

METHOD OF DEACTIVATING POLYMERIZATIONCATALYSTS

The present invention relates to a method for the deactivation of polymerization catalysts.

5 In conventional procedures for the polymerization (both homopolymerization and copolymerization) of olefins using catalysts of the so-called "Ziegler" type, the polymerization mixture obtained after completion of the polymerization is mixed with a large quantity of an alcohol or of water to deactivate the catalyst
10 in the mixture as well as to remove catalyst residues from the mixture. Since such a large quantity of alcohol or water is employed, it becomes necessary to separate these materials as well as to rectify the recovered polymerization solvent and unreacted monomers for reuse. Recently, the advent of highly active supported
15 catalysts has made it possible to dispense with the step of removing catalyst residues, since the amount of catalyst employed is so small that the quantity of catalyst in the polymer can be disregarded. However, it is still necessary to deactivate the catalyst because, if the catalyst is not deactivated, uncontrollable polymerization
20 will proceed during subsequent processing of the polymer, resulting in such defects as fisheyes or incompatible particles in the articles, such as films, produced from the polymer. Thus, although the process is simplified by omitting the step of removing catalyst residues, the use of a large quantity of an alcohol or water,
25 as in conventional processes, offsets this advantage, since it

is still necessary to separate the alcohol or water and to rectify the recovered polymerization solvent and unreacted monomers for reuse.

There is, accordingly, a substantial need for a simplified
5 deactivation method which will render unnecessary separation of the water or alcohol and rectification of recovered solvents and monomers. We have now found, that, by using as the deactivation agent a metallic salt of a fatty acid which contains water, it is possible to effect deactivation with a very small quantity
10 of water (as compared with the large quantity used in conventional processes) and that there is no adverse effect on the recovery of the polymerization solvent and unreacted monomer.

Thus, the present invention consists in a method for deactivating a polymerization catalyst, in which a polymerization mixture
15 formed by polymerising an olefin in the presence of a polymerization catalyst comprising a transition metal compound component and an organometallic compound component is contacted with a water-containing metallic salt of a fatty acid under such conditions that:

20
$$400 \leq \frac{XY}{Z} \leq 9,000$$

in which X is the quantity of said metallic salt in grams, Y is the water content of said metallic salt in weight per cent, and Z is the number of moles of said organometallic compound in the polymerization mixture.

The method of the invention has the following advantages:

1. Water is used in an amount judged sufficient to react with the organometallic compound and thus deactivate the catalyst, without the need for a large quantity of water, as is used in 5 the conventional method. Consequently, the step of separating water from the polymer is unnecessary. The polymerization solvent and unreacted monomers can be recovered and reused for polymerization without rectification, because the recovered materials either contain no water or contain so little water that the polymerization 10 activity is not affected.

2. The fatty acid salt used in the method of the invention is employed in so small an amount that, even if it is retained in the polymer, it does not cause such problems as the presence of incompatible particles or fisheyes or decreased transparency 15 in the final products, e.g. a film.

3. The fatty acid salt also acts as a neutralizing agent for the halogen compounds formed from the catalyst and, as a result, protects from corrosion metals in the production plant and processing unit.

20 The fatty acid metallic salts employed in the method of the present invention are preferably salts of higher fatty acids (from C_8 to C_{22}) with such metals as aluminium, calcium, magnesium, zinc, tin, sodium or lithium; it is, of course, possible to

use a single such salt or a mixture of two or more such salts. Particularly preferred salts are calcium stearate, calcium 12-hydroxystearate, sodium stearate and zinc stearate.

The fatty acid metallic salt as such may be contacted with
5 the polymerization mixture or it may be employed in suspension in a hydrocarbon solvent. The hydrocarbon solvent preferably has at least 3 carbon atoms and we prefer aliphatic saturated or olefinic hydrocarbons having from 3 to 8 carbon atoms. Examples of such compounds include propane, butane, pentane, hexane, heptane,
10 octane, propylene, butene-1, pentene-1, hexene-1, heptene-1 and octene-1; a single such solvent or a mixture of any two or more may be employed. If a hydrocarbon having more than 8 carbon atoms is used, it may, in some instances, remain in the polymer and impart an odour. Where a hydrocarbon is employed, it is
15 preferably used in the least possible amount sufficient to disperse the fatty acid salt. A preferred amount is in the range of from 10 to 1,000 times the weight of the fatty acid salt.

