



(43) International Publication Date
13 November 2014 (13.11.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/180759 A1

(51) International Patent Classification:

CIOG 25/00 (2006.01) CIOG 53/08 (2006.01)
CIOG 29/20 (2006.01)

(21) International Application Number:

PCT/EP2014/059047

(22) International Filing Date:

5 May 2014 (05.05.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

10 2013 104 696.7 7 May 2013 (07.05.2013) DE

(71) Applicant: L'AIR LIQUIDE, SOCIÉTÉ ANONYME
POUR L'ETUDE ET L'EXPLOITATION DES
PROCÉDÉS GEORGES CLAUDE [FR/FR]; 75, quai
d'Orsay, F-75007 Paris (FR).

(72) Inventor: BAUER, Ingo; SchultheiB-Bilger-Str. 4, 61118
Bad Vilbel (DE).

(74) Agent: HEINE, Christian; KNH Patentanwälte Kahlhofer
Neumann RoBler Heine, Postfach 103363, 40024 Düssel-
dorf(DE).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM,
ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: PROCESS FOR REMOVING METALS FROM HIGH-BOILING HYDROCARBON FRACTIONS

(57) Abstract: Subject-matter of the invention is a process for removing metal impurities from hydrocarbon fractions, as they are obtained for example as product of the Fischer-Tropsch synthesis by using a suspended catalyst. According to the invention, the treatment of the feed hydrocarbon fraction is effected by addition of an alkanolamine and by addition of an adsorbent or a cross-linking agent. The metals to be removed are obtained as precipitate or bound to the adsorbent and in both cases can easily be separated with a mechanical separation method, for example the filtration.



WO 2014/180759 A1

Process for Removing Metals from High-Boiling Hydrocarbon Fractions

5 Field of the Invention

This invention relates to a process for removing metals from high-boiling hydrocarbon fractions, in particular for separating catalyst-induced nickel, cobalt and aluminum impurities from the primary products of a hydrocarbon synthesis, for example by the Fischer-Tropsch process.

10

Prior art

Hydrocarbons can be obtained as synthesis products from chemico-catalytical processes, such as for example the Fischer-Tropsch process, the fundamentals of which have been described in detail in the literature, e.g. in Ullmann's Encyclopedia of Industrial
15 Chemistry, Sixth Edition, 1998 Electronic Release, keyword "Coal Liquefaction", chapter 2.2 "Fischer-Tropsch Synthesis". A modern process variant is the conversion of synthesis gas in a suspension of the solid, fine-grained catalyst into the liquid product hydrocarbons (so-called slurry process). There are used highly active catalysts, which as active components contain metals, for example cobalt, on a carrier material, for example
20 alumina, as it is described in the US patent specification US 4,801,573. The International Patent Application WO 98/271 81 A1 - beside numerous other publications - proposes a process for separating the catalyst suspension from the hydrocarbon product. The product hydrocarbons obtained often contain significant amounts of heavy metals. A possible cause of this undesired heavy metal contamination are abrasion and corrosion
25 processes on the catalysts and/or the container material used in the synthesis process. These methods based on mechanical separation methods, however, only are suitable for the separation of particulate metal impurities, but not for separating metals chemically bound in the hydrocarbon phase or dissolved in finely dispersed or colloidal form.

30 In addition to the heavy metal contamination, impurities with the metal of the catalyst carrier matrix (e.g. aluminum) also are observed. The described metal contamination can be disturbing in a further chemico-catalytical conversion of the product hydrocar-

- 2 -

bons, since the same can become active as catalyst poison. In addition, heavy metal contaminations, independent of the substance in which they are contained, represent a potential environmental and health hazard. Particular reference should be made to nickel and cobalt, which are classified as carcinogenic. On the other hand, both heavy metals represent valuable catalyst components, which should be supplied to a recycling process, in order to avoid losses.

From the prior art, various methods for separating metal contaminations from hydrocarbons are known already. For example, the documents AT 205229, DD 26308, EP 0009935 B1, GB 1001 190, US 3449243, US 361 7530 and WO 20091 13095 A2 teach washing processes for removing metal impurities from hydrocarbon phases. The hydrocarbon phases either are treated with aqueous solutions of certain reagents or by addition of reagents into the organic phase with subsequent water wash, in order to dissolve the metal contaminations and transfer the same into the aqueous phase. What is disadvantageous is the expenditure required for the treatment and subsequent separation of the two-phase mixture of hydrocarbon phase and aqueous phase, as well as the necessary treatment of the aqueous phase before its disposal or reuse.

