



US 20020125175A1

(19) **United States**

(12) **Patent Application Publication**  
**Collins et al.**

(10) **Pub. No.: US 2002/0125175 A1**

(43) **Pub. Date:**  
**Sep. 12, 2002**

(54) **PROCESS FOR REDUCING THE ACIDITY OF OIL**

(76) Inventors: **Ian Ralph Collins**, Sunbury on Thames (GB); **Simon Nell Duncum**, Bracknell (GB); **Christopher George Osborne**, Sandhurst (GB)

Correspondence Address:  
**NIXON & VANDERHYE P.C.**  
**8th Floor**  
**1100 North Glebe Road**  
**Arlington, VA 22201 (US)**

(21) Appl. No.: **09/997,239**

(22) Filed: **Nov. 30, 2001**

**Related U.S. Application Data**

(63) Continuation of application No. PCT/GB00/02068,  
filed on May 30, 2000.

(30) **Foreign Application Priority Data**

Jun. 2, 1999 (GB) ..... 9912842.3

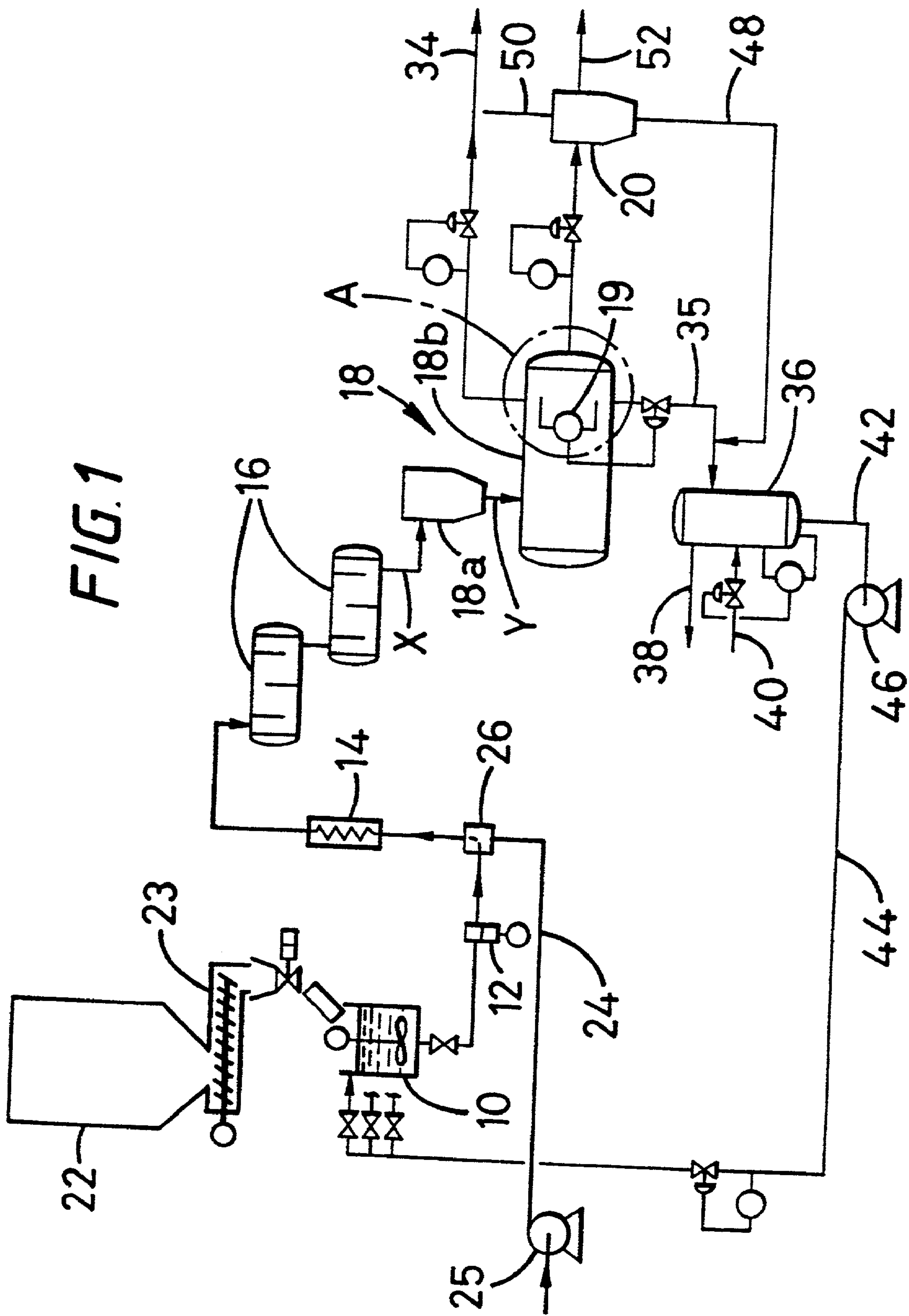
**Publication Classification**

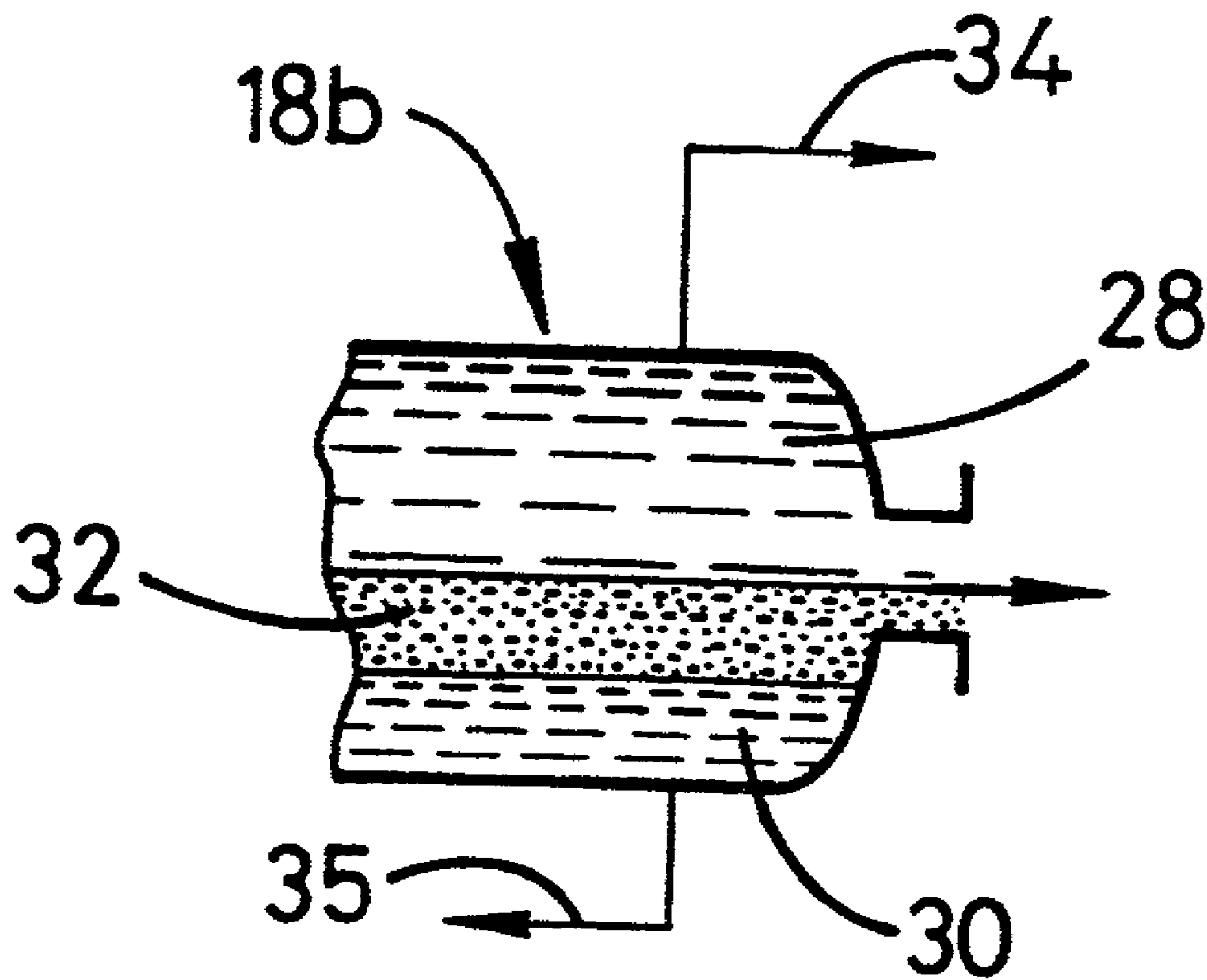
(51) **Int. Cl.<sup>7</sup>** ..... **C10G 19/00**; C10G 19/02

(52) **U.S. Cl.** ..... **208/263**; 208/283

(57) **ABSTRACT**

An improved process is disclosed for removing trace acidic compounds from liquid hydrocarbons. Traces of acidic compounds, including carboxylic acids, H<sub>2</sub>S, naphthenic acids, et al., are present in most hydrocarbon streams. The presence of these acidic compounds is considered deleterious to accepted product specifications. The trace acidic compounds which interfere are removed via injection of a dilute aqueous alkaline solution into the hydrocarbon stream and passage of this stream through a coalescing bed.





*FIG. 2*



**PROCESS FOR REDUCING THE ACIDITY OF OIL**

[0001] This invention relates to a process for the de-acidifying of crude oil and/or a crude oil distillate.