In contacting the polymerization mixture with the fatty acid salt, it is necessary that the following relationship should
20 be observed:

$$400 \leq \frac{XY}{Z} \leq 9,000$$

in which X, Y and Z are as defined above. If $\frac{XY}{Z}$ is less than 400, deactivation does not occur whereas, if $\frac{XY}{Z}$ is greater than 9,000 although deactivation occurs, the recovered solvent and monomer, if used directly in a polymerization process, will cause a marked decline in the polymerization activity.

The water content Y and amount X of the fatty acid metallic salt can be freely selected, so long as the value of $\frac{XY}{Z}$ is within the aforementioned range from 400 to 9,000. It is, however, desirable to increase the water content Y and decrease the amount of metallic salt X in order to reduce the effects on the physical properties of the final product (e.g. occurrence of incompatible particles and fisheyes and decline in transparency). Accordingly, we prefer that the water content Y of the fatty acid metallic salt should be from 1 to 30%, more preferably from 3 to 25%, and most preferably from 6 to 20%, by weight. For example, when the quantity of organometallic compound contained in the polymerization mixture is 1 mole, the values of X and Y may be selected so that the following relationships hold:

$$400 \leq XY \leq 9,000$$

$$20 \leq X \leq 500 \quad (\text{in terms of grams})$$

$$1 \leq Y \leq 30 \quad (\text{in terms of \% by weight})$$

The water-containing metallic salt of the fatty acid may be prepared by allowing the metallic salt to stand for a suitable

period (which may range from several hours to several days) in an atmosphere saturated with water vapour, preferably at ambient temperature or above. The determination of water content may be performed, for example, by the titration method of Karl Fischer.

5 The polymerization processes to which the deactivation method of the present invention is applicable are, of course, known, but briefly, they may be as described below.

10 Olefins which may be polymerized include those having from 2 to 8 carbon atoms, particularly ethylene, propylene, butene-1, pentene-1, 4-methylpentene-1, hexene-1 and octene-1. A single one of these olefins may be polymerized or mixtures of two or more may be polymerized.

15 The polymerization catalyst employed is of the Ziegler type and comprises, as one catalyst component, a transition metal compound, and, as the other catalyst component, an organoaluminium compound.

20 Examples of transition metal compounds include such titanium, vanadium and zirconium compounds as titanium tetrachloride, titanium tetrabromide, titanium tetraiodide, titanium trichloride, alkoxy- and aryloxy-titanium halides of formula $Ti(OR^1)_{(4-p)}X_p$ (in which R^1 represents a hydrocarbon radical, X represents a halogen atom and p is a number such that $0 < p < 4$), vanadium tetrachloride,

vanadium oxytrichloride, zirconium tetrachloride and alkoxy- and aryloxy- zirconium halides of formula $Zr(OR^2)_{(4-q)}X_q$ (in which R^2 represents a hydrocarbon radical, X represents a halogen atom and q is a number such that $0 < q < 4$).

5 The method of the invention is also useful in connection with supported Ziegler catalyst systems, in which the transition metal compound is supported on a suitable carrier. Useful carriers include such inorganic compounds as oxides, hydroxides, chlorides and carbonates of metals and silicon, as well as mixtures or
10 double salts thereof. Examples include magnesium oxide, titanium oxide, silica, alumina, magnesium carbonate, hydroxychlorides of divalent metals, magnesium hydroxide, magnesium chloride, magnesium alkoxides, magnesium haloalkoxides, the double oxide of magnesium and aluminium and the double oxide of magnesium
15 and calcium. Of these, we particularly prefer magnesium compounds.

