

620582

COMMONWEALTH of AUSTRALIA
Patents Act 1952

APPLICATION FOR A STANDARD PATENT

I/We

Shell Oil Company

of

900 Louisiana, Houston, Texas, 77001, United States of America

hereby apply for the grant of a Standard Patent for an invention entitled:

In-reactor stabilization of polyolefins via coated stabilizers

which is described in the accompanying complete specification.

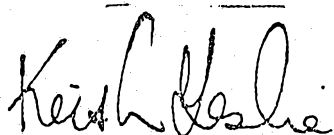
Details of basic application(s):-

<u>Number</u>	<u>Convention Country</u>	<u>Date</u>
147953	United States of America	25 January 1988

The address for service is care of DAVIES & COLLISON, Patent Attorneys,
of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of
Australia.

DATED this TENTH day of JANUARY 1989

To: THE COMMISSIONER OF PATENTS


.....
a member of the firm of
DAVIES & COLLISON for
and on behalf of the
applicant(s)

Davies & Collison, Melbourne

1005696 10/01/89

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COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-1973

DECLARATION IN SUPPORT OF CONVENTION OR
NON-CONVENTION APPLICATION FOR A PATENT
OR PATENT OF ADDITION

Insert title of invention

In support of the Application made for a ~~patent~~ ~~XXXXXX~~ for an invention
entitled: "In-reactor stabilizatio of polyolefins via
coated stabilizers"

Insert full name(s) and address(es)
of declarant(s) being the appli-
cant(s) or person(s) authorized to
sign on behalf of an applicant
company.

I RAND N. SHULMAN, Assistant General Counsel
~~XXX~~
of: SHELL OIL COMPANY, a Corporation organised
and existing under the laws of the State of
Delaware, United States of America of:900,
Louisiana, Houston, Texas 77001, United States
of America.

Cross out whichever of paragraphs
1(a) or 1(b) does not apply

do solemnly and sincerely declare as follows :-

1(a) relates to application made
by individual(s)
1(b) relates to application made
by company; insert name of
applicant company.

~~I am the applicant~~ ~~XXXXXX~~ ~~patent~~ ~~XXXXXX~~
~~We are~~ ~~XXXXXX~~ ~~patent of addition~~ ~~XXXXXX~~
or (b) I am authorized by
SHELL OIL COMPANY,

Cross out whichever of paragraphs
2(a) or 2(b) does not apply

the applicant..... for the ~~patent~~ ~~XXXXXX~~ to make this declaration on its behalf
~~XXXXXX~~ ~~XXXXXX~~

2(a) relates to application made
by inventor(s)
2(b) relates to application made
by company(s) or person(s) who
are not inventor(s). Insert full
name(s) and address(es) of inven-
tors.

~~I am the inventor~~ ~~XXXXXX~~ ~~XXXXXX~~
~~We are~~ ~~XXXXXX~~ ~~XXXXXX~~

or (b). ANANDA MOHAN CHATTERJEE, an Indian citizen

of: 14411 Locke Lane, Houston, Texas 77077, United
States of America.

State manner in which applicant(s)
derive title from inventor(s)

~~is~~ ~~are~~ the actual inventor..... of the invention and the facts upon which the applicant ~~is~~ ~~are~~
~~is~~ ~~are~~ entitled to make the application are as follows :-

"The Applicant would, if a patent were granted upon
an application made by the Inventor , be entitled to
have the patent assigned to it"

Cross out paragraphs 3 and 4
for non-convention applications.
For convention applications,
insert basic country(s) followed
by date(s) and basic applicant(s).

3. The basic application..... as defined by Section 141 of the Act ~~was~~ ~~made~~
~~United States of America~~ ~~was~~ ~~made~~
in U.S.A. No. 147,953 on the 25th January, 1988
by ANANDA MOHAN CHATTERJEE
in on the
by
in on the
by

4. The basic application..... referred to in paragraph 3 of this Declaration ~~was~~ ~~made~~
the first application..... made in a Convention country in respect of the invention the subject
of the application.

Insert place and date of signature.

Declared at HOUSTON TEXAS this 15th day of December 1988

Signature of declarant(s) (an
attestation required)

Rand N. Shulman
RAND N. SHULMAN -
ASSISTANT GENERAL COUNSEL.....

Note: Initial all alterations.

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(54) Title
IN-REACTOR STABILIZATION OF POLYOLEFINS VIA COATED STABILIZERS

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(71) Applicant(s)
SHELL OIL COMPANY

(72) Inventor(s)
ANANDA MOHAN CHATTERJEE

(74) Attorney or Agent
DAVIES COLLISON CAVE , 1 Little Collins Street, MELBOURNE VIC 3000

(56) Prior Art Documents
US 4659506

(57) Claim

1. A coated additive particle suitable for use in an olefin polymerization reaction, which comprises a core comprising at least one antioxidant for a polyolefin, and a coating comprising at least one wax which is solid at the polymerization temperature and which comprises a polyolefin wax selected from polypropylene wax, polybutylene, polyethylene wax, and a mixture of at least two of these.

