(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 June 2015 (11.06.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/084761 A1

(51) International Patent Classification:
C10G 31/08 (2006.01) *C10G 33/06* (2006.01)
C10G 33/02 (2006.01)

(21) International Application Number:
PCT/US2014/068001

(22) International Filing Date:
2 December 2014 (02.12.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/911,153 3 December 2013 (03.12.2013) US

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(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, 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, ST, 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: DESALTER EMULSION SEPARATION BY EMULSION RECYCLE

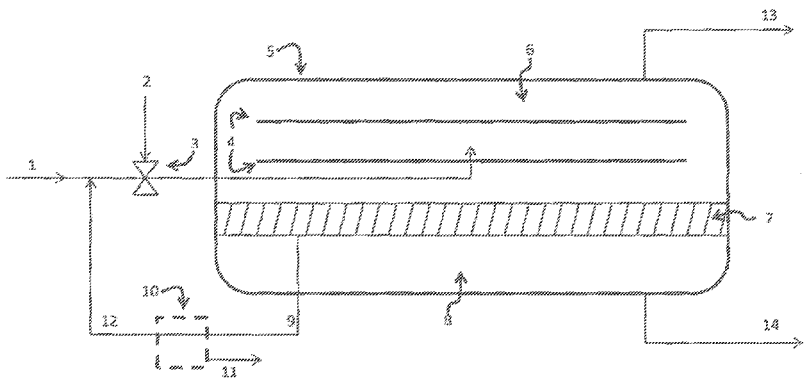


Fig. 1

(57) Abstract: A petroleum desalting process in which fluid from interracial boundary layer between the settled water layer and the settled oil layer or emulsion-water layer in the vessel is withdrawn from the desalter and recycled to the crude oil inlet of the desalter to improve separation of the oil and water phases.

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DESALTER EMULSION SEPARATION BY EMULSION RECYCLE

Field of the Invention

[0001] This invention relates to petroleum desalters and their operation.

Background of the Invention

[0002] Crude petroleum normally contains salts that may corrode refinery units; salt is removed from the crude oil by a process known as "desalting", in which hot crude oil is mixed with water and a suitable demulsifying agent to form a water-in-oil emulsion which provides intimate contact between the oil and water, transferring salt into the water. The salty emulsion is then passed into a high voltage electric field inside a closed separator vessel. The electric field forces water droplets to coalesce, forming larger water droplets. As the water droplet volumes increase, they settle to the bottom of the tank under gravitation. The desalted oil forms at the upper layer in the desalter from where it is continuously drawn off for distillation. The salty water is withdrawn from the bottom of the desalter. .

[0003] During operation of desalter units, a stable emulsion phase (also known as a "rag layer") of variable composition and thickness forms above the interface between the oil-continuous phase and the water-continuous phase at the bottom of the desalter. Certain crude oils contain natural surfactants (e.g. asphaltenes and resins) which tend to form a barrier around the water droplets in the emulsion, preventing coalescence and stabilize the emulsion in the desalting vessel. Finely-divided solid particles in the crude may also act to stabilize the emulsion, and it has been found that solids-stabilized emulsions present particular difficulties. Solids coated with crude oil components, such as those found in oil sands, are thought to be particularly effective in forming stable emulsions. This emulsion phase may become stable and persistent in the desalting vessel. The growth of stable emulsion layer reduces workable volume and may short the electric circuit and force unplanned and costly desalter shut down. To mitigate the rag

layer buildup in some cases, emulsion is withdrawn from the unit; alternatively or in addition, costly demulsifiers may be added to the oil phase upstream of the desalter although with limited success.

[0004] Additionally, processing crudes with high rag layer formation tendencies in current desalter configurations may cause poor desalting (salt removal) efficiency due to solids build up at the bottom of the vessel, and/or a solids-stabilized rag layer leading to erratic level control and insufficient residence time for proper water/oil separation. Solids-stabilized emulsion layers have become a major desalter operating concern, generating desalter upsets, increased preheat train fouling, and deteriorating quality of the brine effluent and disruption of the operation of the downstream wastewater treatment facilities.

[0005] Refinery sites which process high solids-content crudes (characterized as containing more than 150 ppm inorganic solids) have the most pervasive problems with emulsion formation. Heavy crude oils and bitumens from Western Canada which contain elevated levels of small clay fines and other small solids are particularly prone to forming large volumes of highly stable emulsion and with such feeds, growth of the rag layer is more prevalent. These feeds are, however, being introduced to refineries in greater quantities despite two main disadvantages related to the efficacy of desalting. First, the viscosity of these crudes can be quite high, so transport of water through the feed is slower than in high API gravity crude. Second, the density mismatch between water and oil is lower, so the gravitational energy gradient is reduced compared to higher API gravity crudes. Growth of the rag layer in the desalter requires either the amount of crude passed through the desalter is reduced or removal of the rag layer from the desalting vessel for external treatment.

[0006] The water content of the rag layer could range from 20 to 95% water with the balance being hydrocarbon (normally full range crude oil) and up to 5 weight percent inorganic solids. Precipitated asphaltenes, waxes, and paraffins may also be found at elevated levels in the rag layer (compared to the incoming crude oil) which combine with particulates (solids), to bind the mixture together to form a complex structure that is highly stable. Intractable emulsions of this kind comprising oil, water and solids make

adequate separation and oil recovery difficult. Often, these stable emulsions arising from the desalter are periodically discarded as slop streams. This results in expensive treating or handling procedures or pollution problems as well as the fact that crude oil is also lost with these emulsions and slop streams.

[0007] Emulsions must be separated into well-defined oil and water phases before they can be reintroduced to refinery process units (e.g. crude distillation, coker, etc.) or a waste water treatment plant. These stable emulsions may not be completely separated by heating and conventional gravity settling and require specialized separation equipment.