 The method of the present invention may also be employed with a catalyst system in which the transition metal component is the reaction product of an organomagnesium compound and a transition metal compound of formula $Ti(OR^3)_{(4-r)}X_r$ (in which
20 R^3 represents a hydrocarbon radical, X represents a halogen atom and r is a number such that $0 < r < 4$) for example titanium tetrahalides, alkoxytitanium compounds, aryloxytitanium compounds, alkoxytitanium halides and aryloxytitanium halides.

 The catalyst component of unsupported transition metal compounds is described, for example in Japanese Patent Applications Kokai

(i.e. published but unexamined) No.34478/72, No.16298/76, No.20986/76, No.46598/76, No.110793/77, No.9288/78, No.125986/75, No.107294/77 and No.155199/77.

5 Pertinent examples of the catalyst components of supported transition metal compounds are described, for example, in Japanese Patent Publications No.39037/79, No.40273/79, No.40274/79 and No.23561/80, Japanese Patent Applications Kokai No.126785/75, No.84884/76 and No.133408/80, and in Japanese Patent Applications No.51641/79, No.165341/79 and No.9200/80.

10 The organometallic compound, which is the other essential component of the catalyst system may be, for example: a trialkyl-aluminium, such as triethylaluminium, tripropylaluminium, trisobutyl-aluminium, tributylaluminium or trihexylaluminium; a dialkylaluminium monohalide, such as diethylaluminium chloride, dipropylaluminium
15 chloride, diisobutylaluminium chloride, dibutylaluminium chloride or dihexylaluminium chloride; an alkylaluminium dihalide, such as ethylaluminium dichloride, propylaluminium dichloride, isobutyl-aluminium dichloride, butylaluminium dichloride or hexylaluminium dichloride; another organoaluminium compound, such as ethylaluminium
20 sesquichloride, propylaluminium sesquichloride, isobutylaluminium sesquichloride, butylaluminium sesquichloride or hexylaluminium sesquichloride; or an organozinc compound. A single one of these organometallic compounds may be used or it is possible to use two or more of them.

The polymerization may be carried out by the method of slurry polymerization, solution polymerization or gas phase polymerization. Liquid phase polymerization processes, such as solution or slurry polymerization, are preferably conducted by supplying the olefin continuously to an inert solvent containing the transition metal compound and the organometallic compound at a reaction temperature which may range from ambient temperature to 250°C and under a reaction pressure which may range from atmospheric pressure to about 100 atmospheres (101 bars). However, the polymerization temperature and pressure are not limited to these ranges and, for example, higher temperatures and/or pressures may be used. When an α -olefin having from 3 to 8 carbon atoms (e.g. propylene, butene-1 or pentene-1) is used as the monomer, the liquid phase polymerization can be conducted using the monomer itself as solvent. A molecular weight regulator, for example hydrogen, can be used. The polymerization can be carried out either continuously or batch-wise. Examples of inert solvents which may be employed as the polymerization solvent include aliphatic hydrocarbons (e.g. propane, butane, pentane, hexane, heptane or octane), alicyclic hydrocarbons (e.g. cyclohexane or cycloheptane) and aromatic hydrocarbons (e.g. benzene, toluene, or xylene). A single one of these solvents or a mixture of two or more thereof may be employed.

Contact of the fatty acid metallic salt with the polymerization mixture may be effected by adding the metallic salt itself or a suspension of the salt in a hydrocarbon to the polymerization

5 mixture, e.g. in a polymerization vessel or polymerization termination tank, and agitating the mixture to mix it thoroughly. It is also possible to effect the contact by mixing the salt with a polymer cake obtained by separating a solid polymer from the polymerization mixture by suitable means, e.g. centrifugation, filtration or flush evaporation.

10 Gas phase polymerization may be carried out by the fluidized bed method or by agitation at the polymerization temperature, which may range from ambient temperature to 100°C, and under a pressure of, for example, from atmospheric pressure to about 100 atmospheres (101 bars). Contact of the polymerization mixture with the fatty acid metallic salt may be effected by methods similar to those employed in the case of liquid phase polymerization.

