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(54) Title: PROCESS FOR PRODUCING SALT FROM WASTE AQUEOUS STREAMS OF ORGANIC PEROXIDES PRODUCTION

(57) Abstract: Process for producing a salt comprising NaCl and/or KCl from the aqueous effluents from one or more organic peroxide production processes, said process comprising the following steps (a) ensuring the pH of the aqueous effluents to be in the range 1-5, (b) separating the effluents in a liquid organic layer and an aqueous layer, (c) removing the organic layer, (d) raising the pH of the aqueous layer to a value in the range 6-14, and (e) crystallizing the salt from the aqueous layer having a pH in the range 6-14.

PROCESS FOR PRODUCING SALT FROM WASTE AQUEOUS STREAMS OF ORGANIC PEROXIDES PRODUCTION

The present invention relates to a process for producing salt, more in particular NaCl and/or KCl-containing salt, from chemical production process effluents, more in particular organic peroxide production effluents.

The production of various organic peroxides, such as diacyl peroxides, peroxyesters, and peroxydicarbonates, involves the reaction of an acid chloride or chloroformate with an organic hydroperoxide or H_2O_2 under alkaline conditions. Depending on the specific process, the alkaline conditions are obtained by the addition of NaOH, KOH, or a combination thereof.

As a side-product, a significant amount of salt (KCl and/or NaCl) is formed. Also other salts, such as Na_2SO_4, may be present. The high salt concentration is generally such that direct processing of the aqueous salt-containing effluents to a biological waste water treatment unit is not allowed.

Instead of diluting the effluents, it is more attractive from an environmental and economical perspective, to isolate the salt in such a form that it can find use in other processes, such as textile production, leather tanning, or chlor-alkali processes.

The salt(s) may be recovered by conventional evaporative crystallization. However, direct processing of the effluents in such a system leads to safety and operating issues. First of all, a dangerously concentrated organic peroxide residue phase may be formed in the crystallizer. Furthermore, the resulting salt may contain peroxide residues and/or high organic impurity levels that either preclude it from re-use or may lead to health and safety issues upon re-use of salt. In addition, settling of benzoic acid residues, present in effluents from processes using benzoyl chloride as reactant, may cause scaling and purging problems. And finally, higher carboxylic acids (≥8 carbon atoms) or their salts, present in effluents from processes using higher acid chlorides as reactant, may end up in the aqueous layer and may cause foaming, thereby decreasing the capacity of the crystallizer.

In order for the salt to be suitable for re-use, it should not contain more than 1000 ppm, preferably not more than 500 ppm, even more preferably not more than 300 ppm, and most preferably not more than 200 ppm of organic impurities, based on the weight of dry salt. This content of organic impurities is defined as the non-purgeable organic compound (NPOC) content, which can be determined as described in the examples below.

It has now been found that, in order to mitigate these problems and to obtain a salt that is suitable for re-use, the effluent is first acidified to a pH in the range 1-5, an organic liquid layer is subsequently separated off, and the pH of the effluent is then raised again to a value in the range 6-14.
The acidification allows benzoic acid and higher carboxylic acids, commonly present in the process streams when producing organic peroxides, into the organic layer, which allows their separation from the aqueous layer before crystallization. The subsequent high pH serves to prevent corrosion of stainless steel crystallization equipment and/or to prevent precipitation of organic acids.

The invention therefore relates to a process for producing a salt comprising NaCl and/or KCl from the aqueous effluents from one or more organic peroxide production processes, said process comprising the following steps:

a) ensuring the pH of the aqueous effluents to be in the range 1-5,
b) separating the effluents in a liquid organic layer and an aqueous layer,
c) removing the liquid organic layer,
d) raising the pH of the aqueous layer to a value in the range 6-14,
e) crystallizing the salt from the aqueous layer having a pH in the range 6-14.