[0008] One of the most common industry practices is to separate the stable emulsion into separate water, oil and solids phases using 3-phase centrifuges (decanter centrifuges). The centrifuge separation is often enhanced with the use of chemical emulsion breakers, heating and/ or depressurizing the emulsion to facilitate the process. US 2012/0024758 (Love) proposes a technique in which the emulsion "rag" layer is withdrawn from the separator vessel at a rate that maintains the height of the emulsion layer approximately constant so as to permit withdrawal of the rag layer at a fixed level from the vessel. The withdrawn emulsion is then processed outside the vessel through a stacked disk centrifuge. Currently practiced centrifuge separation approach has, however, numerous reliability and cost drawbacks centering on the separation of the oil and water phases before they can be reintroduced to refinery process units (e.g. crude distillation, coker, etc.) or the waste water treatment plant.

[0009] As one problem area arises from the relatively high viscosity of the emulsions formed from heavy oil feeds, various proposals for dilution of the emulsions to reduce their viscosity have been made. US Patent No. 3,396,100 (Pettefer), for example, proposes the separation of oil and water in the rag layer by the direct addition of naphtha or kerosene to the rag layer in the separation tank without withdrawal of the rag layer; the injection of the diluent into the interfacial zone acts to release the solids otherwise retained in the layer so that they settle out into the water layer as a residue.

[0010] US Patent No. 4,200,550 (Scherrer) discloses withdrawal of the rag layer that is tested to determine the amount of stable emulsion, water, and oil. If there is more than

a certain amount of rag layer in the withdrawn sample, then a demulsifier is injected directly into the desalter.

[0011] US Patent No. 5,219,471 (Goyal) discloses dilution of the rag layer with an aromatic hydrocarbon followed by centrifugation to separate the phases.

[0012] US Patent No. 4,824,555 (Paspek) discloses a method in which the stable emulsion is removed from the desalter and a hydrocarbon with a high vapor pressure is added under high pressure in a separate vessel.

[0013] U.S. Patent No. 5,882,506 (Ohsol) describes method for treating desalter rag layer emulsions, for the recovery of processable oil values by adding a sufficient amount of a light hydrocarbon diluent to the emulsion to lower its overall viscosity and to reduce the specific gravity of the oil phase. The diluted emulsions are subjected to flashing at emulsion-breaking conditions after which the oil is recovered from the various streams created in the flashing steps.

[0014] A related process is described in U.S. Patent No. 4,938,876 (Ohsol) in which emulsions are rendered more amenable to gravitational and cyclonic separation by causing a portion of the normally water-dispersed phase to flash into vapor by suddenly reducing pressure on the emulsion which has been heated by direct contact with superheated water and/or steam. The envelope around each droplet is thus shattered so the dispersed phase can be coalesced and separated by gravity, or enhanced gravity forces, when there is a sufficient divergence of specific gravity and a low viscosity. Suitable anti-emulsion chemicals are often added to prevent re-emulsification. These processes, however, are energy-intensive requiring significant amounts of heat in the flash vaporization.

[0015] A different approach is suggested in U.S. Patent No. 4,722,781(Swartz). A portion of the rag layer is returned to the crude oil feed stream, upstream of water and chemical addition, and without any additional processing. A slip stream comprising the portion which is not returned to the crude oil feed is drawn off to avoid solids contaminant buildup. This slip stream is diluted with a light hydrocarbon material to

break the emulsion and the oil reduced in solids content is then recovered by settling and decantation. Oil is removed from a tank after the water and oil layers have settled. The oil phase and rag layer may be removed together from the desalter and taken to a second vessel in which they are separated.

[0016] Co-pending U.S. Provisional Patent Application Serial No. 61/774,957, filed 8 March 2013 (EM Family No. 2013EM063), describes an improved mode of desalter operation in which for withdrawal of a portion of the emulsion layer is withdrawn from the desalter vessel through one or more external withdrawal headers according to the thickness and position of the emulsion layer with the selected withdrawal header(s) being controlled by sensors monitoring the position and thickness of the emulsion layer. The withdrawn emulsion layer is then routed as such or with the desalter water effluent to a settling tank or directly to another unit for separation and reprocessing.

[0017] Co-pending U.S. Provisional Patent Application Serial No. 61/828,963, filed 30 May 2013 (EM Family No. 2013EM170), describes an improved mode of desalter operation in which a portion of the emulsion layer from the desalter vessel is withdrawn for treating the emulsion layer withdrawn from the desalter vessel in order to separate it into its oil and water components along with any solids brought along with it. This treatment comprises diluting the withdrawn emulsion with added water or oil to destabilize the emulsion and permit its subsequent separation. The desalting method is operated by forming a settled water layer containing the dissolved salts with a settled supernatant, desalted oil layer and an intervening emulsion layer formed from the oil and the water. A portion of the emulsion is withdrawn through one or more withdrawal ports or headers and diluted with an added fluid, typically water or an added hydrocarbon feedstock, to destabilize the emulsion which is then separated, optionally with the aid of an electrostatic precipitator in a separator vessel which itself may be a desalter type vessel operating with a high voltage electric filed to facilitate the separation.

[0018] Co-pending U.S. Provisional Patent Application Serial No. 61/882358, filed 25 September 2013 (EM Family No.2013EM259, Brian D. Albert et al.), describes a desalting process in which the oil/water emulsion layer which forms in the desalter vessel between the settled oil and water layers is separated into the oil and water

components by direct contact with a heated, high boiling hydrocarbon acting as a heating medium to transfer heat from the heating medium to the emulsion. This has the effect of breaking the emulsion and then at least partly vaporizing the water content of the emulsion in a flash drum downstream from the desalter vessel. The preferred heating medium is an atmospheric or vacuum resid, both of which have the advantage of being readily available and of not introducing additional light hydrocarbon vapors into the flash drum along with the water vaporized from the emulsion.