The invention is further illustrated by the following Examples.

15

EXAMPLE 1

(a) Synthesis of transition metal compound catalyst component

20 Into a four-necked 1 litre flask, provided with a stirrer, a reflux condenser and a dropping funnel, were placed 35.0 g of magnesium turnings of a grade suitable for Grignard reagents. The flask was then flushed thoroughly with nitrogen in order to remove completely the air and moisture and then 125 g of butyl chloride and 500 ml of dibutyl ether were charged into the dropping funnel to form a solution. About 30 ml of this solution were

added dropwise onto the magnesium in the flask to start the reaction. After the reaction had started, the dropwise addition was continued, so as to allow the reaction to proceed smoothly. At the end of the reaction, unreacted magnesium was removed by filtration through a glass filter.

A four-necked 100 ml flask, provided with a stirrer, a dropping funnel and a thermometer, was flushed thoroughly with nitrogen in order to remove the air and moisture. Into the flask were charged 23.8 ml (50 mmoles) of the solution of butylmagnesium chloride in dibutyl ether prepared as described above. This solution was stirred and, whilst it was stirred, 8.5 g of silicon tetrachloride were slowly added dropwise through the dropping funnel to form a white precipitate. When all of the silicon tetrachloride had been added, the precipitate was filtered from the dibutyl ether and washed with 50 ml of purified heptane. The washing and filtration steps were repeated 5 times, after which the precipitate was dried in vacuo at room temperature, to give 6.1 g of a white solid.

6.0 g of this white solid were dipped into 30 ml of titanium tetrachloride in a four-necked 100 ml flask, and the mixture was heated at 100°C for 1 hour. When the reaction was complete, the solid matter was washed repeatedly with heptane, until no more titanium tetrachloride could be found in the washings. There were obtained 4.8 g of the transition metal compound catalyst component.

(b) Preparation of deactivation agent

A petri dish containing 5 g of calcium stearate was left standing for 200 hours at room temperature in a tightly closed desiccator containing distilled water on the bottom. The initial
5 water content of the calcium stearate was 0.8% by weight, determined by the Karl Fischer method. After the calcium stearate had stood for 200 hours in the desiccator, its water content had increased to 19.4%, although there was no appreciable change in its properties (agglomeration and flowability) as a result of this increased
10 water content. 470 mg of the resulting calcium stearate was then suspended in 50 ml of heptane, which had been thoroughly dehydrated by treatment with Molecular Sieve 4A - a 10 ml portion of this suspension was used as the deactivation agent.

(c) Polymerization

15 A 1 litre stainless steel autoclave provided with an electromagnetic induction stirrer was thoroughly flushed with nitrogen and heated to 70°C. To the autoclave were added, with stirring, 500 ml of heptane (which had been thoroughly dehydrated and deoxygenated), 2.0 mmoles of triethylaluminium and 5.1 mg of the solid
20 catalyst component obtained as described in step (a) above. Hydrogen was added to a gauge pressure of 5 kg/cm² (4.9 bars), and then ethylene was fed in to a gauge pressure of 15 kg/cm² (14.7 bars), to commence polymerization. Polymerization was continued for 1 hour at 70°C, whilst maintaining a total pressure

of 15 kg/cm² (14.7 bars), by replenishing the ethylene, as necessary.

(d) Deactivation treatment

After completion of the polymerization, the supply of ethylene was discontinued. A 10 ml portion of the suspension prepared as described in step (b) was forced into the autoclave by a nitrogen pressure of 30 kg/cm² gauge (29.4 bars). On addition of the suspension, evolution of heat in the autoclave quickly subsided and the decrease in internal pressure caused by absorption of ethylene was no longer observable, indicating that the polymerization had been terminated by deactivation of the catalyst. The unreacted ethylene, hydrogen and nitrogen were then purged. The contents of the autoclave were removed, freed from heptane by filtration and dried in vacuo at 60°C to give 40 g of polyethylene powder.