8. A process for producing a coated additive particle as claimed in any one of claims 1 to 7 which comprises melting said wax, fluidizing with a hot gas particles of said antioxidant, spraying the molten wax on the heated fluidized antioxidant particles, and maintaining the resulting fluidized additive particles at a temperature such that the formation of fibres is prevented and discrete coated additive particles are formed.

16. A process according to claim 15 wherein the polymerisation catalyst is a magnesium supported titanium

halide/aluminum alkyl catalyst system comprising

(i) a procatalyst component obtained by reacting a magnesium compound of the formula $MgR'R''$ wherein R' is an alkoxide or aryloxy group or a halogen, and R'' is an alkoxide, alkyl carbonate, aryloxy or halogen with a halide of tetravalent titanium and an electron donor, contacting the halogenated product with a halide of tetravalent titanium, washing it to remove unreacted titanium and electron donor, contacting the halogenated product with a halide of tetravalent titanium, washing it in an inert solvent to remove unreacted titanium compounds and recovering the solid product;

(ii) a cocatalyst component comprising an organoaluminum compound which is diethyl aluminum chloride, ethyl aluminum dichloride, ethyl aluminum sesquichloride or triethyl aluminum; and

(iii) a selectivity control agent which is diphenyldimethoxysilane, paraethoxy benzoate, ethyl paratoluate, ethyl paramethoxy benzoate, phenyltriethoxysilane or 2,2,6,6-tetramethyl piperidine.

620582

ORIGINAL
COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952
COMPLETE SPECIFICATION

NAME & ADDRESS
OF APPLICANT:

Shell Oil Company
900 Louisiana
Houston Texas 77001
United States of America

NAME(S) OF INVENTOR(S):

Ananda M. CHATTERJEE

ADDRESS FOR SERVICE:

DAVIES & COLLISON
Patent Attorneys
1 Little Collins Street, Melbourne, 3000.

COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:

In-reactor stabilization of polyolefins via coated stabilizers

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

This invention relates to coated additives for a variety of uses including: (a) addition to a polymerization reactor, to produce non-extruded product which contains stabilizer, and (b) preparation of concentrates or

5 masterbatches of additives or pigments via a non-extrusion route. It also relates to a process for producing such additives as well as to a process for incorporating the additives into polyolefins during olefin polymerization.

Prior art methods for incorporating dry additives
10 into polymers have involved polymerizing a monomer, and then adding stabilizers to the resulting polymer by extrusion or other melt mixing techniques, thereby producing pellets. Stabilizers have traditionally not been added directly to the polymerization reactor because neat stabilizers often
15 deactivate the polymerization catalyst and terminate the polymerization reaction. Various disadvantages are associated with such melt mixing techniques, including an appreciable downtime for cleaning of the blending equipment, heat sensitivity of some additives, and pelletization
20 problems, particularly with very high melt flow $> 0.166\text{g/sec}$ ($> 100\text{ g/10 min}$) polypropylene resins.

Amongst prior disclosures of methods of blending additives with polymers, US-A-3,591,409 describes preparing a composition by high intensity blending of a mixture of

particulate thermoplastic resin, hydrocarbon wax, and particulate solid additive at high temperatures. This method requires that all ingredients be placed in the mixer at once, without the separate pretreatment of any one of the
5 components of the mixture.

A variety of patents teach methods for making discrete particles or capsules containing different kinds of fill materials. US-A-4,306,993 discloses a method for making microcapsules which can be used to tag books, paper
10 currency and explosives and explosive devices.

DE-A-2,160,852 discloses microcapsules containing wetting agents, and US-A-4,224,422 discloses a curable epoxy resin polyisocyanate system useful as an adhesive. The curable one part system comprises a rupturable impermeable
15 microcapsule having shell walls of a crosslinked interfacial polyurethane-polyether reaction product of an aromatic polyisocyanate. US-A-4,382,326 describes acrylate copolymer microsphere structures using glycerol and cycloaliphatic polyepoxides filled with a liquid Lewis acid-glycerol
20 complex. Tacky spherical acrylate copolymer particles are disclosed in US-A-4,098,945, which teaches a liquid-filled capsule having a microporous capsule wall made of a dispersed solid-phase and a continuous phase. Here the capsule forms a single phase in the liquid state but
25 separate phases when cooled to a solid and the volume contraction ratio is at least 1.2:1. The preferred capsules are spherical and the wall is made of the solid, crystalline olefin polymer, an amorphous hydrocarbon resin and an at

least partially crystalline wax capable of separating out as a discontinuous mass.

