 in Purifaction	Yoshiura (Mitsubishi)	14 June 1977
4,016,349	Use of Polar Solvent	McKenna (DuPont)	15 April 1977