The German patent specification DE 1212662 describes a method for the treatment of hydrocarbon oils for the purpose of removing metallic impurities, which are detrimental for the catalysts used in their conversions. It is proposed to treat the contaminated hydrocarbon oils with a solution of hydrogen fluoride in an organic solvent, whereby the metals are transferred into a hardly soluble precipitate which subsequently can be separated with a mechanical separation method. The above-described problems in the treatment of a two-phase mixture of hydrocarbon phase and aqueous phase thereby are avoided. What is disadvantageous, however, is the use of the highly reactive, gaseous hydrogen fluoride for preparing the treatment solution for reasons of occupational safety and handling.

The German patent application 2346058 teaches a method for removing metal-containing foreign substances from a hydrocarbon material by contacting this material with a catalyst under hydrogenation conditions, wherein the metal-containing foreign

substances are reduced to elementary metal, which is separated from the hydrocarbon phase as precipitate. What is disadvantageous here is the expensive procedure for ensuring a rather complete hydrogenation of the metallic impurities, while at the same time avoiding the hydrogenating cracking of the hydrocarbons.

5

The US patent specification US 4,518,484 indicates a method for the treatment of metal-containing hydrocarbon feed streams, which comprises the following steps: (a) contacting the hydrocarbon feed streams in an extraction zone with at least one hydrocarbon solvent with 2 to 10 carbon atoms per molecule under supercritical conditions in the presence of an organophosphorus-based demetalizing agent, (b) discharging a top product from the extraction zone, which contains the hydrocarbons largely liberated from metals, and a bottom product which contains the solvent loaded with the metals. What is to be regarded as disadvantageous is the expensive procedure, in particular the adjustment of supercritical conditions.

15

Subject-matter of the patent application DE 10 2011 013 470 A1 is a process and means for removing metal impurities from hydrocarbon fractions, as they are obtained for example as product of the Fischer-Tropsch synthesis by using a suspended catalyst. The treatment of the feed hydrocarbon fractions is effected with a demetalizing agent, comprising at least one sulfur source and at least one basic compound, under anhydrous conditions. The metals to be removed are obtained as precipitate which can easily be separated with a mechanical separation method, for example the filtration.

20

The US patent specification US 3,617,530 A teaches a process for separating metal impurities such as nickel, vanadium or iron from high-boiling hydrocarbon fractions, wherein an amine-containing solvent and an alkali or alkaline earth metal component is added and the metal impurities are removed by water washing. The disadvantages involved in the use of aqueous media have already been discussed above.

25

Description of the Invention

Therefore, it is the object underlying the present invention to indicate a simple process for removing metal impurities from high-boiling hydrocarbon fractions, which is charac-

30

- 4 -

terized by a simple procedure - in particular without the use of aqueous media -, and which can be carried out without the use of substances with a high hazard potential.

The solution of the object according to the invention substantially results from the features of claim 1 by a process for producing a hydrocarbon fraction poor in metals, wherein the metals are chemically bound in the hydrocarbon fraction or are dispersed in the hydrocarbon fraction in colloidal or finely dispersed form, comprising the following steps:

- (a) providing the metal-containing hydrocarbon fraction in liquid form,
- (b) contacting the liquid, metal-containing hydrocarbon fraction with an alkanolamine,
- (c) contacting the liquid, metal-containing hydrocarbon fraction with a solid, powdery or fine-grained adsorbent or a cross-linking agent,
- (d) separating the metal-containing precipitate with a mechanical separation method,
- (e) discharging a hydrocarbon fraction depleted of metals.

Further advantageous aspects of the process according to the invention can be found in the sub-claims.

For the treatment by the method according to the invention, the feed hydrocarbon fraction must be present in liquid form. Wax-like hydrocarbons, as they are obtained for example as products of the Fischer-Tropsch process, possibly must be molten before the treatment.

Contacting the liquid, metal-containing hydrocarbon fraction with a trialkanolamine and subsequently with a solid, powdery or fine-grained adsorbent or a cross-linking agent is effected by intensive mixing of the components, for example by stirring.

It is known that alkanolamines such as triethanolamine (TEA) interact with polyvalent metal ions, for example the Al^{3+} ion, and thereby form stable complexes. This effect is utilized in complexometry, in order to mask aluminum ions in aqueous solutions. The resulting complex is characterized by a high water solubility and a firm ionic bond between the reactants.

