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(54) Title: REDUCED FOULING IN POLYMERIZATION REACTORS

(57) Abstract: The treatment of a reactor for the gas phase, slurry, solution or high pressure polymerization of ethylene, optionally with comonomers, with a gas comprising not less than 50 volume% hydrogen at a temperature greater than 185 C for time up to about 30 hours reduces any Fe³⁺ (e.g. hematite) to Fe²⁺ (e.g. magnetite). As Fe³⁺ is known to be a catalytic site for deposition of carbon based deposits. A pre start up treatment reduces fouling in the reactor.



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REDUCED FOULING IN POLYMERIZATION REACTORS

TECHNICAL FIELD

The present invention relates to the reduction of fouling in reactors for the polymerization of alpha-olefins in a fluid phase. More particularly the present invention relates to treating the internal surface of the reactor with a reducing agent, particularly hydrogen to reduce fouling.

BACKGROUND ART

There is very little art in the field of treating fluid phase polymerization reactors to reduce the iron at the reactor surface to reduce fouling.

There are a number of patents relating to reducing static in gas phase reactors by incorporating chemicals such as "water add back" (U.S. patent 4,855,370 to Chirillo et al.,) controlling the voltage on the reactor wall where sheet formation is likely to occur (U.S. patent 4,532,311 to Fulks et al.,) and treating the internal reactor surface with a chrome containing compound prior to polymerization (U.S. patent 4,876,320 to Fulks et al.) These patents are all directed at reducing static electrical charges on the wall of a gas phase reactor.

United States patent 3,842,060 issued Oct. 15, 1974 to McDonald et al., assigned to Dart Industries Inc. teaches a method to reduce the gradual build up of polymer on the inside wall of a high pressure tubular reactor. The patent teaches to continuously add between about 10 and 150 ppm by volume of hydrogen to the feed for a high pressure tubular reactor. The patent does not suggest that the treatment could be carried out prior to the reaction. The reference teaches away from the subject matter of the present invention.

United States patent 5,501,878 issued March 26, 1996 to Barendregt et al, assigned to Mannesmann Aktiengesellschaft and KTI Group B.V. teaches treating transfer line exchangers (TLE) made of boiler steel in a thermal cracking process to produce alpha olefins, with hydrogen to reduce Fe_2O_3 to Fe_3O_4 to reduce the formation of coke in the TLE. The Fe_2O_3 is believed to be a catalyst site for the formation of coke from ethylene or propylene. The composition of the steel is described as "boiler" steel in the abstract and at line 23 of Col. 1. However, the only composition suggested in the disclosure is 15Mo3 (Col. 1 line 30 and the examples). A 15 Mo steel would contain 15 % molybdenum. This is well outside of the range of steels contemplated in the present

invention. The reference teaches that the reaction is a gas phase cracking reaction and teaches away from a liquid phase polymerization reaction.

U.S. patent 7,056,399 issued June 6, 2006 to Cai et al., assigned to NOVA Chemicals (International) S.A. also teaches treating transfer line exchangers. The transfer line exchanger is first cleaned (decoked), then reduced and then further treated with various chemicals such as sulphides, disulphides and disulfirams. This teaches away from the subject matter of the present invention in that the present invention does not require further treatment with the sulphur containing compounds.

While this art has been available for a number of years, as far as Applicant can determine no one has thought of applying the art to fluid, preferably liquid polymerization reactions.

The present invention seeks to provide a process to reduce fouling in a fluid, preferably liquid, phase alpha olefin polymerization reactor by reducing the internal surface of the reactor. It is known that Fe_2O_3 (Fe^{3+}) is a site for the production of coke in cracking reactors the presence of alpha olefins. Reducing the Fe_2O_3 removes the site for the alpha olefin to attach to the wall of the reactor. Deposits at such sites may slough off at various stages leading to a range of fouling from gels to black specks.

DISCLOSURE OF INVENTION

In one embodiment the present invention provides a process to reduce fouling in a fluid alpha olefin polymerization reactor having an internal steel surface comprising less than 10 weight % Mo, comprising prior to polymerization subjecting the internal steel surface to reduction by exposure to gaseous hydrogen at a temperature greater than 185°C for a time from 15 minutes to 30 hours, with shorter times at higher temperatures.

In a further embodiment the gas comprises not less than 70 volume % hydrogen and the temperature is from 240°C to 360°C for a time from 10 hours to half an hour with shorter times at higher temperatures.