A portion of the dried powder was placed on a piece of SS-41 flat plate, which had been mirror-finished with a 300 gauge sandpaper, and the powder was hot-pressed at 280°C and 150 kg/cm² gauge (147.1 bars) for 3 minutes. The plate carrying the pressed sheet was kept overnight in a desiccator containing water. As a control, a similar SS-41 plate alone was similarly treated in the hot press and left standing overnight. On comparison, there was no observable difference in the degree of corrosion of the two pieces of SS-41 plate, indicating that the polyethylene powder would have no corrosive effect upon such metal apparatus as granulators or injection moulding machines.

EXAMPLE 2

Polymerization was carried out as described in Example 1, except that:

the amount of transition metal compound catalyst component
5 [prepared as described in Example 1(a)] was 3.8 mg;

150 g of butane and 100 g of butene-1 were used in place of the 500 ml of heptane; and

the polymerization temperature, hydrogen partial gauge pressure and ethylene partial gauge pressure were 60°C, 5.0 kg/cm²
10 (4.9 bars) and 10 kg/cm² (9.8 bars), respectively.

The catalyst in the polymerization mixture was deactivated by addition of 10 ml of the suspension prepared as described in Example 1(b). Heat evolution quickly subsided, indicating termination of polymerization by deactivation of the catalyst.
15 There were obtained 97 g of an ethylene/butene-1 copolymer in powdered form.

EXAMPLE 3

Polymerization and deactivation were carried out as described in Example 2, except that 3.5 mg of the transition metal compound
20 catalyst component prepared as described in Example 1(a) were used and 500 mg of humidified calcium stearate, prepared as described in Example 1(b), were used as the deactivation agent. The results obtained are shown in Table 1. The yield of powdered ethylene/butene-1 copolymer was 89 g.

EXAMPLE 4

Calcium stearate was humidified as described in Example 1(b), except that the humidification time was 50 hours. At the end of this time, the water content was 5.0 % by weight (Karl Fischer). A suspension of 360 mg of the humidified calcium stearate in 20 ml of heptane (dehydrated as in Example 1) was used as the deactivation agent. Polymerization and deactivation were carried out as described in Example 2, except that 4.0 mg of the transition metal compound catalyst component prepared as described in Example 1(a) were used and the deactivation agent was as described above. The results obtained are shown in Table 1. The yield of ethylene/butene-1 copolymer powder was 101 g.

EXAMPLE 5

A 1 litre stainless steel autoclave provided with an electromagnetic induction stirrer was thoroughly flushed with nitrogen. Into the autoclave were charged 10.5 mg of commercial grade titanium trichloride, 2.0 mmoles of diethylaluminium chloride and 300 g of liquified propylene. Polymerization was allowed to proceed at 70°C for 4 hours.

At the end of this time, deactivation was carried out using 10 ml of the same suspension as was used in Example 1. The results obtained are shown in Table 1. The yield of polypropylene was 30.5 g.

EXAMPLE 6

(a) Synthesis of transition metal compound catalyst.

Into a 500 ml flask, provided with a stirrer, a reflux condenser and a dropping funnel, were placed 17.2 g (0.7 mole) of powdered magnesium. The flask was heated at 120°C for 2 hours whilst passing dry nitrogen through it in order to remove completely moisture adsorbed on the internal surfaces of the flask and on the magnesium powder. Into the dropping funnel were then charged 63 ml (0.6 mole) of butyl chloride and 347 ml of diethyl ether, to form a solution. This solution was added dropwise to the magnesium in the flask over a period of 75 minutes, whilst maintaining the internal temperature of the flask at 60°C. When all of the solution had been added, the reaction was allowed to proceed under reflux for a further 60 minutes. The flask was then cooled to room temperature and unreacted magnesium was filtered off through a glass filter. The filtrate contained 1.48 moles of Grignard reagent per litre, as determined by hydrolysing with 1 N aqueous sulphuric acid and back-titrating with 1 N aqueous sodium hydroxide.