[0002] Crude oil and distilled fractions thereof may contain acid impurities such as naphthenic acid. Typical Total Acid Number (TAN) values, as measured by ASTM Method D0664, for such acidic oils are in the range of 0.5 to 4 mg KOH/g. These acid impurities can cause corrosion problems, particularly in refinery operations where temperatures of 200° C. and above are encountered. For this reason, it is desirable to reduce the acidity of crude oils, for example, by reducing the amount of naphthenic acid present.

[0003] Various methods for deacidifying crude oil and/or crude oil distillate (hereinafter "oil") are known. In a conventional de-acidification process, an alkali such as aqueous sodium hydroxide or aqueous potassium hydroxide is contacted with the oil to neutralise any acid present. The reaction produces an aqueous phase comprising water, and alkali metal naphthenate. This aqueous phase has to be removed from the deacidified oil, before the oil can be used or sold.

[0004] According to U.S. Pat. No. 4,199,440, alkali metal naphthenates are chemically similar to soap, and tend to emulsify hydrocarbon and aqueous phases. This emulsion interferes with the efficient separation of the deacidified oil and aqueous phase. The solubility of alkali metal naphthenates in the aqueous phase, however, increases as the concentration of alkali in the aqueous phase decreases. Thus, by using a dilute solution of sodium or potassium hydroxide, the tendency of alkali naphthenate to emulsify hydrocarbon phases is reduced. Accordingly, the problem of emulsion formation may be alleviated by using a dilute solution of the aqueous base.

[0005] EP 0 881 274 endeavours to improve the process of U.S. Pat. No. 4,199,440 by avoiding the formation of a stable emulsion. According to EP 0 881 274, stable emulsions are formed when bases are added to oil at an oil to base ratio of 1:1 or less. Thus, in the process of EP 0 881 274, oil is added to aqueous base at an oil to base ratio of 1:3 to 1:15. By treating the oil in this manner, an unstable dispersion of oil in a continuous aqueous base phase is produced. This unstable emulsion is easily broken, allowing the alkali metal naphthenates and aqueous base to be conveniently removed from the oil phase.

[0006] A problem with EP 0 881 274 is that it requires large volumes of aqueous base to be used. This makes the process relatively uneconomic, particularly when very large volumes of oil require treatment. Thus, it is desirable to reduce the volume of aqueous base required to deacidify a given quantity of oil.

[0007] WO 97/08270 describes a process in which the volume of aqueous base employed is relatively small. Specifically, the reference describes a deacidification process in which a Group IA or Group IIA metal oxide, hydroxide or hydroxide hydrate is contacted with crude oil in the presence of from zero to 7 wt % water. When a Group IA compound is employed, the process does not require the addition of water. When a Group IIA metal compound is employed, a small amount of water must be present to render the base effective for neutralising acid. The treatment produces a treated crude having a reduced acidity. Any solid suspended in the oil after treatment is separated by centrifugation.

[0008] Whilst this process may be effective for treating oil on a small-scale, it cannot be used to treat large quantities of oil in an efficient manner. This is because the rate of deacidification is limited by the constraints of having to centrifuge the entire volume of oil treated.

[0009] We have now found that with certain bases, a demulsifier can be employed to ensure that even in the presence of relatively low concentrations of water, oil can be treated with base to produce at least three separate phases: an oil-rich phase consisting essentially of deacidified oil, an aqueous phase consisting essentially of water, and an interface layer disposed between the oil-rich phase and aqueous phase. The interface layer comprises accumulated solids, such as neutralisation salts. The interface layer is immiscible with both the deacidified oil and water, and is thus easily removed.

[0010] According to the present invention, there is provided a process for de-acidifying crude oil and/or crude oil distillate, said process comprising:

[0011] (a) contacting crude oil and/or crude oil distillate with a Group IIA metal hydroxide in the presence of water, wherein water is present in a concentration of 0.01 to 100 wt % of the crude oil and/or crude oil distillate; and

[0012] (b) introducing a demulsifier to the mixture of crude oil and/or crude oil distillate, Group IIA metal hydroxide and water, in an amount effective to cause the mixture to separate into an oil-rich phase, an aqueous phase and an interface layer disposed between the oil-rich phase and aqueous phase.

[0013] Steps a) and b) of the present invention may be carried out at a temperature of 5 to 200° C., preferably 10 to 70° C., most preferably, 20 to 50° C., and especially 30 to 40° C. Thus, the crude oil and/or crude oil distillate may be heated using an external or dedicated heat source. However, preferably, the process is carried out without heating the crude oil and/or crude oil distillate.