In a further embodiment the alpha olefin is ethylene alone or together with one or more alpha olefins selected from the group consisting of C_{3-8} alpha olefins.

In a further embodiment polymerization is conducted at a temperature from 75°C to 330°C and at pressures from 0.78 MPa (110 psi) to 345 MPa (50,000 psi).

In a further embodiment the polymerization reactor has an internal steel surface comprising less than 0.4 weight % carbon, less than 1.5 weight % Mn, less than 2

weight % of Cr, less than 3 weight % of Ni, less than 1 weight % of Mo and the balance iron.

In a further embodiment the alpha olefins are dissolved or dispersed in not less than 30 weight % of a solvent or diluent.

5 In a further embodiment the alpha olefins are dispersed in not less than 50% of diluent and the reaction is conducted at a temperature from 82°C to 99°C and a pressure from 0.760 MPa to 6.8 MPa.

10 In a further embodiment the alpha olefins are dissolved in not less than 65% of a solvent and the reaction is conducted at a temperature from 120°C to 250°C and a pressure from 4 MPa to 31 MPa.

In a further embodiment there is less than 10 wt% of a solvent in the reactor and the reaction is conducted at a temperature from 150°C to 250°C and a pressure from 138 MPa to 344 MPa.

In a further embodiment the alpha olefin is ethylene.

15 In a further embodiment the polymerization is carried out in the gas phase.

The above embodiments may be combined in whole or in part individually or in combination with each other.

20 In a further embodiment of the present invention there is provided a process to reduce black specks in an ethylene polymer produced in a fluid, preferably liquid, phase reactor comprising treating the reactor according to the above embodiments.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a schematic drawing of the quartz reactor unit (QRU) used to perform the experiments.

25 Figure 2 is a plot of the time for reduction of iron on the steel surface using 100 volume % hydrogen at various temperatures.

BEST MODE FOR CARRYING OUT THE INVENTION

30 The present invention is applicable to any alpha olefin polymerization process which takes place in the fluid phase, preferably liquid phase. Fluid phase alpha olefin polymerization reactions may take place over a broad range of temperature and pressure conditions from 75°C to 330°C and at pressures from 0.78 MPa (110 psi) to 345 MPa (50,000 psi). This includes gas phase reactions, and preferably slurry reactions, solution reactions and high pressure reactions.

For gas phase, slurry and solutions polymers the reactions are catalyzed typically with a catalyst selected from the group consisting of:

1. a chrome base catalyst, typically chromium oxide or a silyl chromate on a silica support, activated with an aluminum compound such as an aluminum alkyl compound which may be halogenated (e.g. trimethyl aluminum, triethyl aluminum, diethyl aluminum chloride etc.) or an alkyl aluminum alkoxide (e.g. diethyl aluminum alkoxide);
2. a Ziegler natta catalyst typically a combination of a transition metal compound such as a halide (e.g. TiCl_3 , TiCl_4 ,) or a transition metal alkoxide ($\text{Ti}(\text{OEt})_4$, etc.) a magnesium compound (MgCl_2 , EtMgBu , etc) and an aluminum compound as noted above; and
3. a single site catalyst such as a bridged or unbridged metallocene (e.g. Cp_2ZrX_2 etc.) activated with a complex aluminum compound (MAO) or an ionic activator (e.g. a borate such as trityl borate) or a mixture thereof.

High pressure polymerizations may be conducted thermally without a catalyst or in the present of a free radical initiator (e.g. a peroxide).

The polymerization may take place over a broad range of conditions at a temperature from 75°C to 330°C and at pressures from 0.78 MPa (110 psi) to 345 MPa (50,000 psi). This encompasses gas phase, slurry, solution and high pressure polymerizations.

Gas phase reactions may take place over a range of temperatures and pressures from about 75°C to about 110°C , typically from 82°C to 99°C and at pressures from 0.76 MPa (110 psi) to 3.4 MPa (about 500 psi). The gas phase comprises the monomers, typically one or more C_{2-6} alpha olefins, such as ethylene, 1-butene and 1-hexene, saturated gaseous hydrocarbons such as C_{2-6} alkanes, inert gases such as nitrogen, chain transfer agents such as hydrogen and optionally from about 10 to 40, preferably about 13 to 35, most preferably from about 15 to 25 weight % of a condensable alkane for heat removal from the reaction. The reaction stream is passed through a bed of catalyst and growing polymer particles at a pressure and rate sufficiently high to keep the bed fluidized. Generally there is an expanded portion at the top of the reactor to reduce the gas velocity and cause fines and polymer particles to fall back into the bed. The polymer is removed from the bed using a series of pressure lock valves and a receiving chamber and degassed. The unreacted monomers and the rest of the components in the gas phase leave the reactor and pass through a

compressor and a heat exchanger to compress and cool the gas and if present cause a condensable gas to form a suspended liquid phase (i.e. droplets). Additional monomer is added to the recycle stream and it enters the reactor beneath a disperser plate and again passes upward through the fluidized bed.