Summary of the Invention

[0019] According to the present invention, a fluid stream that includes the interface between the effluent water and fluid above is removed from the desalter. Additionally, this fluid can be recycled back to the crude feed into the desalter, preferably to be returned upstream of the mix valve that creates the water-in-oil emulsion before it is sent to the desalting vessel. The fluid that is withdrawn and taken to recycle includes fluid extracted from the boundary layer at the interface of the water and the supernatant emulsion including oil-wet solids which stabilize the emulsion layer. The addition of a small amount of rag layer to crude oil and water before emulsification not only does not inhibit performance, it enhances water separation by reusing the trapped demulsifier for better water resolution. In one variant of the process, a hydrocarbon diluent is used to aid the separation of the oil from the solids in the settler.

[0020] In operation, the desalting is carried out by mixing a crude oil to be desalted with water and passing the mixture of oil and water to the desalter vessel. The emulsion enters the desalting vessel between electrodes at a high voltage. Water droplets coalesce in the electric field and settle towards the bottom of the tank under gravitational forces. An emulsion layer formed from the oil and the water and emulsion-stabilizing solids forms between the settled water layer and the settled oil layer; water is removed from the water layer through a water outlet conduit at the bottom of the vessel and desalted oil is removed from the oil layer through an oil outlet conduit at the top of the vessel. An emulsion outlet for removing an emulsion stream from the emulsion layer is provided in the vessel and this is connected to an optional settling drum interposed between the

emulsion outlet of the desalter vessel and the recycle conduit to reduce the amount of non-emulsified water returned to the process.

Drawings

[0021] In the accompanying drawings:

[0022] Figure 1 is a simplified diagram of a petroleum crude desalter unit with a desalter vessel and an initial emulsion settling drum with an emulsion recycle line for returning rag layer emulsion to the inlet of the desalter;

[0023] Figure 2 is a graph showing the water resolution (cm^3, (CC)) in tests with (filled squares) and without (open squares) stable refinery emulsion added to laboratory-prepared emulsions.

[0024] Figure 3 is a graph showing the water resolution (cm^3, (CC)) in tests with (filled squares) and without (open squares) stable refinery emulsion added to laboratory-prepared emulsions.

Detailed Description

[0025] In its most common form with electrostatically induced separation in the settler vessel, the desalting process first mixes the crude or crude blend with water using a mixing valve or other equivalent device to produce an oil/water emulsion to ensure good contact between the oil and the water to favor removal of soluble salts by the water. The resulting emulsion is then exposed to an electric field to initiate the coalescence of the water droplets inside of the desalter vessel or separator. With time, the feed emulsion separates into an aqueous phase, an oil phase, and a solids phase which settles to the bottom of the vessel and is withdrawn there. The aqueous phase contains salts and suspended solids derived from the crude oil. The oil phase is recovered as desalted crude from the top of the desalter vessel and normally is sent to an atmospheric distillation unit for further processing into feedstocks for motor fuel, lubricants, asphalt and other ultimate products and uses such as petrochemical production. The aqueous phase is

further processed in a water treatment plant. Depending upon the crude or combination of crudes and the mixing intensity, an excessive stable emulsion (rag) layer may form in between the oil phase and the aqueous phase. Typically, this emulsion layer which could contain 20 to 95 % v/v water accumulates until it becomes too close to the electrodes of the desalter. This uncontrolled growth, if continued, may ultimately short-circuit the electrodes, resulting in a complete shutdown of the desalter and a loss of oil and water separation. If the emulsion layer is allowed to grow downwards, then an unacceptable oil contamination of the aqueous phase may ensue, exceeding the capability of the associated water treatment plant to process the brine to an acceptable environmental quality. Prudent operating practice therefore calls for the water level to be maintained at a substantially constant level in the vessel.

[0026] Conventionally, the practice is to process the crude with a single stage desalter. Some units operate with two separator vessels in series where the water is cascaded countercurrently to the crude to maximize salt removal. The separator vessel typically uses gravity and an imposed electric field to coalesce and separate oil-water emulsions into the oil and the wastewater effluent. Separators are available from a variety of commercial sources.

[0027] The wash water used to treat the crude oil may be derived from various sources and the water itself may be, for example, recycled refinery water, recirculated wastewater, clarified water, purified wastewater, sour water stripper bottoms, overhead condensate, boiler feed water, clarified river water or from other water sources or combinations of water sources. Salts in water are measured in parts per thousand by weight (ppt) and could range from fresh water (<0.5 ppt), brackish water (0.5-30 ppt), saline water (30-50 ppt) to brine (over 50 ppt). Although deionized water may be used to favor exchange of salt from the crude into the aqueous solution, de-ionized water is not normally required to desalt crude oil feedstocks although it may be mixed with recirculated water from the desalter to achieve a specific ionic content in either the water before emulsification or to achieve a specific ionic strength in the final emulsified product. Wash water rates may be between approximately 5% and approximately 7% by volume of the total crude charge, but may be higher or lower dependent upon the crude oil source and quality. Frequently, a variety of water sources are mixed as determined by

cost requirements, supply, salt content of the water, salt content of the crude, and other factors specific to the desalting conditions such as the size of the separator and the degree of desalting required.

[0028] The desalting process comprises the conventional steps of mixing a crude oil to be desalted with added water and passing the mixture of oil and water to a desalter vessel to form a settled water layer containing salts dissolved from the oil in the lower portion of the vessel which is removed as effluent as well as a settled supernatant, desalted oil layer in the upper portion of the vessel. The emulsion layer formed from the oil and the water and comprising emulsified oil, water, and solids, forms at the interface between the settled water layer and the settled oil layer.

[0029] According to the present invention, a fluid stream including fluid from the settled water-emulsion interface and the emulsion layer is removed from the desalter vessel for recycling to the inlet of the desalter. Preferably, all or part of the withdrawn emulsion layer is taken to a settler drum in which an initial resolution can be affected prior to the recycle. The initial separation can be assisted by the injection of an additive, if desired, e.g. by the addition of demulsifiers or other means. If desired, additional quantities of oil diluent, preferably a distillate fraction such as FCC cycle oil, gas oil, diesel or kerosene may be added to the settler to improve resolution of the withdrawn emulsion.