A 1 litre flask, provided with a stirrer and a dropping funnel, was thoroughly flushed with dry nitrogen. Into the flask were charged 500 ml of heptane and 39 g (0.17 mole) of tetraethoxytitanium. The heptane solution of tetraethoxytitanium in the flask was vigorously stirred, whilst 100 ml (0.14 mole)

of the diethyl ether solution of Grignard reagent were added dropwise through the dropping funnel over a period of about 1 hour, whilst maintaining the temperature of the reaction system always at 3-4°C. After all of the solution had been added, the reaction was allowed to continue for 3 hours at room temperature. The reaction product solidified and became suspended in the liquid medium. The suspended matter was allowed to settle and was then separated from the supernatant, washed 5 times, each time with 100 ml of heptane, and dried, to give 36 g of a solid reaction product having a dark blue colour.

(b) Preparation of deactivation agent

55 mg of humidified calcium stearate, prepared as described in Example 1(b), were suspended in 10 ml of heptane which had been thoroughly dehydrated with Molecular Sieve 4A. The resulting suspension was used as the deactivation agent.

(c) Polymerization and deactivation

Polymerization was carried out as described in Example 2, except that 6.6 mg of the transition metal compound component prepared as described in step (a) above and 2 mmoles of diethylaluminium chloride were used. Deactivation was then effected by adding the deactivation agent prepared as described in step (b) above. The results obtained are shown in Table 1. The yield of the ethylene/butene-1 copolymer powder was 21 g.

EXAMPLE 7

A humidified fatty acid metallic salt was prepared as described in Example 1(b), except that sodium stearate was used in place of the calcium stearate and the humidification time was 100 hours.

5 The water content was 13.2% by weight (Karl Fischer). 137 mg of this humidified sodium stearate were suspended in 10 ml of heptane, which had been thoroughly dehydrated with Molecular Sieve 4A. The resulting suspension was used as the deactivation agent.

10 Polymerization was then carried out as described in Example 2, except that 4.8 mg of the transition metal compound catalyst component were used. Deactivation was then effected by adding the deactivation agent prepared as described above. The results obtained are shown in Table 1. The yield of ethylene/butene-1
15 copolymer powder was 120 g.

Table 1

Example No.	Fatty acid metallic salt		Hydrocarbon (ml)	Organo-metallic compound Z (mole)
	X (g)	Water content Y (wt.-%)		
1	Ca stearate 0.094	19.4	Heptane 10	$\text{Al}(\text{C}_2\text{H}_5)_3$ 0.002
2	" 0.094	19.4	" 10	" 0.002
3	" 0.5	19.4	None	" 0.002
4	" 0.36	5.0	Heptane 20	" 0.002
5	" 0.094	19.4	" 10	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ 0.002
6	" 0.055	19.4	" 10	" 0.002
7	Na stearate 0.137	13.2	" 10	$\text{Al}(\text{C}_2\text{H}_5)_3$ 0.002

Table 1 continued

$\frac{XY}{Z}$ (g/mole)	Olefin being polymerized	Deactivation ability
912	Ethylene	Termination of polymerization
912	Ethylene butene-1	"
4850	"	"
900	"	"
912	Propylene	"
534	Ethylene butene-1	"
904	"	"

EXAMPLE 8

(a) Synthesis of transition metal compound catalyst component

In a four-necked flask, which had been thoroughly flushed with nitrogen, 22.4 g of dried magnesium turnings and 14.4 ml of butyl chloride were allowed to react in 500 ml of heptane in the presence of 0.02 g of iodine at 90°C for 7 hours, to yield a white, finely granular reaction product. After completion of the reaction, unreacted magnesium was removed from the suspension of the reaction product. The solvent was then removed from the suspension by filtration and the product was dried in vacuo, to give a powder of butylmagnesium chloride, which was found, on analysis, to contain 23.0% by weight of magnesium and 58.5% by weight of chlorine.