Liquid-filled capsules for the controlled release of fertilizers having a microporous wall of crystalline polyolefin, hydrocarbon resin and a wax are disclosed in 5 US-A-4,002,453. US-A-3,985,840 describes microspheres prepared by forming a homogeneous molten liquid phase using a solid crystalline olefinic polyer, a hydrocarbon resin and at least partially crystalline wax, and wherein the liquid 10 phase is allowed to cool and the wax separates out as a

discontinuous mass dispersed throughout the matrix.

US-A-3,977,992 discloses a controlled release capsule prepared from 2% wax, 5% hydrocarbon resin and the remainder of crystalline olefinic polymer such as polyethylene.

5 It has long been desired to find a method of cheaply blending stabilizers, antioxidants and other additives into polymers in a reactor without compounding or extruding, in such a way that these additives are dispersed throughout the polymer. It has also been desired to achieve
10 a method of blending additives into polymers without requiring the use of solvents. The present invention seeks to achieve these goals by providing coated additive particles that can act as an antioxidant when incorporated in a polymer matrix and which can be thus
15 incorporated during polymerization at short notice and with good efficiency.

 Accordingly, the present invention provides a coated additive particle suitable for use in an olefin polymerization reaction, which comprises a core comprising at
20 least one antioxidant for a polyolefin and a coating comprising at least one wax which is solid at the polymerization temperature and comprises polypropylene wax, polybutylene wax, polyethylene wax or a mixture of at least two of these.

25 The invention also provides a process for producing such a coated additive particle, which comprises melting a wax, fluidizing with a hot gas particles of said antioxidant, spraying the molten wax on the heated fluidized antioxidant particles, and maintaining the resulting fluidized additive
30 particles at a temperature such that the formation of fibers is prevented and discrete coated additive particles are formed.



The invention further provides a process for providing in-reactor stabilization of a polyolefin during a polymerization reaction which comprises polymerizing the olefin in the presence of coated additive particles as
5 hereinbefore described and a polymerization catalyst.

The coated additive particles of the present invention comprise a core of at least one antioxidant and a coating of wax which is solid at the polymerization temperature and which comprises polypropylene wax,
10 polybutylene wax, polyethylene wax or a mixture of at least two of these. In one embodiment, the wax coating represents from 15% to 85% of the total weight of the particle, the percentages being based on the total composition of the particle.

15 The coated additive particles suitably have diameters from 100 to 8000 μm . The antioxidant may be, for example, 1,3,5-trimethyl-2,4,6-tris
(3,5-di-tert-butyl-4'-hydroxybenzyl) benzene (A); octadecyl
3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) propionate (B),
20 tetrakis[methylene (3,5-di-tert-butyl-4-hydroxy-
hydrocinnamate)] methane (C);
tris[3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate (D);
3,5-di-tert-butyl-4-hydroxyhydrocinnamic acid triester with
1,3,5-tris(2-hydroxyethyl)-s-triazine-2,4,6(1H,3H,5H)-trione
25 (E); 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)
1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (F); bis-[3,3-bis(4'
hydroxy-3'-tert-butyl-phenyl)-butanoic acid]-glycolester (G);
2,2'-methylene-bis-(4-methyl-6-tertiary-butyl-phenol)-tereph-
thalate (H); 2,2-bis[4-(2-(3,5-di-tert-butyl-4-hydroxy-



hydrocinnamoyloxy)ethoxy-phenyl]propane (I),
 calcium bis-[monoethyl(3,5-di-tert-butyl-4-hydroxy-
 benzyl)phosphonate](J); 1,2-bis(3,5-di-tert-butyl-4-hydroxy-
 hydrocinnamoyl)hydrazine (K) or 2,2'-oxamido bis-[ethyl
 5 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (L).

Owing to their melting points, antioxidants A, D,
 F, G, H, J, K, and L can be coated by an isotactic propylene
 homopolymer wax. Antioxidants A and C to L inclusive, are
 suitably coated by polyethylene wax of melting point
 10 100-105°C.

Additives suitable for use either separately from,
 or blended with, the above antioxidants include processing
 stabilizers such as phosphites and phosphonites; acid
 acceptors such as metal stearates, metal oxides, and
 15 hydrotalcites (for example Kyowa Chemical Industries' DHT-4A
 and DHT-4C); nucleating agents; lubricants; antistatic
 agents; fillers such as barium sulfate, clay, calcium
 carbonate silicates and magnesium oxide; pigments such as
 titanium dioxide, zinc oxide, lead chromate, cadmium
 20 sulfides, cadmium selenide, zinc sulfide and basic carbonate
 of white lead; stabilizers such as tribasic lead sulfate,
 basic lead chlorosilicate, dibutyl tin oxide and other salts
 of lead, zinc, cadmium and tin; flame retardants such as
 antimony oxide; ultra-violet stabilizers, slip agents,
 25 anti-block agents, and other solid additives which enhance
 the properties and processability of a polyolefin to which
 they are added.