[0030] Depending upon the crude or combination of crudes and the mixing intensity, the emulsion layer forms between the oil phase and the aqueous phase in the desalter vessel. Crudes with high solids contents present a particularly intractable problem since the presence of the solids, often with particle sizes under 5 microns, may act to stabilize the emulsion, leading to a progressive increase in the depth of the rag layer with the stability of the emulsion varying inversely with decreasing particle size. The present invention is especially useful in its application to challenged crudes containing high levels of solids, but it may also be applied to benefit the desalting of high asphaltene content crudes which also tend to stabilize the emulsion layer in the desalter.

[0031] The fluid that is withdrawn from the desalter vessel and recycled back to the desalter inlet should include the interfacial layer between the oil and the water at the bottom of the desalter so that fluid from the boundary layer is included in the withdrawal stream. While withdrawal of the emulsion-water interface will mean that there will be some water withdrawn as well as the rag layer, close monitoring and control of the position of the interface by regulation of the water (brine) drawdown rate relative to the feed rate coupled with control of withdrawal technique, principally the withdrawal rate, can minimize the amount of water removed with the interfacial layer. The position of the interface may be monitored with a level detector such as the commercially available level probes, for example, the Agar™ probes from Agar Corporation Inc., 5150 Tacoma Drive, Houston, TX 77041. Probes of this type typically provide continuous 4 to 20 mA output signals that are proportional to the water/oil ratio at their individual locations inside the desalter with the output signal suitable for conventional monitoring and control systems.

[0032] Density profilers may be used to indicate the extent of the different phases within the desalter vessel so that the interfaces between the oil, emulsion, and water phases can be monitored and controlled. One type of density profiler is described in US 6,633,625 (Jackson/Johnson Matthey) using collimated ionizing radiation beams with an axially distributed radiation detector array in which each detector is associated with one of the beams to produce an output signal in response to incident radiation. In a typical commercial density profiler a dip pipe extending into the vessel through a flange holds an array of low-energy gamma sources with a collimator with holes at each source level. These holes direct a narrow beam of radiation toward a selected detector so that each source is matched to the radiation source in the same plane. The liquid between the dip pipes will attenuate the radiation with the intensity of the detected radiation proportional to the density of the intervening liquid, thus providing an output signal indicative of the liquid at each source/detector plane. Various density profilers are commercially available such as the Nitus™ system from Thermo Fisher Scientific, the Tracerco™ Profiler from Johnson Matthey, the Delta Controls IPT (Interface Position Transmitter) and the Ohmart Vega MDA interface profiler. The profiler typically operates from an internal drywell with multi-level radiation sources with internal or external detectors for each interface level. The type with internal drywell detectors has the advantage of easy

installation while the external detectors are less sensitive to temperature and do not require cooling to preserve their integrity.

[0033] The outputs from level detectors may be transmitted for analysis, for instance, by wire or fiber-optic link to an integrated, programmable logic controller that collects the information and calculates the density profile which is used to control the emulsion withdrawal. A preferred technique for making a controlled withdrawal of the proper interfacial fluid is described in co-pending U.S. Provisional Patent Application Serial No. 61/774,957, filed 8 March 2013 (EM Family No. 2013EM063, to which reference is made for a description of the technique), in which the emulsion layer is withdrawn from the desalter vessel through one or more external withdrawal headers according to the thickness and position of the emulsion layer with the selected withdrawal header(s) being controlled by sensors monitoring the position and thickness of the emulsion layer. This technique may be used to effect withdrawal of the interfacial layer according to the position of this layer as determined by the level detector(s). As described in the application, withdrawal may be affected through valves at different levels in the desalter vessel according to the position of the top of the layers in the vessel with each valve under the control of the density profiler and the associated control circuitry. If desired, the profiler may be adapted to indicate the liquid composition only in the region where the interfacial layer is expected to form.

[0034] Figure 1 shows a simplified schematic of a crude petroleum desalter unit in which the incoming crude oil feed to be desalted enters by way of line 1 and is mixed with fresh water feed from line 2 in mixing valve 3 to emulsify the water into the oil before the mixture is introduced into the desalter vessel 5. Under the high voltage electric field induced by means of electrode grids 4, the separation of the oil phase 6 and the water phase 8 takes place with the emulsion phase (rag layer) 7 forming at the interface between the oil and water phases. The recycle stream 9 from the emulsion layer is withdrawn at the interface with the water (brine) layer so that the recycle stream includes material from the interfacial boundary layer. The recycle stream is taken from the vessel and may then pass to optional separation vessel 10 to permit a gravitational separation of the oil and water phases with water being withdrawn by way of line 11 to reduce the volume of recycled water passing by way of line 12 into the incoming crude

oil feed in line 1. Desalted oil is withdrawn from an outlet in the upper portion of the vessel and passes to refinery processing in line 13; salty water (brine) containing salts washed out of the crude is withdrawn from an outlet at the bottom of the vessel through line 14 and sent to waste water recovery.

[0035] In normal operation of the desalter, continuous withdrawal of fluid from the interfacial boundary layer with the emulsion is the preferred mode of operation with withdrawal at a rate equal to its rate of generation so that optimal, stable conditions for the removal of dissolved salts are maintained in the desalter. The use of the intermediate withdrawal ports between the uppermost and lowermost ports is useful since they permit withdrawal of emulsion with an oil/water ratio between the maximum and minimum values set in the density profiler, with selection of the withdrawal port or ports being made according to the most appropriate emulsion composition (oil/water ratio). Withdrawal may be effected through one or more of the ports simultaneously. If the emulsion layer has grown to extend itself downwards in the vessel, a sequential withdrawal sequence may be used with withdrawal commenced at the lowest withdrawal port until the water level has reached that port, at which time, withdrawal at that level can be terminated and initiated through the higher level ports in turn as the water level in the vessel rises.