5 Slurry reactions may take place over a range of temperatures and pressures from about 75°C to about 110°C, typically from 82°C to 99°C and at pressures from 0.76 MPa (110 psi) to 6.8 MPa (about 1000 psi). In a slurry reaction the olefins and monomers are typically dispersed in a hydrocarbon diluent such as mixture of one or more C₄₋₈ saturated hydrocarbons and aromatic hydrocarbons. Typically the reactor is
10 a loop reactor with one or more settling legs. The reactor contents, diluent, monomer and polymer (and chain transfer agent) circulate around the loop portion of the reactor. The diluent in the loop portion of the reactor is present in an amount of at least 50 weight %, typically at least about 60 weight % of the reactor contents (i.e. the polymer may be up to about 40 weight % of the reactor contents in the main loop). In the
15 settling leg of the reactor the diluent concentration may range from 40 to 50 weight % and the polymer may be present in an amount from about 60 to 50 weight %.

Solution reactions may take place over a range of temperatures and pressures from about 120°C to about 250°C, typically from 180°C to 220°C and at pressures from 4 MPa to 31 MPa (about 1900 to about 15,000 psi) typically from about 6 to 10 MPa
20 (about 2900 to about 4800 psi). The polymer concentration may be as high as about 35 weight %, but typically is about 10 to 15 weight %. The concentration of solvent in the reactor is not less than about 65 weight %, typically from about 90 to 85 weight %.

High pressure reactions take place over a range of temperatures from about 150°C to 250°C, typically from about 180°C to about 230°C and at pressures from 103
25 MPa (15000 psi) to 345 MPa (about 50,000 psi) typically from 138 MPa (20,000 psi) to 276 MPa (40,000 psi). The solvent or diluent if present is present in an amount of less than 10 weight %, preferably less than 3 weight %, most preferably less than 1.5 weight %. Preferably a minimum amount or no solvent or diluent is present and the liquid phase is monomer.

30 Typically, apart from high pressure polymerization, the above polymerization processes may be used to produce homopolymers and copolymers. The alpha olefin is selected from the group consisting of C₂₋₈ alpha olefins. Typically the copolymer will generally contain less than about 15 weight %, preferably less than 10 weight % of

comonomer selected from the group consisting of C₃₋₈ alpha olefins. Some typical alpha olefin comonomers for ethylene include 1-butene, 1-hexene and 1-octene (typically present only in solution processes).

5 The high pressure reaction is typically used to produce homopolymers of ethylene, although in some cases where propylene is used as a chain transfer agent small amounts, typically less than 3 weight %, preferably less than 2 weight % of propylene may be incorporated into the polymer.

10 The steel used to construct reactors for the above processes is typically a carbon steel without a high chrome or nickel content. The steel typically comprises not less than about 90 weight % of Fe and less than about 10 weight % Mo, preferably less than 5 weight % Mo, most preferably less than 2 weight % Mo, desirably less than 1 weight % Mo. The steel may have a composition comprising less than 0.4 weight % carbon, less than 1.5 weight % Mn, less than 2 weight % of Cr, less than 3 weight % of Ni, less than 1 weight % of Mo and the balance iron. One suitable steel comprises from 15 0.3 to 0.4, preferably from 0.3 to 0.38 weight % carbon, from 0.7 to 1.5 weight %, preferably from 0.7 to 1 weight % of Mn, from 0.8 to 2, preferably from 0.8 to 1.2 weight % of Cr, from 0.5 to 3 weight %, preferably from 0.5 to 2.5 weight % of Ni, from 0.5 to 1 weight %, preferably from 0.5 to 0.65 weight % of Mo and the balance of iron.