The coating of the additive particles comprises a

a polyolefin wax which comprises polypropylene wax, polybutylene wax, polyethylene wax or a mixture thereof. In producing the particles, the initial heating of the wax is suitably carried out at a temperature from 110°C to 180°C. One
5 embodiment involves heating the fluidized additive particles to be coated to a temperature from 150°C to 180°C.

In the process for providing in-reactor stabilization of a polyolefin according to the present invention, which comprises polymerizing an olefin in the
10 presence of coated additive particles as hereinbefore described and a polymerization catalyst, the coated additive particles are suitably added directly to the polymerization reactor. Polymerization with a titanium halide/aluminum alkyl catalyst system is particularly suitable. In one
15 embodiment, the polymerization catalyst is a magnesium supported titanium halide/aluminum alkyl catalyst system comprising;

(i) a procatalyst component obtained by reacting a magnesium compound of the formula $MgR'R''$ wherein R' is an
20 alkoxide or aryloxy group or a halogen, and R'' is an alkoxide, alkyl carbonate, aryloxy or halogen with a halide of tetravalent titanium and an electron donor, contacting the halogenated product with a halide of tetravalent titanium, washing it to remove unreacted
25 titanium and electron donor, contacting the halogenated product with a halide of tetravalent titanium, washing it in an inert solvent to remove unreacted titanium compounds and recovering the solid product;



(ii) a cocatalyst component comprising an organoaluminum compound which is diethyl aluminum chloride, ethyl aluminum dichloride, ethyl aluminum sesquichloride or triethyl aluminum; and

5 (iii) a selectivity control agent which is diphenyldimethoxysilane, paraethoxy benzoate, ethyl paratoluate, ethyl paramethoxy benzoate, phenyltriethoxysilane or 2,2,6,6-tetramethyl piperidine.

The coated additive particle according to the
10 invention suitably comprises in its core one or more of a variety of additives, examples of which include acid acceptors, processing stabilizers, antioxidants, metal deactivating agents, nucleating agents, pigments, heat stabilizers, light stabilizers, lubricants, antiblock
15 agents, antistatic agents, and slip additives which are capable of enhancing the properties and processability of the polyolefin. Typically, the concentration of additive ranges from about 5% to about 85% of the total mass of the particle.

20 The present invention thus involves at least two aspects;

- (1) the formation of a novel coated additive particle comprising a core of additive and a coating of a polymer wax, and
- 25 (2) the incorporation of the novel, coated additive particles within a polymer matrix during polymerization in a reactor, wherein the particle coating acts as a barrier between the catalyst system and the ^{antioxidant} ~~additive~~ during



. polymerization.

The outer coating material may be either of a natural or synthetic wax. Typical examples of suitable coating materials include hydrocarbon waxes, preferably 5 polyolefin waxes such as polypropylene and polyethylene and paraffin wax, ester waxes, such as spermaceti, mineral waxes such as montan wax, amide waxes such as ethylene distearamide and ethylene diorescorcinolamide, halogenated hydrocarbon waxes such as chlorinated paraffin waxes and 10 chlorinated naphthalenes, and ketone waxes such as stearone.

The outer coating of the particle comprises at least one polyolefin wax derived from ethylene, propylene or butene-1. A hydrocarbon wax, such as a polypropylene wax with a weight average molecular weight of 10,000 to 30,000 15 and which is primarily isotactic (such as Hoechst Wax PP 230) is an example of a suitable coating. Also copolymers of ethylene and propylene, copolymers of propylene and butene-1, and copolymers of ethylene with at least one other alpha olefin containing from 2 to 18 carbon atoms in the repeating 20 unit and more preferably containing from 2 to 8 carbon atoms are suitable. The term "polyolefin" as applied to the coating thus is intended to comprehend both homopolymers and copolymers.

The wax selected for the outer coating should not cause color formation, staining, or degradation of the base



polymer composition in which the coated particles are to be incorporated. The wax of the outer coating should be relatively easy to incorporate into the polymer. More specifically the outer coating should not be reactive with
 5 the base polymer. If a polypropylene wax is used as the coating material, it (in low concentration) can be left in the final polypropylene composition.

The melting point of the coating wax should be at least high enough so that the outer coating remains solid at
 10 room and storage temperatures. It is preferred that the coating material soften or melt at from 100°C to 180°C for convenience of its incorporation during propylene polymerization.

Waxes and wax-like materials are suitably employed
 15 alone or in mixtures of various proportions as the coating layer. A particularly suitable outer coating comprises polypropylene. The individual components of the coating are typically melted together before being coated on the core of additive. This melting usually occurs at temperatures from
 20 150°C to 180°C. The coating can then be applied to the additive core by a heating and/or blending and/or spraying operation.