To a slurry of 5.4 g of powdered butylmagnesium chloride, prepared as described above, in 50 ml of heptane were added 50 ml of a heptane solution containing 3.2 g of phenol. The mixture was allowed to react at about 25°C for 1 hour. At the end of this time, the mixture was freed from the solvent by filtration and then mixed with a mixture of 4.3 ml of diethyl ether and 100 ml of heptane. The resulting mixture was again allowed to react at about 25°C for 1 hour, after which the reaction product was separated by filtration, and mixed with 21.0 ml of titanium tetrachloride, whilst cooling at 0°C. The mixture was then allowed to react at 136°C for 2 hours. After completion of the reaction, the resulting slurry was cooled to about 25°C and the reaction product was washed with heptane, until no more titanium tetra-

chloride could be detected in the washings. The resulting catalyst component was then dried in vacuo, to give a pale reddish-brown powder, which was found, on analysis, to contain 2.4% by weight titanium, 21.0% by weight magnesium and 66.0% by weight chlorine.

(b) Polymerization

Into a 2 litre stainless steel autoclave, in which the air had been replaced by propylene, were charged 1.5 mmoles of triethylaluminium, 1.5 mmoles of diethylaluminium chloride, 0.75 mmoles of ethyl p-anisate and 600 ml of heptane (which had been thoroughly dehydrated and purified). 43.8 mg of the solid catalyst component prepared as described in step (a) above were added, after which 240 ml (standard state - i.e. the amount supplied was that which occupies 240 ml at 0°C and 1 atmosphere - 0.98 bar) of hydrogen were forced into the autoclave. The internal temperature of the autoclave was raised to 60°C, after which feeding of propylene began. Whilst maintaining the internal pressure of the autoclave at 10 kg/cm² gauge (9.8 bars), by replenishing the propylene, polymerization was continued for 1 hour at 70°C.

(c) Deactivation treatment

After polymerization had been effected for 1 hour, as described above, 20 ml of a suspension of 1 g of powdered calcium stearate (having a water content of

2.4% by weight, prepared as described in Example 1(b)) in heptane were forced into the autoclave by a nitrogen pressure of 20 kg/cm² gauge (19.6 bars), whilst continuing

the supply of propylene. As soon as the suspension had been introduced into the autoclave, no more weight decrease (measured on a platform scale of 1 g reciprocal sensibility) of the cylinder supplying propylene could be observed, indicating that polymerization had terminated. After the point at which the decrease in the weight of this cylinder had ceased to be observable, the temperature and pressure in the autoclave were maintained for a further 1 hour. The polypropylene formed was then removed from the autoclave and its catalytic activity was investigated and found to be 4030 g polypropylene per g catalyst. This value coincided, within an error of 2%, with that obtained from a similar experiment, in which the catalyst activity was determined after polymerization had been terminated with a large volume of ethanol. It was confirmed that the polymerization had been completely terminated with the water-containing calcium stearate of this invention.

EXAMPLE 9

(a) Polymerization

Into a 2 litre stainless steel autoclave, in which the air had been replaced by propylene, were charged 3 mmoles of diethylaluminium chloride and 600 ml of heptane (which had been thoroughly dehydrated and purified). 57.2 mg of a commercial grade titanium trichloride catalyst component were added, after which 240 ml

(standard state) of hydrogen were forced into the autoclave. The internal temperature of the autoclave was raised to 60°C and then propylene was fed into the autoclave. The internal pressure of the autoclave was maintained at 6 kg/cm² gauge (5.9 bars) by replenishing the propylene and polymerization was continued for 2 hours at 70°C.

(b) Deactivation treatment

After polymerization had been effected for 2 hours, as described above, 20 ml of a suspension of 1.5 g of powdered sodium stearate (water content 2.0% by weight) in heptane were forced into the autoclave using a nitrogen pressure of 15 kg/cm² gauge (14.7 bars), whilst maintaining the supply of propylene. As soon as the suspension had been introduced, it was no longer possible to observe any weight decrease in the cylinder supplying propylene, indicating that the polymerization had been terminated.