[0014] In step a), crude oil and/or crude oil distillate (hereinafter "oil") is contacted with Group IIA metal hydroxide in the presence of water, to produce water and neutralisation salts. This contacting step is preferably carried out by adding the hydroxide to the oil, such that a water-in-oil type emulsion is produced. This neutralisation reaction causes the acidity of the oil to be reduced, which enables the treated oil (oil-rich phase) to be used directly, to be exported, to be sold or to be further processed, for example, by fractional distillation.

[0015] Suitable Group IIA metal hydroxides include barium hydroxide, magnesium hydroxide, and preferably, calcium hydroxide. Group IIA metal hydroxides tend to be relatively insoluble in water (and oil), such that any excess hydroxide remains substantially undissolved in the aqueous phase (and oil-rich phase). Thus, the aqueous phase consists essentially of water and is either neutral, or only very mildly alkaline.

[0016] The concentration of water employed in step a) is 0.01 to 100 wt % of oil. Water is believed to aid the neutralisation reaction by catalysing the transfer of hydrogen ions between the oil and base (Group IIA metal hydroxide). Water is also required for the formation of the aqueous phase

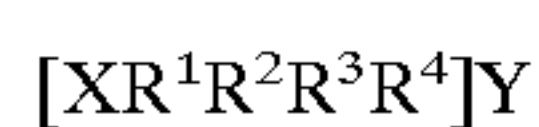


and interface layer. For these reasons, water may have to be added to the reaction mixture. Some crude oils and/or crude oil distillates, however, may themselves contain sufficient water to aid the transfer of hydrogen ions and to form the aqueous phase and interface layer. In such cases, the addition of water may not be necessary.

[0017] Water is also produced during the deacidification reaction, and therefore the water concentration increases during the process of the present invention. For water to be generated in this manner, however, at least some traces of water must be initially present in the reaction mixture of step a).

[0018] Preferably, water concentrations of 0.01 to 30, more preferably 0.01 to 25 wt %, even more preferably, 0.1 to 20 wt % of oil, most preferably, 3 to 20 wt %, and especially 10 to 15 wt % of oil are employed.

[0019] A phase transfer agent may also be added to the reaction mixture formed in step a). This phase transfer agent may further catalyse the neutralisation reaction by aiding the transfer of hydrogen ions between the oil and base (Group IIA metal hydroxide). A suitable phase transfer agent is represented by the formula:



[0020] wherein

[0021] X is N or P, and preferably, is N;

[0022] Y is Cl, Br or I and preferably, is Br;

[0023]  $R^1$  is an alkyl group having a carbon number in the range of 10 to 20, preferably, 14 to 18;  $R^1$  is preferably a straight chain alkyl group; and

[0024]  $R^2$ ,  $R^3$ ,  $R^4$  are each independently an alkyl group having a carbon number in the range of 1 to 5, preferably, 1 to 4.

[0025] Preferably,  $R^2$ ,  $R^3$  and  $R^4$  are the same alkyl group.

[0026] Another suitable phase transfer agent is represented by the formula:



[0027] wherein X and Y are defined above;

[0028]  $R^5$  and  $R^6$  are each independently an alkyl group having a carbon number in the range of 10 to 20, preferably, 14 to 18;  $R^5$  and  $R^6$  are preferably straight chain alkyl groups; and

[0029]  $R^7$  and  $R^8$  are each independently an alkyl group having a carbon number in the range of 1 to 5, preferably, 1 to 4.

[0030] Preferably,  $R^5$  and  $R^6$  are the same. Preferably, also  $R^7$  and  $R^8$  are the same.

[0031] Specific examples of phase transfer agents include cetyltrimethyl ammonium bromide (CTAB), didodecyltrimethyl ammonium bromide, tetrabutyl ammonium bromide (TBAB) and tetrapentyl ammonium bromide. Phase transfer agent concentrations of 0.01 to 40 wt %, preferably 5 to 20 wt % and most preferably, 5 to 15 wt % based on the weight of Group IIA metal hydroxide are employed.

[0032] An emulsifier may be also be added to the reaction mixture formed in step a). Examples of suitable emulsifiers include sorbitan monooleate, sorbitan monostearate, sorbi-

tan trioleate, sorbitan monopalmitate, sorbitan tristearate, non-ionic block co-polymers, polyoxyethylene stearyl alcohols, polyoxyethylene cocoa amines, fatty amine ethoxylates, polyoxyethylene oleyl alcohols, polyoxyethylene stearyl alcohols, polyoxyethylene cetyl alcohols, fatty acid polyglycol esters, glyceryl stearate, glyceryl oleate, propylene glycol stearate, polyoxyethylene oleates, polyoxyethylene stearates, diethylene glycol stearate, and fatty acid polyamine condensates. Preferably, the emulsifier is a fatty acid polyalkylene polyamine condensate (preferably those condensates sold under the Trademark Atlox LP6 or Hypermer LP6), a fatty amine ethoxylate (preferably Hypermer™ B246) or sorbitan monooleate. Suitably, the concentration of emulsifier is less than 5% wt oil, preferably less than 1% wt oil.