One or more coatings are applied to the ~~additive~~^{antioxidant}
 core by spraying or by any other suitable technique. For
 25 example, an ~~additive~~^{antioxidant} powder is heated and fluidized using hot air. At the same time the coating material is heated until it melts and it is then sprayed onto the fluidized
~~additive~~^{antioxidant} powder. The liquid coating material is added to



the fluidized ^{antioxidant}~~additive~~ in an amount sufficient to form coated additive particles having the desired diameter. The core comprising the ^{antioxidant}~~additive~~ is suitably coated with two or more layers to form the coated particles. Optimum operating
 5 conditions for the fluidized bed are shown in Table I.

Following the completion of the coating step, the coated additive particle is introduced into the polymerization reactor for incorporation into the polymer. This incorporation typically takes place without any
 10 additional solvents or diluents.

For gas phase fluidized bed polymerization of the olefin, the coated additive particles are suitably introduced into the fluidized zone of monomer in the reactor. Depending on the particular ^{antioxidant}~~additive and its~~
 15 ~~function~~, the amounts to be incorporated into the polymer are varied in accordance with the percentages known to the art to achieve the desired polymer properties.

In addition to coated additive and monomer, a catalyst system comprising cocatalyst, selectivity control
 20 agent and procatalyst is typically added to the polymerization reactor. The coated particles are suitable for use in all types of polymerization, such as liquid pool polymerization, gas phase polymerization, solvent slurry polymerization, and polymerization processes disclosed in
 25 US-A-4,414,132 AND US-A-4,329,253. Sieved fractions of the coated additives can also be added to the polymerization reactor.

Good results are obtained with polypropylene wax



^{antioxidant}
 coatings on solid ~~additives~~, for incorporation into
 polypropylene. The wax coating serves to prevent early or
 inadvertent deactivation of the catalyst by the ^{antioxidant} ~~additive~~
 underlying the coating. One important advantage of this
 5 occurs in further melt processing of the polymer by the
 customer, in that, in the extruder, the frictional or
 applied heat causes the wax coating to melt and thereby
 promotes dispersion of the additive throughout the resin.
 Since the polypropylene wax is predominantly isotactic, it
 10 can be left in the final product.

^{antioxidant}
 From 5 to 85% by weight of ~~additive~~ (based on the
 total weight of the particle) is typically used in coated
 particles for stabilizing a polyolefin. Tests have been
 conducted on a number of different kinds of ^{antioxidant} ~~additives~~
 15 (coated with polypropylene wax), including "Irganox" 3114
 ("Irganox" is a Registered Trade Mark), an additive for
 polymers and particularly useful as a stabilizer for
 polypropylene compositions.

The novel wax-coated additives can reduce abrasion
 20 of the surfaces of processing machinery, and thereby reduce
 undue wear and erosion of metal surfaces in contact with the
 final resin composition (including the working parts of the
 processing equipment). Screw and barrel cleaning presents
 problems in these types of operations. Metal contamination
 25 caused by abrasion is a serious source of discoloration and
 degradation of the resins and the use of the novel coating
 additive particles reduces the magnitude of this problem.

^{antioxidant}
 Wax-coated ~~additives~~ can minimize the dusting



tendencies of the finely divided ^{antioxidant} ~~additives~~, and thereby prevent the generation of toxic dusts and minimize dust explosion hazards.

The coated additive particles are advantageously
5 used in polymers such as polypropylene, chlorosulfonate
polyethylene, ethylene-propylene copolymer rubbers,
ethylene-propylene terpolymers, (and butyl, butadiene-
styrene, silicone, acrylonitrile rubbers. They are also
suitable for use in plastics such as polyvinyl chloride
10 polymers and copolymers, polyethylene and copolymers,
polypropylene, polyvinylidene chloride, polystyrene,
polyimides, polyamides, polyacetals,
acrylonitrile-butadiene-styrene, polycarbonates,
polycaprolactone, poly(ethylene oxide), chlorinated
15 polyethylene, polymethyl methacrylate, and polyaromatic
sulfones.

The process of the present invention can be
advantageously employed to produce efficiently a resin
containing dispersed ^{antioxidant} ~~additives~~ without the need for further
20 extrusion pelletization of the resin. This means that
polymerization to produce a highly stable product can be
accomplished with an expenditure of a minimum of man-hours
and minimal equipment costs compared with known techniques.