- 5 -

It has been found that even under anhydrous conditions, as they exist in high-boiling hydrocarbon fractions, alkanolamines are capable of interacting with aluminum ions by forming an aluminum-alkanolamine complex. Other metals, for example nickel, also can be included in such complexes. Hasin et al. in *Mj. Int. J. Sci. Tech.* 2008, 2(01), 140-149, for example describe such nickel-aluminum complexes as preliminary stage for the synthesis of nickel-aluminate spinels.

The multifunctionality of the alkanolamines permits to bind said metal complexes either to polar solids surfaces of suitable adsorbents or to couple them with each other by addition of cross-linking agents and thus form larger particles or agglomerates which promote the formation of metal-containing flocculations or precipitates. In both cases, an immobilization of the metal-alkanolamine complex is achieved and a separation from the hydrocarbon fraction is achieved. Useful multifunctional alkanolamines include ethanolamine, diethanolamine, triethanolamine as well as the mono-, di- and trialkanolamines of higher alcohols. The precipitates formed on the adsorbents loaded with the metal-alkanolamine complexes then can be separated from the hydrocarbon fraction by means of a suitable mechanical separation method, for example by filtration, whereby a depletion of the metal content of the hydrocarbon fraction is achieved. What is, however, also possible is the separation by means of sedimentation, decantation, centrifugation, adsorption or absorption processes, and by electrostatic or electrochemical separation processes.

Further preferred aspects of the invention

In a preferred aspect of the invention a trialkanolamine such as triethanolamine (TEA) is used as alkanolamine. The same can be stirred into the hydrocarbon fraction to be treated, wherein it is homogeneously dissolved in the hydrocarbon. Due to the three alkanol groups present in the TEA molecule, it is able to particularly effectively bind to polar adsorbents or to be cross-linked with suitable cross-linking agents.

In one aspect of the invention, the metal-alkanolamine complexes are bound to polar adsorbents, wherein preferably SiO_2 -containing adsorbents of natural or synthetic origin

- 6 -

are used. Under treatment conditions, such adsorbents are inert to the hydrocarbon fraction to be treated.

Particularly preferably, there are used SiO_2 -containing adsorbents on the basis of acid-treated bentonites or on the basis of silica gel. They are commercially available, for example under the trade names Tonsil® (Clariant) or Trisyl® (Grace).

In a further aspect of the invention, a diisocyanate-based cross-linking agent is added. The OH groups of the alkanol radicals thereby are bound to the base body of the diisocyanate via urethane bonds and thus linked with each other.

According to the invention, the separation of the metal-containing, hardly soluble precipitate is effected by means of a mechanical separation method, preferably by filtration, sedimentation, decantation or centrifugation or with combinations of these methods. What is, however, also possible is the separation by applying adsorption or absorption processes as well as electrostatic or electrochemical separation processes.

Exemplary embodiments and numerical examples

Further developments, advantages and possible applications of the invention can also be taken from the following description of non-limiting exemplary embodiments and numerical examples. All features described form the invention per se or in any combination, independent of their inclusion in the claims or their back-reference.

General procedure when carrying out the invention

The hydrocarbon fraction to be demetalized is mixed with an alkanolamine in a suitable tank and by simultaneously thorough mixing brought to a temperature of 100 to 200 °C, in order to transfer wax-like products into the liquid state. In this temperature range, the formation of a metal-alkanolamine complex is effected after addition of the alkanolamine. Said complex initially is present finely dispersed, which is revealed by a distinct turbidity as compared to the starting sample. After an extended tempering phase over several minutes up to one hour at said temperature, a partial aggregation of the turbidity is to be observed. There are obtained flocculations, which can easily, but not

- 7 -

quantitatively, be separated by filtration. For its complete removal, as described above, a further chemical or physical step is necessary, which either is carried out subsequently as separate process or is carried out in the same reaction tank. In the last-mentioned case, the further chemical or physical step can be carried out in parallel or subsequent
5 to the addition of the alkanolamine.

Example 1: Formation and partial separation of the metal-alkanolamine complex

1 kg of a hydrocarbon mixture (wax fraction from the Fischer-Tropsch synthesis), with a total metal content of 485 ppm (nickel 140 ppm, cobalt 35 ppm, aluminum 310 ppm)
10 were molten at 100 °C. The melt was mixed with 4 g triethanolamine which was homogeneously distributed in the liquid hydrocarbon phase by vigorous stirring while heating to 190 °C. Subsequently, the mixture was kept at this temperature for 15 minutes while stirring. When this temperature was reached, a distinct turbidity could be observed already. During the cooling phase (at about 140 °C) flocculations were formed, which re-
15 mained suspended in the reaction mixture. These flocculations partly could be separated from the entire reaction mixture by means of a fluted filter. The analysis of the still turbid filtrate revealed a total metal content of 213 ppm (nickel = 63 ppm, cobalt = 20 ppm, and aluminum = 130 ppm).