It should be noted that CN 108423908 discloses a process in which effluents from an organic peroxide process are treated, the process comprising the steps of acidifying the effluents, isolating 4-methylbenzoic acid in solid form by precipitation and increasing the pH of the remaining fluid to a value of between 5 and 7, and next isolating NaCl by a precipitation step. The purpose of the process as disclosed in CN 108423908 is mostly the isolation and recovery of unreacted 4-methylbenzoic acid and not primarily the recovery of salt in high purity. It has been surprisingly found that when in step b) the separation is a liquid-liquid separation wherein an organic and an aqueous liquid phase are separated, the purity of the salt as isolated is clearly improved, the salt contains a significant lower amount of (non-purgeable) organics than in the process disclosed in CN 108423908. Alternatively said, would in the process of CN108423908 one wish to obtain salt with an increased low organics amount, further purification steps would be needed which would make the process unattractive and lead to isolation of less of such salt as any purification step will go with loss of some yield.

The aqueous effluent

The aqueous effluents result from the production of a diacyl peroxide, peroxyester, peroxycarbonate, or peroxydicarbonate by reacting an acid chloride or chloroformate with an organic hydroperoxide or H_2O_2 under alkaline conditions.

Examples of peroxyesters are tert-butyl peroxybenzoate, tert-amyl peroxybenzoate, cumyl peroxybenzoate, 1,1,3,3-tetramethylbutyl peroxybenzoate tert-butylperoxy isobutyrate, tertamylperoxy isobutyrate, 1,1,3,3-tetramethylbutyl peroxyisobutyrate, cumyl peroxyisobutyrate, cumyl peroxyneodecanoate, 1,1,3,3-tetramethylbutyl peroxyneodecanoate, tert-amyl peroxyneodecanoate, tert-butyl peroxyneodecanoate, 1,1,3,3-tetramethylbutyl peroxypivalate, tert-amyl peroxypivalate, tert-butyl peroxypivalate, cumyl peroxypivalate 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate, tert-amyl peroxy-2-ethylhexanoate, tert-butyl peroxy-2-ethylhexanoate, cumyl peroxy-2-ethylhexanoate tert-amyl peroxyacetate, tert-butyl peroxyacetate, cumyl peroxyacetate, tert-butyl peroxy-3,5,5-trimethylhexanoate, tert-amyl peroxy-3,5,5-trimethylhexanoate, and cumyl peroxy-3,5,5-trimethylhexanoate.

Preferred peroxyesters are tert-amyl peroxypivalate, tert-butyl peroxypivalate, tert-amyl peroxy-2-ethylhexanoate, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxy-3,5,5-trimethylhexanoate, cumyl peroxyneodecanoate, and tert-butyl peroxyneodecanoate.

Examples of peroxycarbonates are tert-butyl peroxy-2-ethylhexyl carbonate, tert-amyl peroxy-2-ethylhexyl carbonate, cumyl peroxy-2-ethylhexyl carbonate, tert-butyl peroxy-2-ethylhexyl carbonate, 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexyl carbonate, tert-butyl peroxyisopropylcarbonate, tert-amyl peroxyisopropylcarbonate, cumyl peroxyisopropylcarbonate, tert-butyl peroxyisopropylcarbonate, and 1,1,3,3-tetramethylbutyl peroxyisopropyl carbonate.

A preferred peroxycarbonate is tert-butyl peroxy-2-ethylhexyl carbonate.

Examples of diacyl peroxides are di-isobutyryl peroxide, di-n-butyryl peroxide, di-isopentanoyl peroxide, di-n-pentanoyl peroxide, di-2-methylbutanoyl peroxide, di-hexanoyl peroxide, di-octanoyl peroxide, dibenzoyl peroxide, acetyl isobutyryl peroxide, cyclohexylcarbonyl acetyl peroxide, acetyl benzoyl peroxide, lauroyl acetyl peroxide, hexanoyl acetyl peroxide, propionyl isobutyryl chloride, propionyl benzoyl peroxide, di(p-methylbenzoyl) peroxide, di(o-methylbenzoyl) peroxide. dilauroyl peroxide, di(3,5,5-trimethylhexanoyl) peroxide, and didecanoyl peroxide. Preferred diacyl peroxides are di-isobutyryl peroxide, acetyl isobutyryl peroxide, dibenzoyl peroxide, di(p-methylbenzoyl) peroxide, di(o-methylbenzoyl) peroxide, dilauroyl peroxide, and di(3,5,5-trimethylhexanoyl) peroxide.