The production of concentrates or masterbatches of
25 stabilizer, pigments and other additives is an important
segment of the polymer industry. Before fabrication the
concentrates (containing additive) are blended with an
amount of polymer, to achieve a desired final additive



concentration. Additive concentration in the masterbatch can be controlled by controlling the coating layer thickness. The current concentrate manufacturing technology involves extrusion (often with expensive twin-screw equipment) or other mechanical mixing process. Screw and
5 barrel cleaning, maintenance problems, energy cost, heat sensitivity of some additives and pelletization often present problems in such operations. The present invention presents a lower energy, non-extrusion route to additive or pigment concentrate preparation.

10 The invention is further illustrated by the following Examples, in which all parts and percentages are by weight unless otherwise specified.

Examples 1 to 3 and Comparative Example 1

Preparation of Additive mixtures

15 The additives used were "Irganox" 3114 (available from Ciba-Geigy Corporation), "Ultranox" 626 (available from Borg Warner Chemicals), and ZnO ("Kadox" 25) (available from New Jersey Zinc Company). ("Ultranox" and "Kadox" are Registered Trade Marks).

20 Two stabilizer mixtures were prepared. Mixtures 126-1 and 126-2 (same composition) contained "Irganox" 3114, "Ultranox" 626 and zinc oxide in the weight ratio 10:5:4. Mixture 126-5 contained "Irganox" 3114 and ZnO in the weight ratio 10:4. These mixtures were prepared by dry blending
25 the solid stabilizer particles.

Coating of additives

Fluidized bed coating experiments were conducted

at Coating Place Incorporated (Verona, Wisconsin), using the Wurster process, described in H.S. Hall and R. E. Pondell, Chapter 7, in "Controlled Release Technologies: Methods, Theory and Applications", Vol. II, A.F. Kydonieus, Ed. CRC Press, Boca Raton, FL, 1980. In this process the coating material is sprayed or atomized through a nozzle onto a fluidized bed of solid core material.

A fluidized bed equipped with a spray nozzle in the bottom of the reactor was used to prepare the coated particles. The coating wax, which was Hoechst Wax PP 230, which is predominantly isotactic polypropylene with weight average molecular weight of about 25000 and softening point (Ring and Ball) of about 158°C, was delivered to the fluidized additive bed with a Zenith gear pump.

The coating chamber was 10cm (4 inches) in diameter at the bottom and 15cm (6 inches) at the top. The spray nozzle was mounted at the base of this chamber. The molten polypropylene wax was delivered by a heated Zenith gear pump (1.75 cc/revolution) to the spray nozzle. Here the atomizing air produced a fine spray of the polypropylene wax which coated the stabilizer particles in the fluid bed. The operating conditions were as set out in Table I.

TABLE I

	Fluidizing Air Temp (°C)		Fluidizing Air Flow Rate m ³ /s (SCFM)	RPM of Pump	Atomizing Air Pressure Kpa (psi)		Atomizing Air Flow Rate m ³ /s (SCFH)	Polypropylene Wax Line Temp (°C)
	<u>In</u>	<u>Out</u>						
Comparative								
Example 1	104	65	0.0179 (38)	20	207	(30)	9.83x10 ⁻⁴ (125)	220
Example 1	154	104	0.0165 (35)	20	207	(30)	9.83x10 ⁻⁴ (125)	232
Example 2	160	77	0.0142 (30)	18	138	(20)	6.21x10 ⁻⁴ (79)	238
Example 3	154	77	0.0142 (30)	18	138	(20)	6.45x10 ⁻⁴ (82)	238

In comparative Example 1, 456 g stabilizer mixture 126-1 was fluidized by air, with the objective of coating it with polypropylene wax. The coating was not successful, because the polypropylene wax formed fiber after exiting the nozzle, instead of atomizing. The fiber formation was caused by the relatively low inlet temperature of the fluidizing air (104°C).

In Example 1 500 g stabilizer mixture 126-2 was coated with 504 g polypropylene wax at a fluidizing air inlet temperature of 184°C during a 24 minute run. The coated particles, which contained 50% weight stabilizer, showed visibly larger particle size than the starting stabilizers.

In Example 2 1 kg stabilizer mixture 126-5 was coated with 200 g polypropylene wax at a fluidizing air inlet temperature of 160°C during a 14 minute run. The coated particles contained 83% by weight of stabilizer.

In Example 3 1 kg of the coated product from Example 2 was further coated with 200 g polypropylene wax at a fluidizing air inlet temperature of 154°C during a 14 minute run. The coated particles contained 69% by weight stabilizer.