20 When repeating the experiment under identical conditions, but with reduced triethanolamine addition of 2 g/kg, there was merely observed a formation of turbidity and no formation of flocculations.

Example 2: Formation of a metal-alkanolamine complex and subsequent adsorption to
25 active surfaces

Analogous to exemplary embodiment 1, 1 kg of hydrocarbon mixture (wax fraction from the Fischer-Tropsch synthesis) was each pretreated with 2 g/kg and with 4 g/kg of triethanolamine. A filtration step for separating the flocculations formed was omitted. To the melt cooled to 150 °C there were each added 5 g Trisyl® (silicic acid product, com-
30 mercial preparation of W.R. Grace Corporation). Subsequently, the mixtures were stirred for 10 min at 150 °C. Thereafter, the suspension could very easily be separated by from the entire reaction mixture by means of a fluted filter.

The analysis of the filtrates revealed no detectable concentration of nickel, cobalt and aluminum (< 10 ppm detection limit).

5 In an analogously conducted experiment with original wax by addition of twice the amount of Trisyl® (10 g/kg) and without the pretreatment carried out in exemplary embodiment 1, a total metal content of about 93 ppm (nickel 12 ppm, cobalt 6 ppm, aluminum 75 ppm) was analysed in the filtrate.

10 Example 3: Formation of a metal-alkanolamine complex and subsequent adsorption to active surfaces

Analogous to exemplary embodiment 1, 1 kg of hydrocarbon mixture (wax fraction from the Fischer-Tropsch synthesis) was each pretreated with 2 g/kg and with 4 g/kg of triethanolamine. A filtration step for separating the flocculations formed was omitted. To
15 the melt cooled to 150 °C there were each added 5 g Tonsil® (bleaching product, commercial preparation of Clariant AG). Subsequently, the mixtures were stirred for 10 min at 150 °C. Thereafter, the suspension could very easily be separated by from the entire reaction mixture by means of a fluted filter.

20 The analysis of the filtrates revealed no detectable concentration of nickel and cobalt (< 10 ppm detection limit). The aluminum concentration was 13 ppm during the pretreatment with 2 g/kg of triethanolamine and 7 ppm during the pretreatment with 4 g/kg of triethanolamine.

In an analogously conducted experiment with original wax by addition of the same
25 amount of Tonsil® (5 g/kg) and without the pretreatment carried out in exemplary embodiment 1, a total metal content of about 344 ppm (nickel 86 ppm, cobalt 18 ppm, aluminum 240 ppm) was analysed in the filtrate.

30 Example 4: Formation of a metal-alkanolamine complex and subsequent cross-linkage by addition of a diisocyanate

Analogous to exemplary embodiment 1, 1 kg of hydrocarbon mixture (wax fraction from the Fischer-Tropsch synthesis) was each pretreated with 4 g/kg of triethanolamine. A

- 9 -

filtration step for separating the flocculations formed was omitted. To the melt having a temperature of 180 °C there were each added 4 g of diphenylmethane-4,4'-diisocyanate (methylene-bis-phenyl-isocyanate, MDI, CAS No. 101-68-8). Subsequently, the mixtures were stirred for 10 min at 180°C. Thereafter, the resulting coarsely flocculent turbidity could very easily be separated by from the entire reaction mixture by means of a fluted filter.

The analysis of the filtrate revealed no detectable concentration of nickel, cobalt and aluminum (< 10 ppm detection limit).

In an analogously conducted experiment with the same hydrocarbon mixture by addition of the same amount of MDI (4 g/kg) and without the triethanolamine addition carried out in exemplary embodiment 1, an almost unchanged metal content of about 407 ppm (nickel 129 ppm, cobalt 28 ppm, aluminum 250 ppm) was analysed in the filtrate as compared to the starting sample.