20 The interior surface of the reactor is treated with a reducing gas typically hydrogen, or a mixture comprising not less than 50 volume % hydrogen and up to 50 volume % of an inert gas such as helium, nitrogen and argon. Preferably, the gas mixture comprises not less than 75 volume %, preferably not less than 90 volume %, of hydrogen and correspondingly up to 25 volume %, preferably up to 10 volume % of one or more inert gases selected from the group consisting of helium, nitrogen and argon, 25 preferably nitrogen.

When the treatment gas comprises 100 volume % of hydrogen the reactor may be treated for a time from 15 minutes to 30 hours at a temperature of at least 185°C, with longer times at lower temperatures. Typically the temperature for treatment will be from 240°C to 360°C at times from about 10 hours to about 15 minutes respectively. 30 For gas mixtures which are more dilute in hydrogen the times would be proportionally increased relative to the amount of dilution with the inert gas. When the treatment gas comprises not less than 70 volume % hydrogen and the temperature is from 240°C to 360°C the treatment time may be from 10 hours to half an hour with shorter times at

higher temperatures. When the treatment gas comprises not less than 90 volume % of hydrogen and the temperature is from 240°C to 360°C the treatment time may be from 8 hours to about 20 minutes with shorter times at higher temperatures.

Preferably, the treatment reduces the iron at interior the reactor surface to Fe⁺² without the formation of submicron iron powder or dust (e.g. iron particles having a size less than about 0.5, typically less than 0.2, most preferably less than about 0.15 microns).

The present invention will now be illustrated by the following example.

The experiments were carried out in two steps first using a muffle furnace to oxidize and a quartz reactor unit (QRU) to reduce which is schematically shown in Figure 1.

Coupons of steel having the composition of that in NOVA Chemicals' high pressure reactor were initially pre-oxidized for 4 hours in a muffle furnace at 870°C in an air flow to form hematite (Fe₂O₃). The degree of pre-oxidization was calculated by weight gain of the sample. For all samples the degree of oxidation was greater than 95%.

The coupon was then transferred to the QRU where the coupon was placed in the quartz tube of the QRU and brought to temperature. Dry hydrogen was flowed through the unit and the weight loss of the sample was measured until there was theoretically up to 100% conversion of the hematite to magnetite (Fe₃O₄).

The QRU comprises a quartz tube 1 in a furnace 5. The quartz tube has an inlet 2 and an outlet 3 for gases. Coupons 4 are mounded inside the quartz tube 1 and a stream of gas passes over the coupons at the desired temperature.

A typical run of the QRU In the experiments the coupons 4 were placed in the quartz tube 1. The quartz tube 1 was pressurized to test for leaks. If there were no gas leaks the quartz tube is purged with 500 standard cubic centimeters per minute (sccm) of N₂ for one hour. The N₂ flow rate is reduced to 250 sccm during heating. When the set temperature is reached the N₂ flow rate is reduced to from 0 to 375 sccm. A flow of H₂ is started at a rate from 500 to 125 sccm. This is continued at the set temperature for a period of time up to 25 hours according to the experimental matrix. When the run time has been reached the reactor is cooled at a rate of 2°C per minute until a temperature of 100°C is reached and then the H₂ flow is stopped and the N₂ flow is set

at 500 sccm. The metal coupons 4, are removed from the quartz tube when the reactor cools to below 50°C.

The coupon was then removed from the test unit and a potassium thiocyanate solution as an indicator for Fe(III) was applied to the surface of the sample. If the surface turned red it indicates the presence of Fe (III) indicating an incomplete reduction of the surface of the sample. If there is no color change all of the Fe(III) had been reduced to Fe(II).

The coupons were treated at a number of temperatures and times and except for the temperatures at 185°C there was complete reduction of the hematite to magnetite.

The test results are set forth in Table 1.

TABLE 1

Temperature	Time	Theoretical reduction of Fe(III) to Fe(II)	Thiocyanate test
185° C	26 hr	About 92 %	Trace of red.
200° C	18 hr	100%	No color change
210° C	14 hr	100%	No color change
240° C	8 hr	100%	No color change
270° C	2 hr	100%	No color change
280° C	2 hr	100%	No color change
295° C	1 hr	100%	No color change
310° C	1 hr	100%	No color change
335° C	30 min	100%	No color change
355° C	20 min	100%	No color change

The results of the tests are plotted in Figure 2. The results show it is possible to reduce Fe(III) on the internal wall of a reactor by treatment with hydrogen gas particularly at temperatures above 230°C for times of less than about 10 hours.