[0036] The emulsion phase in the desalter contains a high concentration of oil, residual water, suspended solids and salts which, in a typical example, might be approximately 70% v/v water, 30% v/v oil, with 5000-8000 pounds per thousand barrels (PTB) (about 14 to 23 g/l.) solids, and 200-400 PTB (about 570 to 1100 mg/l.) salts. The aqueous phase contains salts from the crude oil. The emulsion layer withdrawn from the desalter is preferably routed as such or with the desalter water effluent which is withdrawn with it to the optional settling tank where a partial separation into oil and water phases can take place. The use of the settler is particularly desirable to reduce the amount of non-emulsified water that is recycled with the feed so that, following the separation, the water phase can be returned to the brine from the desalter or sent to the waste water treatment unit. If any significant amount of oil separates from the emulsion in the settler, it can be combined with the desalted oil or sent directly to another unit for processing.

[0037] The emulsion rag layer is removed from the desalter/settler and recycled back to the crude feed to the desalter, is typically returned upstream of the mix valve that creates the water-in-oil emulsion before it is sent to the desalting vessel. Experiments have demonstrated that the addition of a small amount of rag layer to crude oil and water before emulsification not only does not inhibit performance, it enhances water separation. In one variant of the process, a hydrocarbon diluent is used to aid the separation of the oil from the solids in the settler.

[0038] As an initial step in the separation, an additive, typically a demulsifier and/or polymer can be injected into the emulsion to induce settling and so enhance the separation of free water from the emulsion and the oily solids phase. The emulsion is then passed to a settling drum to permit the initial separation to take place; the aqueous phase is removed from the bottom of the settling drum and treated as sour water. The oil which separates can be withdrawn from the top of the drum and passed to refinery processing along with the oil taken from the desalter vessel.

[0039] The initial separation under gravity in the settling drum may be aided by the use of higher temperatures and although the emulsion from the desalter vessel is already at a temperature sufficiently high, e.g. 110 to 145°C (about 230 to 290°F) to favor settling, it is possible to add a heated emulsion from an external source or sources, e.g. from refinery rundowns, crude feed operations, waste water treatment tankage, prior to separation in the settling drum. This may be preferred when operating with heavy, viscous crude feeds. If emulsion from other sources is added, it should be heated to a comparable temperature or higher, e.g. to about 140 or 150°C to facilitate gravity separation when a significant volume of water can be separated. Higher temperatures are favorable to separation, from about 90 to 175°C (about 195 to 350°F). The mixed emulsion stream is then sent to the settling drum where sufficient residence time is allowed for free water to coalesce separating into an aqueous phase and a partially dewatered, oil-enriched emulsion phase. The optimal temperature for the settling should be determined empirically and conditions adjusted accordingly.

[0040] Additional oil diluent, preferably a distillate fraction such as FCC cycle oil, gas oil, diesel or kerosene may be added to the settler if this will improve resolution of

the withdrawn emulsion. The diluent will preferably have a T5 point[1] of at least 200°C (about 390°F) and preferably higher, e.g. 250°C (about 480°F); in order to avoid increasing viscosity to an extent that will make the emulsion intractable, end points or T90[2] above about 450°C (about 840°F) may be excessive and for this reason are less preferred. Light cycle oil from the FCC main column is a preferred diluent, typically having a boiling range of 200 to 400°C (about 400 to 750°F). Typically, the ratio of emulsion to oil diluent will be from 3:1 to 20:1 v/v, and more commonly from 5:1 to 10:1 v/v.

[0041] A portion of the emulsion phase removed from the desalter vessel or the settling drum, if used, is recycled to the crude oil feed inlet, preferably upstream of the desalting water and chemical additions. Experiment has demonstrated, as shown in the Examples, that the addition of a small amount of rag layer to crude oil and water before emulsification not only does not inhibit performance, it enhances water separation by reusing the trapped demulsifier for better water resolution. Typically, the emulsion recycled to the crude oil feed is used in a proportion of up to 0.03:1 of the crude, preferably from 0.005:1 to 0.025:1 of the crude by volume. Since the effect of the recycled emulsion will vary according to the crude as well as the amount and type of chemicals (emulsifier/demulsifier) added in the process, the amount of recycle emulsion to be used should be determined on an empirical basis according to circumstances.

Example 1 - Water separation in the absence of recycled stable emulsion.

[0042] Adequate amounts of salt water (3% NaCl) and of a crude oil A were heated to 85°C 50 ppm of a commercial demulsifier B was added to 90 mL of preheated crude oil and mixed well. 4 mL of the preheated salt water was added to the oil and blended for 10 seconds at half full power (i.e. 60V setting on a Variac) using a Waring™ blender to generate a water-in-oil emulsion. 75 mL of the emulsion was then poured into a transparent vessel of an Electrostatic Dehydration and Precipitation Tester (EDPT) from Inter AV Inc. which was preheated to 90°C. The vessel's cap was tightened and temperature was then increased to 120°C.

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1 Temperature at which 5% by volume distills over.
2 Temperature at which 90% by volume distills over.

[0043] Voltages of 500, 1500, and 3000 V for duration of one minute were applied at 10, 21, and 33 minutes after the EDPT reached 120°C, respectively. A voltage of 3000 V was applied for one minute at 44, 55, and 66 minutes after the EDPT reached 120°C. The amount of the effluent water at the bottom of the vessel was measured at 5, 16, 27, 39, 50, 61 and 72 minutes after the EDPT reached 120°C.

[0044] The variations in the amount of the effluent water with time and voltage are shown in Figure 1 together with data from Example 2. The maximum amount of water observed was 1.7 mL.