Example 5: Formation of a metal-alkanolamine complex and subsequent cross-linkage by addition of a diisocyanate

Analogous to exemplary embodiment 1, 1 kg of hydrocarbon mixture (wax fraction from the Fischer-Tropsch synthesis) was each pretreated with 2 g/kg and with 4 g/kg of triethanolamine. A filtration step for separating the flocculations formed was omitted. To the melts having a temperature of 180 °C the same amount of Lupranat M20 S® (methylene-bis-phenyl-isocyanate, BASF SE) as the amount of triethanolamine (2 g/kg and 4 g/kg) was added by stirring. Subsequently, the mixtures were stirred for 1 min at 180 °C, wherein in both test batches a distinct flocculation could be observed. Thereafter, the resulting coarsely flocculent turbidities could very easily be separated by from the entire reaction mixture by means of a fluted filter.

The analysis of the two filtrates revealed no detectable concentration of nickel, cobalt and aluminum (< 10 ppm detection limit).

- 10 -

In an analogously conducted experiment with the same hydrocarbon mixture by addition of 4 g/kg of Lupranat M20 S® and without the triethanolamine addition carried out in exemplary embodiment 1, a total metal content of about 364 ppm (nickel 120 ppm, cobalt 24 ppm, aluminum 220 ppm) was analysed in the filtrate.

5

Industrial Applicability

The invention provides a process for removing metal impurities from hydrocarbon fractions, which as compared to the processes known from the prior art is characterized by its technical simplicity and by the absence of additional extracting agents, in particular those foreign to the process, such as aqueous solutions. Furthermore, it is advantageous that only substances with low to medium hazard potential are used, and the use of substances with high hazard potential, such as hydrogen fluoride, is avoided.

10

- 11 -

Claims

1. A process for producing a hydrocarbon fraction poor in metals, wherein the metals in the hydrocarbon fraction are chemically bound or dispersed in the hydrocarbon fraction in colloidal or finely dispersed form, comprising the following steps:
 - (a) providing the metal-containing hydrocarbon fraction in liquid form,
 - (b) contacting the liquid, metal-containing hydrocarbon fraction with an alkanolamine,
 - (c) contacting the liquid, metal-containing hydrocarbon fraction with a solid, powdery or fine-grained adsorbent or a cross-linking agent,
 - (d) separating the metal-containing precipitate with a mechanical separation method,
 - (e) discharging a hydrocarbon fraction depleted of metals.
2. The process according to claim 1, **characterized in that** as alkanolamine a trialkanolamine such as triethanolamine (TEA) is used.
3. The process according to claim 1 or 2, **characterized in that** an SiO_2 -containing adsorbent is used.
4. The process according to claim 3, **characterized in that** an adsorbent on the basis of an acid-treated bentonite is used.
5. The process according to claim 3, **characterized in that** an adsorbent on the basis of a silica gel is used.
6. The process according to claim 1 or 2, **characterized in that** a diisocyanate-based cross-linking agent is used.
7. The process according to claim 6, **characterized in that** as cross-linking agent diphenylmethane-4,4'-diisocyanate (MDI) is used.
8. The process according to any of the preceding claims, **characterized in that** as mechanical separation method the filtration, sedimentation, decantation or centrifugation or combinations thereof are used.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/059047

A. CLASSIFICATION OF SUBJECT MATTER INV. C10G25/00 C10G29/20 C10G53/08 ADD.		
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) CIOG		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal , WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 10 2011 013470 AI (AI R LIQUIDE [FR]) 26 January 2012 (2012-01-26) cited in the application paragraph [0024] - paragraph [0026] -----	1-8
A	Wo 2013/054175 AI (INDIAN OIL CORP LTD [IN]) 18 April 2013 (2013-04-18) the whole document -----	1-8
A	GB 2 484 301 A (UNIV BELFAST [GB]) 11 April 2012 (2012-04-11) the whole document -----	1-8
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) on which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search 4 July 2014	Date of mailing of the international search report 14/07/2014	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Iyer-Bal dew, A	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/059047

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 102011013470 AI	26-01 -2012	CN 103025850 A	03-04-2013
		DE 102011013470 AI	26-01-2012
		EP 2598607 A2	05-06-2013
		US 2013180887 AI	18-07-2013
		Wo 2012013581 A2	02-02-2012

Wo 2013054175 AI	18-04 -2013	NONE	

GB 2484301 A	11-04 -2012	AU 2011311317 AI	02-05-2013
		CA 2813490 AI	12-04-2012
		CN 103237870 A	07-08-2013
		EA 201300438 AI	30-01-2014
		EP 2625249 A2	14-08-2013
		GB 2484301 A	11-04-2012
		JP 2013542288 A	21-11-2013
		SG 189303 AI	31-05-2013
		US 2014001100 AI	02-01-2014
		wo 2012046057 A2	12-04-2012