Examples 4 to 8 and Comparative Example 2

Polymerisation

Batch liquid propylene polymerizations were run in a 3dm³ (1 U.S. gallon) autoclave (2.7 liter propylene charge) at 67% for one hour using SHAC 201 catalyst. The

following injections were made sequentially to the reactor containing propylene and hydrogen: (1) mixture of triethyl aluminum (TEA) cocatalyst (see Table II) and diphenyl dimethoxy silane selectivity control agent (40 microliter),
5 (2) "SHAC" 201 catalyst (0.4 ml in mineral oil), available through the Shell Chemical Co., Houston, Texas ("SHAC" is a Registered Trade Mark) and (3) coated additive suspended in mineral oil (except in the case of comparative Example 2). SHAC 201 catalyst is obtained by halogenating a magnesium
10 compound of the formula $MGR'R''$ (wherein R' is an alkoxide or aryloxy group or halogen, and R'' is an alkoxide, alkyl carbonate, aryloxy or halogen) with a halide of tetravalent titanium and an electron donor, contacting the halogenated product with a tetravalent titanium halide,
15 washing it to remove unreacted titanium and electron donor, contacting the halogenated product with a tetravalent titanium halide, washing it in an inert solvent to remove unreacted titanium compounds and recovering the solid product.

20 Xylene solubles (XS) of the resultant polymers were determined as the percentage of material remaining soluble, when cooling a solution of polymer in xylene, from its boiling point to room temperature.

Thermo-oxidative stability of the polypropylene
25 product was determined by both oven aging and oxidative induction time (OIT) measurements. The polypropylene produced in the reactor was compression-molded into 0.25mm (10 mil) thick specimens. For oven aging these 25.4cm x

38.1cm (1-inch X 1.5-inch) specimens were placed in a forced circulation hot air oven maintained at $125 \pm 0.1^\circ\text{C}$. The aging procedure followed the guidelines of ASTM D3012. The samples were inspected daily, and failure was indicated
5 by characteristic powdery disintegration and brittleness of the polymer.

For OIT measurement, about 5 mg of the compression-molded sample was crimped in a Difference Scanning Calorimeter (Perkin-Elmer model DSC-2). The sample
10 was heated to the test temperature under nitrogen, and then the nitrogen gas was replaced by oxygen. From this time ($t=0$) onward, scanning was done in the time mode. A tangent was drawn to the exothermic oxidation peak; the intersection of this tangent with the initial baseline, measured from
15 $t=0$, gave the oxidative induction time or OIT. Note that higher oven life or OIT values indicate greater oxidative stability of the polymer. Polypropylene stability test results are given in Table II which follows:

TABLE II

	Milli- Mole TEA	Coated ^{a)} Additive	Yield kg PP/g Cat	XS (%w)	Bulk Density (g/cm ³)	Oven Life (days) at 125°C	OIT _{170°C} (MIN)	at 190°C
Example 4	1.4	Example 1	6.5	5.7	0.33	> 81	-	47.2
Example 5	2.1	Example 1	7.5	5.5	0.33	> 81	-	32.2
Example 6	1.4	Example 2	7.9	5.3	0.34	10	27.5	-
Example 7	1.4	Example 3	10.5	5.9	0.35	>131	>40	8.6
Example 8	2.1	Example 3	11.4	6.1	0.35	> 69	-	20.3
Comparative Example 2 - (Unstabilized Polypropylene)	-	-	-	-	-	1	4.3	1.1

a) 3.0 grams used

b) hydrogen used was 32 mmole in all runs.

The data in Table II show that the polypropylene produced in the reactor in accordance with the invention (Examples 4 to 8) had good yield and stereoselectivity, and also had significant level of thermo-oxidative stability, as shown by both oven aging and oxidative induction time (OIT) of the polypropylene, compared to polypropylene which was polymerized without the novel particles (Comparative Example 2). Polypropylene yield increased with increasing TEA concentration. The bulk density of the polypropylene was 10 higher than conventional polypropylene powder.

Comparative Example 3

The process according to Example 4 was carried out, but with the coated additive particles replaced by Irganox 3114 and ZnO added directly to the reactor.

No polymer was produced owing to the fact that
5 the additives deactivated the catalyst and stopped polymerisation.

Concentrates suitable for polyethylene (PE)
resins can be prepared in a similar manner to Examples 4 to
8 by fluidized bed coating of additive or pigment by
10 substituting a PE wax for the PP wax.

The claims defining the invention are as follows:

1. A coated additive particle suitable for use in an olefin polymerization reaction, which comprises a core
5 comprising at least one antioxidant for a polyolefin, and a coating comprising at least one wax which is solid at the polymerization temperature and which comprises a polyolefin wax selected from polypropylene wax, polybutylene, polyethylene wax, and a mixture of at least two of these.

10 2. A particle according to claim 1, wherein the coating represents from 15% to 85% of the total weight of the particle.