INDUSTRIAL APPLICABILITY

The present invention reduces the amount of iron (III) on the surface of reactor components in contact with organic feedstock at elevated temperatures. This reduces the tendency for fouling, such as by coking, of the treated components.

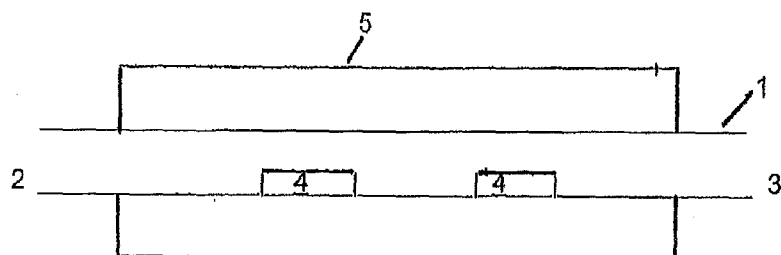
CLAIMS

1. A process to reduce fouling in a fluid alpha olefin polymerization reactor having an internal steel surface comprising less than 10 weight % Mo, comprising prior to
5 polymerization subjecting the internal steel surface to reduction by exposure to a gas comprising not less than 50 volume % hydrogen at a temperature greater than 185°C for a time from 15 minutes to 30 hours, with shorter times at higher temperatures.
2. The process according to claim 1, wherein the gas comprises not less than 70
10 volume % hydrogen and the temperature is from 240°C to 360°C for a time from 10 hours to half an hour with shorter times at higher temperatures.
3. The process according to claim 2, wherein the alpha olefin is ethylene and optionally one or more alpha olefins selected from the group consisting of C₃₋₈ alpha olefins.
4. The process according to claim 3, where in the polymerization is conducted at a
15 temperature from 75°C to 330°C and at pressures from 0.78 MPa (110 psi) to 345 MPa (50,000 psi).
5. The process according to claim 4, wherein said polymerization reactor having an internal steel surface comprising less than 0.4 weight % carbon, less than 1.5 weight % Mn, less than 2 weight % of Cr, less than 3 weight % of Ni, less than 1 weight % of Mo
20 and the balance iron.
6. The process according to claim 5, wherein the alpha olefins are dissolved or dispersed in not less than 30 weight % of a solvent or diluent.
7. The process according to claim 6, where in the alpha olefins are dispersed in not less than 50% of diluent and the reaction is conducted at a temperature from 82°C to
25 99°C and a pressure from 0.760 MPa to 6.8 MPa.
8. The process according to claim 6, wherein the alpha olefins are dissolved in not less than 65 % of a solvent and the reaction is conducted at a temperature from 120°C to 250°C and a pressure from 4 MPa to 31 MPa.
9. The process according to claim 4, wherein there is less than 10 wt% of a solvent
30 in the reactor and the reaction is conducted at a temperature from 150°C to 250°C and a pressure from 138 MPa to 344 MPa.
10. The process according to claim 9, wherein the alpha olefin is ethylene.
11. The process according to claim 5 which is carried out in a gas phase.

12. A process to reduce black specks in an ethylene polymer produced in a fluid phase reactor comprising treating the reactor according to claim 1.