Examples of peroxydicarbonates are di(3-methoxybutyl)peroxydicarbonate, di(2-ethylhexyl)peroxydicarbonate, di-sec-butyl peroxydicarbonate, diisopropyl peroxydicarbonate, dicetyl peroxydicarbonate, di-(4-tert-butylcyclohexyl) peroxydicarbonate, dimyristyl peroxydicarbonate, and di(2-propylheptyl)peroxydicarbonate.

A preferred peroxydicarbonate is di(2-ethylhexyl)peroxydicarbonate .

The aqueous effluents from one individual peroxide production process can be used in the process of the present invention, but it is also possible to use a mixture of aqueous effluents from two or more peroxide production processes. The advantage of using such a mixture is that the (combined) liquid organic phase that is formed and is removed in step b) may serve as extraction solvent for water-soluble organic impurities from the aqueous layer of said mixture.

The aqueous effluents to be used in the process of the present invention generally contain more than 3 wt%, more preferably more than 7 wt%, even more preferably more than 12 wt% of a salt comprising NaCl and/or KCl.

The concentration of organic species in the effluents generally amounts 0.1-10 wt%, more preferably 0.3-7 wt%, most preferably 0.5-4 wt%. Part of these organics consist of organic (hydro)peroxide residues. These residues are generally present in the effluents in a concentration of 0.01 to 4 wt%, preferably 0.05 to 3 wt%, most preferably 0.1 to 2.5 wt%.

Other organic species that can be present in such effluents are peroxide decomposition products (such as acetone, methanol, methylethylketone, ethanol, tert-butanol, or tert-amylalcohol) and solvents (e.g. dimethylphthalate, isododecane, odorless mineral spirits, ethyl acetate, or toluene).

The pH of the effluents to be used in the process is preferably at least 8, even more preferably at least 10, most preferably at least 11.

Step a)

Step a) requires ensuring that the pH of the aqueous effluents is in the range 1-5, preferably in the range 2-4. This means that if the pH is already in that range, no action is required.

However, since the effluents result from processes performed under alkaline conditions, it will generally be required to lower the pH by the addition of acid.

Although many acids can be used, it is preferred to use HCl for effluents containing chloride anions. Should the effluents also contain sulfate anions, H_2SO_4 or $NaHSO_4$ can suitably be used.

Step b)

The acidification of step a) will generally result in the formation of a liquid organic phase. Prior to or during the acidification step a) organic solvent may optionally be added. If no or hardly any liquid organic phase is formed, it is desired to add an organic solvent prior to or during acidification step a) in order to extract organics from the effluent, thereby decreasing fouling and improving the separation of the phases and the safety characteristics of the organic layer. In embodiments wherein the formation of liquid organic phase is so small that no good liquid-liquid separation can be done, organic solvent is added.

This organic solvent is preferably a polar solvent with only limited solubility in water. Examples of suitable solvents are lower phthalates, C_{6-18} carboxylic acids, C_{6-18} alcohols, esters with more than 5 carbon atoms, ethers with more than 5 carbon atoms, alkanes with more than 5 carbon atoms, aromatic compounds with more than 6 carbons, and mixtures of such solvents. Specific examples are 2-ethylhexanol, dimethyl phthalate, oleic acid, diesel oil, isomeric C_{12}-mixtures (e.g. isododecane), mixtures of esters containing dimethyl adipate or diethyladipate, dioctyl adipate, dibutyl sebacate, dibutyl maleate, ethyl benzoate, toluene, xylene, and mixtures thereof.

The liquid organic layer will contain most of the organic components that were present in the effluent, including organic peroxide residues, benzoic acid, alcohols, and higher carboxylic acids.

Step c)

The liquid organic layer that is formed in step b) is removed from the aqueous layer. This can be done in various ways. For instance, it can be performed by gravity settling followed by decanting the upper layer. It can also be done with an oil skimmer, i.e. a device containing a rotating belt or a slowly moving scraper that dips into the organic layer and removes it. The liquid organic layer can also be removed by a liquid-liquid separator, by the application of centrifugal force, by plate separators, by floatation, or by extraction.

The removed liquid organic layer can be transferred to a biological waste water treatment unit; as-is or dispersed in (alkaline) water. The organic layer can also be disposed of as organic liquid waste or, after washing and/or neutralizing, used as fuel. If an organic solvent is added during step b, the organic layer in a preferred embodiment is, optionally purified e.g. by washing with an aqueous alkaline solution, re-used as extraction solvent in step b).