3. A particle according to claim 1 or 2 wherein the core comprises two or more different antioxidants.

15 4. A particle according to any one of the preceding claims wherein the antioxidant is



- 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxy-
benzyl)benzene; octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxy-
5 phenyl)propionate; tetrakis[methylene 3,5-di-tert-
butyl-4-hydroxyhydrocinnamate)] methane;
tris[3,5-di-t-butyl-4-hydroxybenzyl)isocyanurate;
3,5-di-tert-butyl-4-hydroxycinnamic acid triester with
1,3,5-tris(2-hydroxyethyl)-s-triazine-2,4,6(1H,3H,5H)-
10 trione;
1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)
1,3,5-triazine-2,4,6-(1H,3H,5H)-trione;
bis-[3,3-bis(4'-hydroxy-3'-tert-butyl-phenyl)-butanoic acid]-
glycolester;
15 2,2'-methylene-bis-(4-methyl-6-tertiary-butyl-)phenol
terephthalate;
2,2-bis[4-(2-(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyloxy))
ethoxy-phenyl]propane;
calcium bis[monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl)-
20 phosphonate];
1,2-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyl)hydrazine;
or 2,2'-oxamidobis-[ethyl 3-(3,5-di-tert-butyl-
4-hydroxyphenyl)propionate].

5. A particle according to any one of the
25 preceding claims having a diameter of from 100 to 8000 μ m.



6. A particle according to any one of the preceding claims wherein the core comprises a further additive which is an antioxidant, processing stabiliser, acid acceptor, metal deactivating agent, pigment, heat stabilizer, light stabilizer, lubricant, antiblock agent, antistatic agent, slip additive, nucleating agent, filler or flame retardant.
7. Coated additive particles according to claim 1 substantially as described in Example 1, 2 or 3.
8. A process for producing a coated additive particle as claimed in any one of claims 1 to 7 which comprises melting said wax, fluidizing with a hot gas particles of said antioxidant, spraying the molten wax on the heated fluidized antioxidant particles, and maintaining the resulting fluidized additive particles at a temperature such that the formation of fibres is prevented and discrete coated additive particles are formed.
9. A process according to claim 8 wherein the fluidising gas is an inert gas, air or mixture thereof.
10. A process according to claim 8 or 9 wherein the wax is melted at a temperature from 110°C to 180°C.
11. A process according to any one of claims 8 to 10 wherein the fluidizing gas is heated to a temperature from 150°C to 180°C.
12. A process according to any one of claims 8 to 11 wherein the steps are repeated to dispose a second coating on the particle.



13. A process according to claim 8 and substantially as described in any one of Examples 1 to 3.

14. A coated additive particle whenever produced by a process according to any one of claims 8 to 13.

5 15. A process for providing in-reactor stabilization of a polyolefin during a polymerisation reaction which comprises polymerising an olefin in the presence of coated additive particles as claimed in any one of claims 1 to 7 or 14 and a polymerisation catalyst.

10 16. A process according to claim 15 wherein the polymerisation catalyst is a magnesium supported titanium halide/aluminum alkyl catalyst system comprising

(i) a procatalyst component obtained by reacting a magnesium compound of the formula $MgR'R''$ wherein
15 R' is an alkoxide or aryloxy group or a halogen, and R'' is an alkoxide, alkyl carbonate, aryloxy or halogen with a halide of tetravalent titanium and an electron donor, contacting the halogenated product with a halide of tetravalent titanium, washing it to remove unreacted
20 titanium and electron donor, contacting the halogenated product with a halide of tetravalent titanium, washing it in an inert solvent to remove unreacted titanium compounds and recovering the solid product;



(ii) a cocatalyst component comprising an organoaluminum compound which is diethyl aluminum chloride, ethyl aluminum dichloride, ethyl aluminum sesquichloride or triethyl aluminum; and

- 5 (iii) a selectivity control agent which is diphenyldimethoxysilane, paraethoxy benzoate, ethyl paratoluate, ethyl paramethoxy benzoate, phenyltriethoxysilane or 2,2,6,6-tetramethyl piperidine.

10 17. A process according to claim 15 or 16 wherein the olefin polymerisation reaction is a C_2-C_{11} olefin polymerisation reaction.

18. A process according to claim 17 wherein the olefin polymerisation reaction is a propylene or a 1-butene polymerisation reaction.

15 19. A process according to any one of claims 15 to 18 wherein the polymerisation reactor is a gas phase polymerisation reactor.

20. A process according to any one of claims 15 to 18 wherein the polymerisation reactor is a liquid pool
20 polymerisation reactor.

21. A process according to any one of claims 15 to 18 wherein the polymerisation reactor is a solvent/slurry polymerisation reactor.

22. A process according to any one of claims 15
25 to 18 wherein the polymerisation reactor is a solution polymerisation reactor.



23. A process according to claim 15 and substantially as described in any one of Examples 4 to 8.

24. A stabilised polyolefin whenever produced by a
5 process as claimed in any one of claims 15 to 23.

25. A polyolefin incorporating a coated additive particle as claimed in any one of claims 1 to 8 or 14.

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SHELL OIL COMPANY

By Its Patent Attorneys

DAVIES COLLISON CAVE