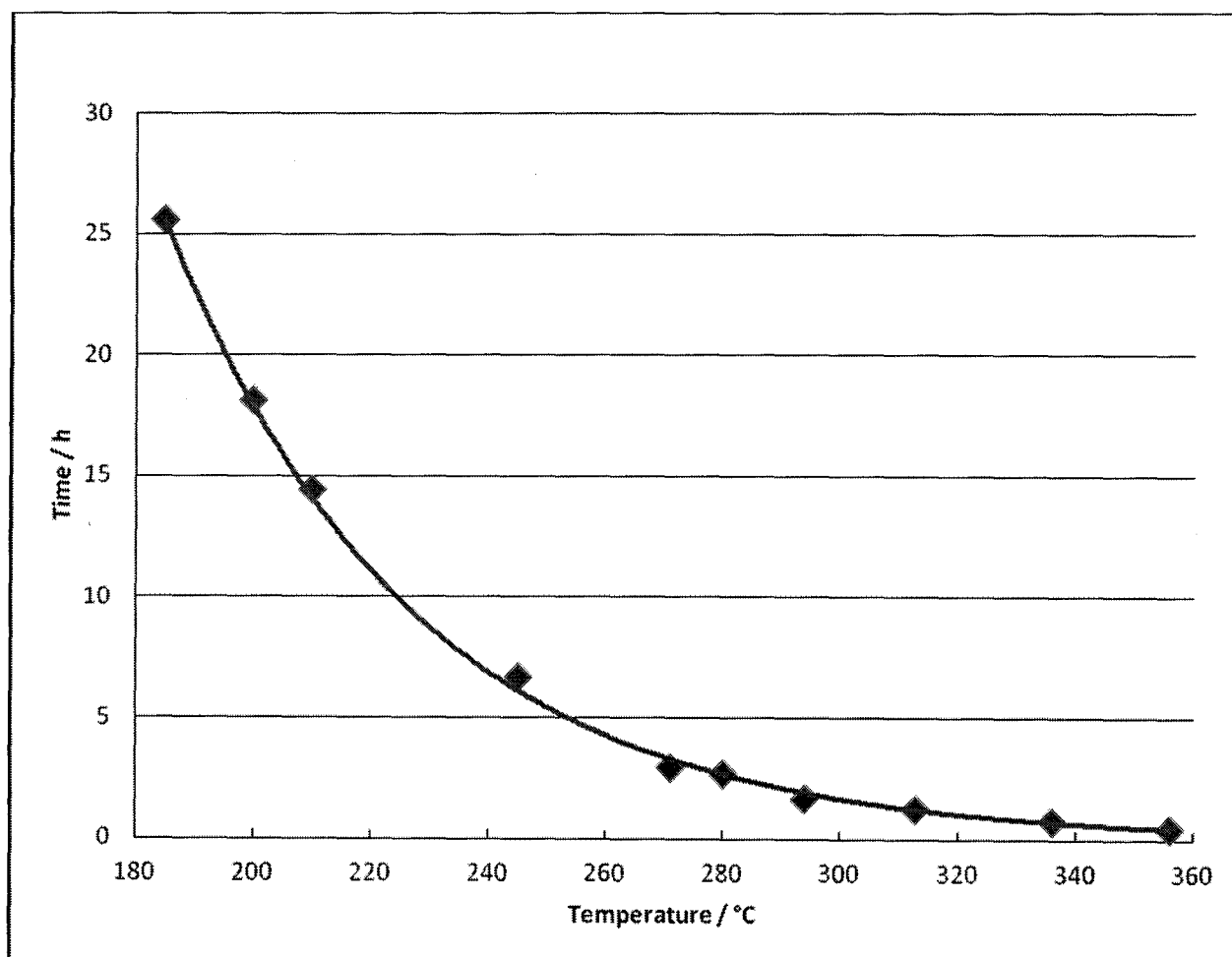
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FIG. 1



2/2

FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER IPC: C08F 2/01 (2006.01) , B08B 17/02 (2006.01) , C08F 10/02 (2006.01) According to International Patent Classification (IPC) or to both national classification and IPC														
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C08F 2/01 (2006.01) , B08B 17/02 (2006.01) , C08F 10/02 (2006.01) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) Database: EPODOC, Scopus, Internet and Canadian Patent Database Keywords: polymerization, corrosion, steel, hematite, magnetite, olefin, hydrogen, fouling and other related search terms														
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>A</td> <td>EP0718322 A2 (CANN, K.J. et al.) 26 June 1996 (25-06-1996) see abstract</td> <td>1-12</td> </tr> <tr> <td>A</td> <td>EP1564211 A1 (FOUARGE, L. et al.) 17 August 2005 (17-08-2005) see abstract and paragraphs 0001 and 0018</td> <td>1-12</td> </tr> <tr> <td>A</td> <td>WAGNER, D., et al., "A Laboratory Study of the Reduction of Iron Oxides by Hydrogen", Sohn International Symposium, San Diego, 27-31 August 2006, Vol. 2, pages 111-120. see whole document</td> <td>1-12</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A	EP0718322 A2 (CANN, K.J. et al.) 26 June 1996 (25-06-1996) see abstract	1-12	A	EP1564211 A1 (FOUARGE, L. et al.) 17 August 2005 (17-08-2005) see abstract and paragraphs 0001 and 0018	1-12	A	WAGNER, D., et al., "A Laboratory Study of the Reduction of Iron Oxides by Hydrogen", Sohn International Symposium, San Diego, 27-31 August 2006, Vol. 2, pages 111-120. see whole document	1-12
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