EXAMPLE 10

Propylene was polymerized for 1 hour, as described in Example 8. The resulting slurry, which still had polymerization activity, was transferred to a filtration tank provided with a stirrer, to separate the polypropylene powder from the polymerization medium. 0.15 g of powdered calcium stearate, which had been adjusted _____

to a water content of 8.3% by weight, were added, with stirring, to the polypropylene powder, to terminate the polymerization. The polymer was dried under a stream of nitrogen at 100°C. The yield of dried polypropylene powder was 160 g. A corrosion test, carried out as described in Example 1(d) indicated that the powder had no corrosive effect on metal.

EXAMPLE 11

Polymerization and deactivation were carried out as described in Example 8, except that the water-containing calcium stearate was added to the polymerization mixture suspended in nitrogen in place of the heptane. It was found that the polymerization was completely terminated by this procedure.

COMPARATIVE EXAMPLES 1, 2 AND 4

Polymerization and deactivation were carried out as described in Example 2, except that from 3.1 to 5.0 mg of the transition metal compound catalyst component prepared as described in Example 1(a) were used and that the deactivation agents were varied in composition and quantity as shown in Table 2. The results are also shown in Table 2.

COMPARATIVE EXAMPLE 3

5 A deactivation agent was prepared by suspending 500 mg of calcium stearate, which had been dried for 8 hours in a vacuum dryer set at 90°C, in 20 ml of heptane, which had been thoroughly dehydrated with Molecular Sieve 4A. Polymerization was then carried out as described in Example 2, except that 3.2 mg of the transition metal compound catalyst component prepared as described in Example 1(a) were used. The method of adding the deactivation agent was the same as in Example 2. The results
10 are shown in Table 2. The yield of ethylene/butene-1 copolymer powder was 81 g.

28

Table 2

Compara- tive Example No.	Fatty acid metallic salt		Hydro- carbon (ml)	Organo- metallic compound Z (mole)
	X (g)	Water con- tent Y (wt.-%)		
1	Ca stearate 0.031	19.4	Heptane 10	Al(C ₂ H ₅) ₃ 0.002
2	" 1.034	19.4	" 20	" 0.002
3	" 0.5	Undetected by Karl Fischer's method	" 20	" 0.002
4	" 2.8	8.1	" 30	" 0.002

Table 2 continued

$\frac{XY}{Z}$ (g/ mole)	Olefin being poly- merized	Deactivation ability
300	Ethylene butene-1	Same decrease in rate of polymerization; polymerization not terminated.
10030	"	Polymerization ter- minated, but the recovered solvent, when reused, inhibited polymerization.
-	"	Polymerization not terminated; no change in rate of polymerization.
11340	"	Polymerization terminated, but the film (30 μ m) made from the polymer showed a great number of incom- patible particles.



CLAIMS:

1. A method for deactivating a polymerization catalyst, in which a polymerization mixture formed by polymerizing an olefin in the presence of a polymerization catalyst comprising a transition metal compound component and an organometallic compound component is contacted with a water-containing metallic salt of a fatty acid under such conditions that:

$$400 \leq \frac{XY}{Z} \leq 9,000$$

in which X is the quantity of said metallic salt in grams, Y is the water content of said metallic salt in weight percent, and Z is the number of moles of said organometallic compound in the polymerization mixture.

2. A method according to Claim 1, in which said salt is calcium stearate, calcium 12-hydroxystearate, zinc stearate or sodium stearate.

3. A method according to Claim 1 or Claim 2, in which said water content Y is from 1 to 30% by weight.

4. A method according to any one of the preceding claims, in which said olefin is one or a mixture of two or more of ethylene,



propylene, butene-1, pentene-1, 4-methylpentene-1, hexene-1 and octene-1.

5. A method according to any one of the preceding claims, in which said metallic salt is added by itself to the polymerization mixture.

6. A method according to any one of claims 1 to 4, in which said metallic salt is added as a suspension in a hydrocarbon to said polymerization mixture.

7. A method according to Claim 1, substantially as hereinbefore described with reference to any one of the foregoing Examples.

8. An olefin polymer when treated by a method according to any one of the preceding claims.