[0033] Optionally a mutual solvent (for the oil-rich and aqueous phases) may be added to the reaction mixture formed in step a). Suitably, the mutual solvent may be a non-ionic amphiphilic solvent, such as an alcohol or preferably a polyol, for example, an alkyltriglycol ether. The alkyl group of the alkyltriglycol ether may be straight or branched chain and suitably has 3-6 carbon atoms, preferably 3-5 carbon atoms. The alkyl group in the alkyltriglycol ether more preferably has 4 carbon atoms and is especially n-butyltriglycol ether (also known as triethylene glycol mono-n-butyl ether). Other suitable glycol ethers include ethylene glycol mono butyl ether and butyl diglycol ether. Without wishing to be bound by any theory, it is believed that these non-ionic amphiphilic solvents, owing to the miscibility gap between the aqueous and oil-rich phases, act to couple oil and water together forming a phase of density intermediate between that of the oil-rich phase and the aqueous phase (hereinafter referred to as "middle phase"). The middle phase exhibits low interfacial tension between the oil and water. The middle phase has a large capacity to solubilise, or dissolve, ionic species and thus can extract the naphthenic acids and/or neutralised naphthenic acid salts from the oil phase. The middle phase may partition into the interface layer or may separate into a distinct phase. Preferably, the mutual solvent is chosen such that the middle phase partitions into the interface layer.

[0034] In a step a) the contacting of the crude oil and/or crude oil distillate (such as gasoline, gas oil, diesel, or kerosene) with the Group IIA metal hydroxide may take place in the presence of an organic diluent such as a  $C_4$ - $C_{16}$  alkane (for example, decane). Preferably, the concentration of the optional organic diluent in step a) is 1 to 100 wt % of oil, for example, 3 to 20 wt % of oil.

[0035] In an embodiment of the present invention, the oil is contacted with a slurry comprising a suspension of the Group IIA metal hydroxide in water. Suitably, the Group IIA metal hydroxide comprises 1-20% w, preferably 2-10% w, more preferably, 5-10% w of the slurry. Optionally the slurry contains at least one of the phase transfer agents mentioned above. Optionally, the slurry contains at least one of the mutual solvents mentioned above.

[0036] Once the Group IIA metal hydroxide is contacted with the oil, the resulting mixture may be stirred or agitated in a mixing unit. The mixture may be stirred using a mechanical stirrer, an ultrasonic stirrer or by bubbling an inert gas through the reaction mixture. The mixing step may last 2 to 30 minutes, preferably, 5 to 20 minutes and most



preferably, 8 to 15 minutes. The mixing step may be carried out at a temperature of 5 to 200° C., preferably 10 to 70° C., most preferably, 20 to 50° C., and especially 30 to 40° C. Preferably, the mixing is carried out without heating the crude oil and/or crude oil distillate.

[0037] After mixing, the reaction mixture may be fed into a coalescer, which may help to agglomerate solid particles in the mixture. This treatment may aid separation of the mixture into an oil-rich phase, aqueous phase and interface layer, when the demulsifier is added in step b).

[0038] In step b), a demulsifier is added to the reaction mixture. After the addition of a demulsifier, the reaction mixture may be allowed to settle, for example, in a settling unit. This causes the reaction mixture to separate into at least three phases: an oil-rich phase, aqueous phase and an interface layer disposed between the aqueous and oil-rich phases. The oil-rich phase may be isolated from the settling unit and used directly, sold or further processed, for example, by fractional distillation.

[0039] The demulsifier ensures that the water present in the reaction mixture separates from the oil phase. Water is present in the aqueous phase, and is usually also present in the interface layer. The aqueous phase may be recovered and purified, before being recycled back to the contacting step a). Water present in the interface layer may also be recovered, purified and recycled to step a). The demulsifier also ensures that any solids present in the reaction mixture (eg unreacted Group IIA metal hydroxide and/or salt of neutralisation) gather as a layer at the interface of the oil-rich and aqueous phases. This interface layer may be regarded as consisting essentially of an aqueous suspension of the solid product (eg calcium naphthenate) of the neutralisation reaction and any unreacted solid base (eg calcium hydroxide). This layer usually also contains some deacidified oil, for example, in an amount of 1-10 wt %, preferably 1 to 5 wt %. Where a mutual solvent is employed, this may preferentially partition into the interface layer. In one embodiment, the deacidified oil is recovered from the interface layer, for example, by using a hydrocyclone, electrostatic coalescer and/or, preferably, a centrifuge. In another embodiment, the interface layer is allowed to settle for sufficient time to allow the deacidified oil to separate from the aqueous phase. The recovered deacidified oil may be used directly, exported or processed.