Example 2: Water separation in the presence of the recycled stable emulsion

[0045] Adequate amounts of salt water (3% NaCl), crude oil A, and a stable emulsion designated ETr5 taken from a tricock of a commercial desalter that used crude oil A, were heated to 85°C. 50 ppm of a commercial demulsifier B was added to 90 mL of preheated crude oil and mixed well. 4 mL of the preheated salt water and 2 mL of the preheated stable emulsion was added to the oil solution and blended for 10 seconds at half full power using a Waring blender to generate a water-in-oil emulsion. 75 mL of the prepared emulsion was then poured in a transparent vessel of the Electrostatic Dehydration and Precipitation Tester (EDPT) from Inter AV Inc. preheated to 90°C. The vessel's cap was tightened and the temperature increased to 120°C. Voltages of 500, 1500 and 3000 V were applied for one minute at 12, 23, and 34 minutes after the EDPT reached 120°C, respectively. A voltage of 3000 V was applied for one minute at 45, 56, and 67 minutes after the EDPT reached 120°C. The amount of the effluent water at the bottom of the vessel was measured at 5, 16, 27, 39, 50, 61 and 72 minutes after the EDPT reached 120°C.

[0046] The variations in the amount of the effluent water with time and voltage are shown in Figure 2 together with data from Example 1. The maximum amount of water observed was 2.8 mL.

[0047] Examples 1 and 2 demonstrate that an addition of stable emulsion at low concentration improves water separation and does not worsen the stability of the original

emulsion. This enhancement in water separation may be due to demulsifier chemicals that could be trapped within the stable emulsion. The recycling of the stable emulsion reuses the trapped demulsifier for better water resolution.

Example 3 - Water separation in the absence of the recycled stable emulsion.

[0048] Adequate amounts of deionized (DI) water and crude oil A were heated to 85°C. 50 ppm of commercial demulsifier B was added to 90 mL of preheated crude oil and mixed well. 4 mL of the preheated DI water was added to the said solution and blended for 10 seconds at half full power using a Waring blender to generate a water-in-oil emulsion. 75 mL of this emulsion was poured into a transparent vessel of the Electrostatic Dehydration and Precipitation Tester (EDPT) preheated to 90°C. The vessel's cap was tightened and temperature was then increased to 120°C.

[0049] Voltages of 500, 1500 and 3000 V were applied for one minute at 10, 21, and 33 minutes after the EDPT reached 120°C, respectively. A voltage of 3000 V was applied for one minute at 44, 55, and 66 minutes after the EDPT reached 120°C. The amount of the effluent water at the bottom of the vessel was measured at 5, 16, 27, 39, 50, 61 and 72 minutes after the EDPT reached 120°C.

[0050] The variations in the amount of the effluent water with time and voltage are shown in Figure 2 together with data from Example 4. The maximum amount of water observed was 2.0 mL.

Example 4 - Water separation in the presence of the recycled stable emulsion ETr3

[0051] Adequate amounts of DI water, crude oil A, and stable emulsion ETr3 (taken from tricock 3 of a commercial desalter that used crude oil A) were heated to 85°C. 50 ppm of a commercial demulsifier B was added to 90 mL of preheated crude oil and mixed well. 4 mL of the preheated DI water and 0.5 mL preheated stable emulsion ETr3 was added to the crude oil solution and blended for 10 seconds at half full power using a Waring blender to generate a water-in-oil emulsion. 75 mL of this emulsion was then poured in a transparent vessel of the Electrostatic Dehydration and Precipitation Tester

(EDPT) that was preheated to 90°C. The vessel's cap was tightened and temperature was then increased to 120°C.

[0052] Voltages of 500, 1500 and 3000 V were applied for one minute at 10, 21, and 33 minutes after the EDPT reached 120°C, respectively. A voltage of 3000 V was applied for one minute at 44, 55, and 66 minutes after the EDPT reached 120°C. The amount of the effluent water at the bottom of the vessel was measured at 5, 16, 27, 39, 50, 61 and 72 minutes after the EDPT reached 120°C.

[0053] The variations in the amount of the effluent water with time and voltage are shown in Figure 3 together with data from Example 3. The maximum amount of water observed was 2.4 mL.

[0054] Examples 3 and 4 demonstrate again that an addition of stable emulsion at low concentration not only does not make the emulsion worse, but improves water separation. This example also shows an enhancement in water separation which may be due to demulsifier chemicals that could be trapped within the stable emulsion. The recycling of the stable emulsion reuses the trapped demulsifier for better water resolution.

Claims

1. A petroleum desalting process which comprises:

mixing a crude oil to be desalted with desalting water and passing the mixture of oil and water to a desalter vessel to form (i) a settled water layer containing salts dissolved from the oil in the lower portion of the vessel, (ii) a settled supernatant, desalted oil layer in the upper portion of the vessel and (iii) an emulsion layer formed from the oil and the water comprising emulsified oil and water at the interface between the settled water layer and the settled oil layer,

removing a stream of emulsion comprising fluid from the boundary layer at the interface between the settled water and the emulsion layer,

recycling a portion of the removed emulsion to the crude oil to be desalted and mixing the recycled emulsion with the crude oil feed.

2. A desalting process according to claim 1 in which the stream of emulsion withdrawn from the desalter vessel includes oil-wet solids from the oil-water or emulsion-water layer in the vessel.

3. A desalting process according to claim 1 in which the withdrawn emulsion stream is settled to effect a partial separation of water and oil from the emulsion to form a water stream and an emulsion stream which is recycled and mixed with to the crude oil feed.

4. A desalting process according to claim 1 in which the recycled emulsion is mixed with the crude oil feed in a proportion up to 0.03:1 v/v of the crude.

5. A desalting process according to claim 4 in which the recycled emulsion is mixed with the crude oil feed in a proportion of 0.005:1 to 0.025:1 v/v of the crude.

6. A desalting process according to claim 1 in which a demulsifying additive is added to the emulsion stream removed from the desalter vessel.

7. A desalting process according to claim 1 in which a hydrocarbon diluent is added to the emulsion stream removed from the desalter vessel.

8. A desalting process according to claim 7 in which the hydrocarbon diluent added to the emulsion stream removed from the desalter vessel has a boiling range from 200 to 400°C.