[0040] Any demulsifier suitable for breaking water-in-oil type emulsions may be employed. Suitably the demulsifier comprises at least one surfactant selected from the group consisting of:

[0041] (a) polyamine salts such as polyester amines, amino methylated poly acrylamide, poly di-methyl amino propyl methacrylamide, poly dimethyl amino ethyl acrylate, poly ethylene imine, poly vinyl pyrrolidone, caprolactam-based polymers and quaternised versions of the above. Suitably, the molecular weight of the polyamine salt is above 3000;

[0042] (b) multifunctional polyethers such as sulfated triglycerides;

[0043] (c) polyethers, such as copolymers of ethylene oxide and propylene oxide and the reaction products of such copolymers with diacids, diepoxides, diisocyanates, aldehydes, and diamines. Suitably, the molecular weight of the polyether is above 2000; and

[0044] (d) p-alkylphenol-formaldehyde resins and ethylene oxide and/or propylene oxide derivatives thereof.

[0045] Suitably, the demulsifier comprises a solution of the surfactant(s) dissolved in a solvent such as monoethylene glycol (MEG), tetraethylene glycol (TEG), butylethylene glycol (BGE), butyldiethylene glycol (EDGE), water, xylene and toluene.

[0046] Suitable demulsifiers may also be prepared by reacting I) an addition product of a phenol and formaldehyde or acetaldehyde, with II) a block polymer containing nitrogen. Preferably, the mole ratio of I to II is 1-20:1. Such demulsifiers are described in U.S. Pat. No. 4,474,682.

[0047] The addition product (I) may be obtained by reacting phenol with formaldehyde or acetaldehyde in a molar ratio of 1:1 to 3, preferably 1:1.8 to 2.2 at a temperature of 50° to 80° C., in the presence of an alkaline catalyst. The block polymer (II) may be obtained by an addition reaction between ethylene oxide, propylene oxide and ethylenediamine, propylenediamine, polyethylenepolyamines, polypropylenepolyamines or mixtures thereof. Preferably, 10 to 80 moles, more preferably, 30 to 70 moles, of ethylene oxide and propylene oxide are added, as a statistical average per nitrogen atom. Typically, the molar ratio of ethylene oxide to propylene oxide is 1:0.5 to 14, preferably, 1:1 to 8. A preferred demulsifier is ML3407™ (supplied by Baker Petrolite).

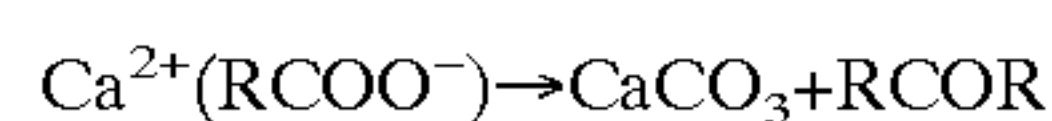
[0048] The concentration of demulsifier employed in step b) may be 0.01 to 5 wt %, preferably, 0.1 to 2 wt % and especially 0.1 to 0.5 wt % of oil.

[0049] The water in the aqueous phase and/or interface layer may have formed during the course of, for example, steps a) and/or b). Alternatively or additionally, the water may have been added some time during the deacidification process.

[0050] The interface layer may represent 1 to 40 vol %, preferably, 5 to 20 vol %, and especially 8 to 11 vol % of the total volume of the reaction mixture. Thus, the volume of fluid required to be processed in, for example, a hydrocyclone, electrostatic coalescer and/or centrifuge is relatively small compared to the total volume of the reaction mixture.

[0051] In certain embodiments of the invention, the interface layer is removed and treated, for example, in a centrifuge, to separate it into a solid layer, an aqueous layer and an oil layer. The oil layer may be recovered, for example, for direct use, export, sale or further processing.

[0052] Solids recovered from the interface layer include unreacted base (Group IIA metal hydroxide) and neutralisation salts. These solids may be converted into useful feedstocks. For example, some calcium salts of organic acids, can be pyrolysed to produce ketones and calcium carbonates according to the following equation:



[0053] Thus, in a preferred embodiment of the present invention, solids recovered from the interface layer are heated to a temperature of 700 to 900° C., preferably, 750 to 850° C. The process is particularly suitable for producing naphthenic ketones, for example, from calcium naphthenates as described in U.S. Pat. No. 5,550,296.

[0054] The process of the present invention may be employed to reduce TAN values of oils to 0 to 2 mg KOH/g, preferably, 0.1 to 0.8 mg KOH/g and especially, 0.1 to 0.5 mg KOH/g.



[0055] The process of the present invention may be carried out on a refinery, or whilst the oil is being transported, for example, in a tanker at sea.

[0056] Embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings in which:

[0057] FIG. 1 is a schematic diagram of an apparatus for carrying an embodiment of the process of the present invention, and

[0058] FIG. 2 shows the area labelled “A” in FIG. 1 in greater detail.