9. A desalting process according to claim 8 in which a hydrocarbon diluent comprising a light cycle oil is added to the emulsion stream removed from the desalter vessel.

10. A desalting process according to claim 7 in which the hydrocarbon diluent is added to the emulsion stream in a proportion of 3:1 to 20:1 v/v.

11. A desalting process according to claim 1 in which the position of the interface between the settled water layer and the settled oil layer or emulsion-water layer in the vessel is detected by means of a level detector.

12. A desalting process according to claim 1 in which the emulsion layer includes emulsion-stabilizing solids.

13. A petroleum desalter which comprises:

a desalter vessel having a crude oil feed inlet for admitting a mixture of crude oil to be desalted with desalting water to form (i) a settled water layer containing salts dissolved from the oil in the lower portion of the vessel, (ii) a settled supernatant desalted oil layer in the upper portion of the vessel and (iii) an emulsion layer formed from the oil and the water and comprising oil and water formed between the settled water layer and the settled oil layer,

a water outlet conduit at the bottom of the vessel for removing water from the water layer,

an oil outlet conduit at the top of the vessel for removing desalted oil from the oil layer,

at least one emulsion outlet for removing an emulsion stream from the interfacial boundary layer between the settled water layer and the settled oil layer or the emulsion-water layer in the vessel,

a recycle conduit connecting the emulsion outlet to the crude inlet.

14. A desalter according to claim 13 in which the desalter vessel has a plurality of vertically spaced emulsion withdrawal points connected to the emulsion withdrawal port.

15. A desalter according to claim 13 in which the emulsion outlet of the desalter vessel is connected to a settling drum having an upper outlet and a lower outlet, to settle the emulsion and remove water from the emulsion, to form an emulsion stream to be withdrawn from the settling drum through its upper outlet and passed to recycle conduit.

16. A petroleum desalter which comprises:

a desalter vessel having a crude oil feed inlet for admitting a mixture of crude oil to be desalted with desalting water to form (i) a settled water layer containing salts dissolved from the oil in the lower portion of the vessel, (ii) a settled supernatant desalted oil layer in the upper portion of the vessel and (iii) an emulsion layer formed from the oil and the water and comprising oil and water formed between the settled water layer and the settled oil layer,

a water outlet conduit at the bottom of the vessel for removing water from the water layer,

an oil outlet conduit at the top of the desalter vessel for removing desalted oil from the oil layer,

a level detector for detecting the position of the interface between the settled water layer and the settled oil layer or the emulsion-water layer in the vessel,

at least one emulsion outlet for removing an emulsion stream from the interfacial boundary layer between the settled water layer and the settled oil layer or the emulsion-water layer in the vessel,

a conduit connecting the emulsion withdrawal port to a settling drum having an upper outlet and a lower outlet, to settle the emulsion and remove water from the emulsion, to form an emulsion stream to be withdrawn from the settling drum through its upper outlet,

a second conduit connecting the upper outlet of the settling drum to a recycle conduit connecting the upper outlet of the settling drum to the crude oil feed inlet.

17. A desalter according to claim 16 which includes an inlet for a hydrocarbon diluent to the recycle conduit.

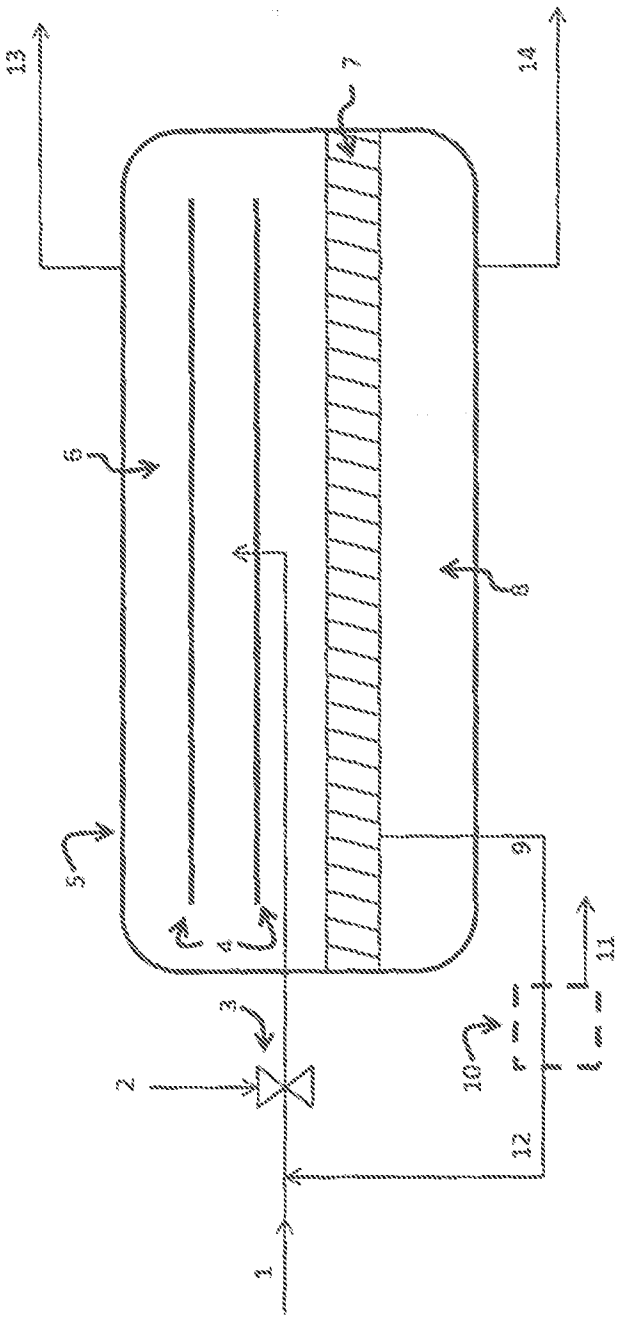


Fig. 1

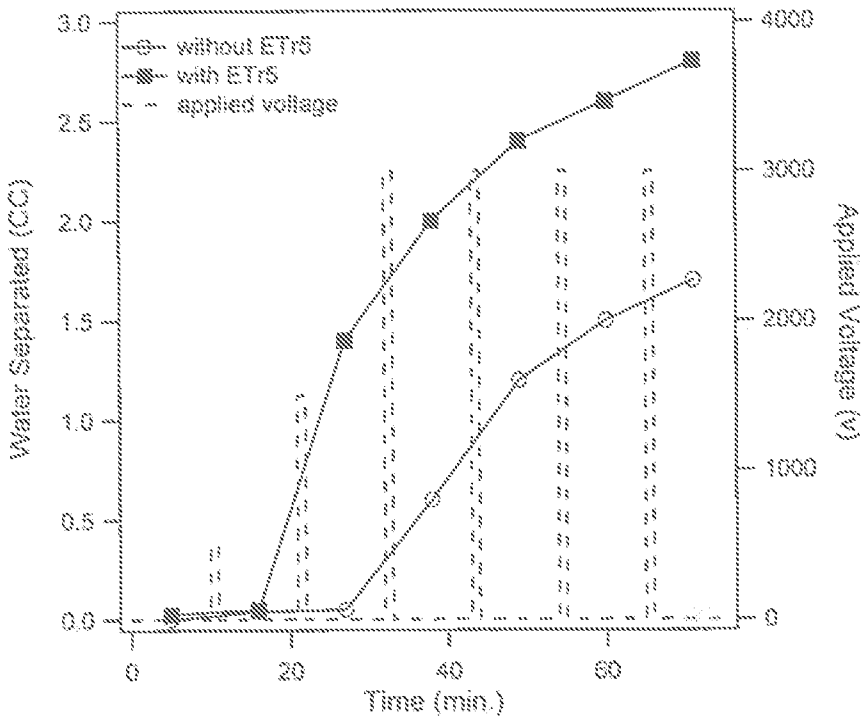

without ETrS
with ETrS
applied voltage
Water Separated (CC)
Applied Voltage (v)
Time (min.)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
4000
3000
2000
1000
0
0
20
40
60

Fig. 2

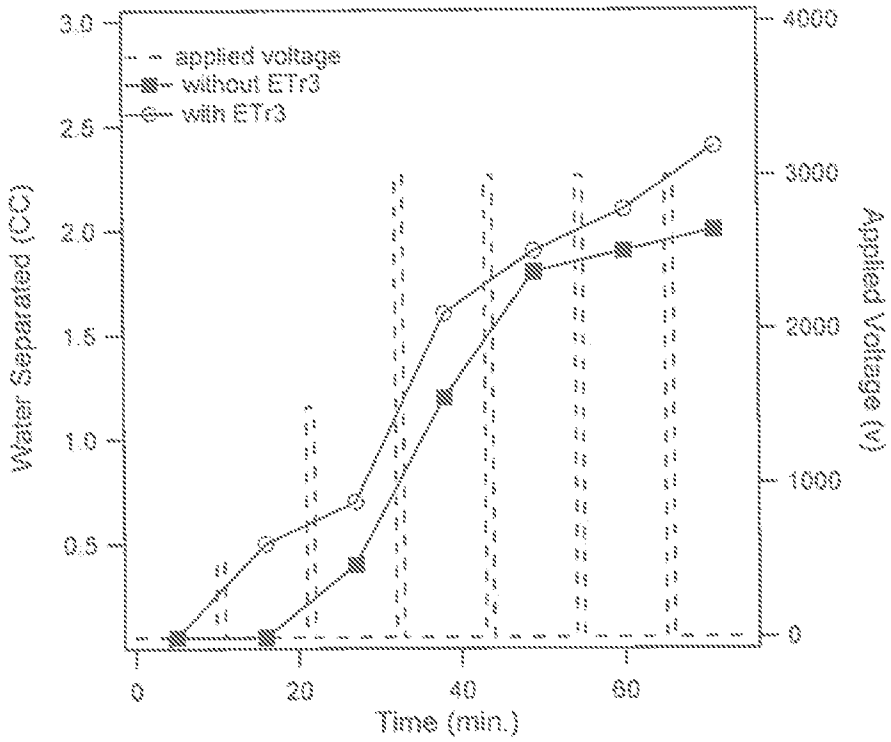

applied voltage
without ETr3
with ETr3
Water Separated (CC)
Applied Voltage (v)
Time (min.)
3.0
2.5
2.0
1.5
1.0
0.5
4000
3000
2000
1000
0
0
20
40
60

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/068001

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G31/08 C10G33/02 C10G33/06
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)
C10G

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 830 957 A (RHODES HUBERT F) 15 April 1958 (1958-04-15)	1-6, 11-13, 15-17
Y	column 2, lines 26-72 column 3, line 39 - column 4, line 17 figures 1,2,5 column 5, lines 1-5	7-10,14

X	US 4 722 781 A (SWARTZ CHARLES J [US] ET AL) 2 February 1988 (1988-02-02)	1,2, 4-10,12, 13
Y	column 2, lines 48-67	7-10,14
A	column 3, lines 19-37; figure 1	3,11, 15-17

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[X] Further documents are listed in the continuation of Box C.

[X] 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

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"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	Date of mailing of the international search report
19 February 2015	27/02/2015

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/068001

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2002/033356 A1 (HONDA TATSUHO [JP] ET AL) 21 March 2002 (2002-03-21)	14
A	paragraphs [0013], [0030]; figures 1,2	1-13, 15-17
A	WO 2010/134822 A1 (AKER PROCESS SYSTEMS AS [NO]; SMUIN DONALD R [CA]; D SOUZA LOUIS [CA];) 25 November 2010 (2010-11-25) page 12; figures 5,6	1-17
A	US 2013/082005 A1 (SAMS GARY W [US] ET AL) 4 April 2013 (2013-04-04) paragraphs [0014], [0015], [0019], [0024]; figure 1	1-17

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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