[0059] Referring to FIGS. 1 and 2, the apparatus comprises at least one slurry mixing tank 10 (preferably 1-3 slurry mixing tanks), an injection pump 12, a static mixer 14, a series of reaction tanks 16, a coaslecer 18 and a centrifuge 20. The slurry mixing tank 10 is coupled to a supply 22 of calcium hydroxide via a weigh hopper 23. Suitably the supply 22 of calcium hydroxide is a bulk storage hopper, preferably 2 bulk storage hoppers. The static mixer 14 is fed with acid crude oil via line 24 and feed pump 25.

[0060] In use, calcium hydroxide, water and a phase transfer agent (for example, CTAB) are introduced into the slurry mixing tank 10, where a slurry is formed comprising 5-10% calcium hydroxide by weight of slurry.

[0061] The neutralisation reaction is initiated when the slurry is contacted with the acidified oil. This occurs when the slurry is added to the acid crude via an injection quill 26. The resulting reaction mixture passes through the static mixer 14, where the mixture is dispersed, and then into the reaction tanks 16, where it has a residence time of between 5 and 20 minutes, The neutralisation reaction predominantly takes place in the reaction tanks 16.

[0062] During neutralisation, calcium hydroxide acts as a base, and reacts with any acid present in the oil to produce a neutralisation salt and water. Examples of neutralisation salts include calcium naphthenate. Like calcium hydroxide, this compound is substantially insoluble in water and oil but acts as an emulsifier for the crude oil/slurry mixture. The neutralisation reaction is catalysed by the presence of water.

[0063] The reaction mixture emerging from the reaction tanks 16, is fed into the coalescer 18. The coalescer 18 comprises a cyclonic coalescer 18a, and a separator coalescer 18b. The cyclonic coalescer promotes the agglomeration of the solid particles prior to entering the separator coalescer 18b. Once the mixture is transferred into the separator coalescer 18b, the reaction mixture is allowed to separate, in the presence of a demulsifier, into an oil-rich phase 28, an aqueous phase 30 and an interface or “ragging” layer 32 The level of the aqueous phase 30 in the separator coalescer 18b is controlled by means of a level controller 19. The demulsifier may be added to the mixture at point X, Y or both (see FIG. 1). The interface layer 32 is disposed between the oil-rich phase 28 and the aqueous phase 30 (see FIG. 2).

[0064] The oil-rich phase 28 consists essentially of deacidified oil. This phase 28 is the least dense of the three phases, and is withdrawn from the separator coalescer 18b via line 34. Once withdrawn, the oil-rich phase 28 is ready for use, export, or further processing, for example, by fractional distillation.

[0065] The aqueous phase 30 consists essentially of water, and is transferred from the separator coalescer 18b into a water break tank 36 via line 35. Oil contaminated water is withdrawn from the water break tank 36 via line 38 and is passed to a clean-up stage (not shown). Clean water is recycled to the slurry mixing tank 10 via lines 42 and 44 and water recycle pump 46. Fresh water 40 may be added to the tank 36, if required.

[0066] The interface layer 32 is an aqueous suspension comprising calcium naphthenate and water and some deacidified oil. Other insoluble solids such as unreacted calcium hydroxide may also be present in this phase. This interface layer 32 and optionally a portion of the oil rich phase 28 is introduced into the centrifuge 20, where it is separated into three streams, each consisting essentially of water 48, deacidified oil 50 and solids 52. The rate of withdrawal of the interface layer is controlled so as to achieve a constant loading of insoluble solids in the interface layer 32 of the separator coalescer 18b. The water is recycled back to the slurry mixing tank 10 via the water break tank 36, and the oil is introduced from the centrifuge 20 to the clean oil stream 34 which is withdrawn from the separator coalescer 18b. The solids stream 52 comprises calcium naphthenate and unreacted calcium hydroxide, and can be processed into useful chemical feedstocks, for example, by pyrolysis (not shown).

EXAMPLE 1

[0067] In this Example, an acidic crude oil was contacted with a slurried mixture of calcium hydroxide, phase transfer agent (CTAB) and water.

[0068] Calcium hydroxide (0.10 g), surfactant (CTAB, 10 wt % based on the weight of Ca(OH)<sub>2</sub>), and water (5 g) were mixed into a slurry in a preliminary step. 100 g of acidified oil (FPS/Hard, TAN=1.14 mg KOH/g) and 5 g decane (organic diluent) were then contacted with the slurry at a temperature of 40° C. The resulting mixture was stirred for 10 minutes and a demulsifier (E3407,2 drops) was added. The mixture was then allowed to settle. After 5 minutes, the mixture separated into three phases: an oil-rich phase, an aqueous phase, and an interface layer. The TAN value of the oil was measured 20, 30 and 40 minutes after the addition of the demulsifier, and recorded as shown in the Table below.

EXAMPLE 2

[0069] The above procedure was repeated except that the preliminary slurrying step was omitted. Instead, the oil and decane were contacted directly with a non-slurried mixture of calcium hydroxide, water and surfactant. As can be seen from the Table below, the TAN of the oil is not reduced at as high a rate as when a slurry is employed. However, the TAN is nevertheless reduced to an acceptable degree.

TABLE

Example	Surfactant additive	Water (%)	Mixing time (minutes)	TAN BP 408 Acidity mg KOH/g Elapsed Time (minutes)		
				20	30	40
1	CTAB	5	10*	0.13	0.15	0.11
2	CTAB	5	10*	0.21	0.20	0.19



1. A process for de-acidifying crude oil and/or crude oil distillate, said process comprising:

- (a) contacting crude oil and/or crude oil distillate with a Group IIA metal hydroxide in the presence of water, wherein water is present in a concentration of 0.01 to 100 wt % of the crude oil and/or crude oil distillate; and
- (b) introducing a demulsifier to the mixture of crude oil and/or crude oil distillate, Group IIA metal hydroxide and water, in an amount effective to cause the mixture to separate into an oil-rich phase, an aqueous phase and an interface layer disposed between the oil-rich phase and aqueous phase.

2. A process as claimed in claim 1, wherein step a) is carried out by adding the Group IIA metal hydroxide to the oil, such that a water-in-oil type emulsion is produced.

3. A process as claimed in claim 1, wherein the Group IIA metal hydroxide is at least one hydroxide selected from the group consisting of barium hydroxide, magnesium hydroxide, and calcium hydroxide.

4. A process as claimed in claim 1, wherein the concentration of water employed in step a) is between 0.01 and 30 wt % of the oil.

5. A process as claimed in claim 1 which further comprises adding a phase transfer agent to the reaction mixture formed in step a).

6. A process as claimed in claim 5, wherein the phase transfer agent is selected from the group consisting of cetyltrimethyl ammonium bromide (CTAB), didodecyltrimethyl ammonium bromide, tetrabutyl ammonium bromide (TBAB) and tetrapentyl ammonium bromide.

7. A process as claimed in claim 1, which further comprises adding an emulsifier to the reaction mixture formed in step a).

8. A process as claimed in claim 7, wherein the emulsifier is selected from the group consisting of sorbitan monooleate, sorbitan monostearate, sorbitan trioleate, sorbitan monopalmitate, sorbitan tristearate, non-ionic block co-polymers, polyoxyethylene stearyl alcohols, polyoxyethylene cocoa amines, fatty amine ethoxylates, polyoxyethylene oleyl alcohols, polyoxyethylene stearyl alcohols, polyoxyethylene cetyl alcohols, fatty acid polyglycol esters, glyceryl stearate, glyceryl oleate, propylene glycol stearate, polyoxyethylene oleates, polyoxyethylene stearates, diethylene glycol stearate, and fatty acid polyamine condensates.

9. A process as claimed in claim 1 which further comprises adding a mutual solvent to the reaction mixture formed in step a).

10. A process as claimed in claim 9, wherein the mutual solvent is a glycol ether.

11. A process as claimed in claim 1, wherein the demulsifier comprises at least one surfactant selected from the group consisting of:

- (a) polyamine salts;
- (b) multifunctional polyethers;
- (c) polyethers; and
- (d) p-alkylphenol-formaldehyde resins and ethylene oxide and/or propylene oxide derivatives thereof.

12. A process as claimed in claim 11, wherein said at least one surfactant is dissolved in a solvent selected from the group consisting of monoethylene glycol (MEG), tetraethylene glycol (TEG), butylene glycol (BGE), butyldiethylene glycol (BDGE), water, xylene and toluene.

13. A process as claimed in claim 1, wherein the demulsifier is prepared by reacting I) an addition product of a phenol and formaldehyde or acetaldehyde, with II) a block polymer containing nitrogen.

14. A process as claimed in claim 1, wherein the concentration of demulsifier employed in step b) is 0.01 to 5 wt % of oil.

15. A process as claimed in claim 1, which further comprises the step of

- c) recovering the oil-rich phase formed in step b) from the aqueous phase and interface layer.

16. A process as claimed in claim 15, which further comprises

- d) recovering the aqueous phase formed in step b),
- e) purifying this aqueous phase, and
- f) recycling purified water obtained from this aqueous phase to step a).

17. A process as claimed in claim 16, which further comprises

- g) removing the interface layer formed in step b) and separating this layer into a water layer, an oil layer and a solid layer.

18. A process as claimed in claim 17, wherein the oil layer formed in step g) is recovered.

19. A process as claimed in claim 17, wherein at least part of the water layer formed in step g) is recycled to step a).

\* \* \* \* \*