If desired, volatile organic compounds, such as acetone, methanol, acetic acid, formic acid, isobutyric acid, n-butyric acid, pivalic acid, tert-amyl hydroperoxide, and tert-butyl hydroperoxide, may be removed by steam stripping. This can be done after acidification step a) and before or after removal of the liquid organic layer.

Steam stripping is generally conducted within a temperature range of 90-120°C and a pressure of 0.1-0.2 Mpa.

The resulting vapor stream can be condensed and sent to a biological waste water treatment unit.

Step d)

After separating off the liquid organic layer, the pH of the aqueous layer is increased to a value in the range 6-14, preferably 7-13, more preferably 8-13, even more preferably 9-13, and most preferably 11-13, in order to prevent corrosion of the crystallization equipment used in step e) and/or to prevent precipitation of organic acids.

The pH is preferably raised by the addition of KOH or NaOH.

Step e)

The salt can be crystallized in various ways. One of these ways is evaporative crystallization. The crystallization temperature and pressure depend on the boiling temperature of the salt solution and on the crystallizer configuration. The temperature will generally be between 50 and 150°C; the pressure between 50 mbar and 4 bar.

The crystallizer can be any of the conventional types, such as a forced-circulation crystallizer powered by Mechanical Vapor Recompression (MVR) or a steam-powered single-effect or multi-effect crystallizer, optionally combined with Thermal Vapor Recompression (TVR); or simply a spray dryer.

For KCl crystallization, cooling crystallization is also possible.

For NaCl crystallization, a 2-effect or 3-effect steam-powered crystallizer or an MVR is preferred.

Crystallization results in a salt slurry. If required for quality reasons, this slurry can be washed using, e.g., a (pusher) centrifuge, elutriation leg, wash column or wash vessel. Washing can be done with clean water or with a brine, for instance the brine from a previous wash cycle. The salt is collected from the slurry as 'wet salt' by means of gravity settling, centrifugation, filtration, or any other suitable solid-liquid separation technique. The filtrate may be disposed of or (partly) recycled to step a) or step e).

The wet salt may also in an embodiment be washed on a filter or another suitable piece of equipment after it has been separated from the adhering liquid.

If desired, the resulting (washed or non-washed) 'wet' salt can be dried. Drying can be performed in any conventional dryer, for instance a fluid bed dryer or a belt dryer.

The resulting salt preferably has a moisture content of less than 10 wt%, more preferably less than 5%, and after drying preferably less than 0.5 wt%.

It preferably contains, based on dry salt weight, less than 1000 ppm, more preferably less than 500 ppm, even more preferably not more than 300 ppm, and most preferably not more than 200 ppm of non-purgeable organic compounds (NPOC), so that it is suitable for re-use.

If desired, an anti-caking agent can be added to the salt. Examples of anti-caking agents are sodium hexacyanoferrate (yellow prussiate of soda, YPS), or silica.

Anti-caking agents are generally added in amounts of 5-100 ppm.

The obtained salt can be used disposed of as waste, but is preferably re-used. It can be re-used in various applications, such as textile production, leather tanning, fertilization, or chlor-alkali processes.

EXAMPLES

In all Examples, the NPOC was measured using a Shimadzu TOC (total organic carbon) analyzer. First, salt was dissolved in water and made acidic by adding

HCl, after which it was purged with N_2. After that, the sample was combusted at 680°C in a tube, in presence of a Pt-catalyst. The formed CO_2 was determined with a nondispersive infrared (NDIR) detector and the amount of carbon was calculated versus an external standard (potassium hydrogen phthalate).

Example 1

30 l of a mixture of several aqueous waste streams from organic peroxide production processes were added to a pilot scale reactor. The mixture had a pH of 10.5 and the following approximate composition:

NaCl	15 wt%
Sodium benzoate	1 wt%
Sodium 2-ethylhexanoate	2 wt%
Tert-butyl hydroperoxide	2 wt%
Water	balance

The mixture was acidified to pH 2.5 by the addition of a 30 wt% HCl solution, followed by the addition of 0.5 wt% dimethylphthalate (based on the total weight of the mixture). A clear organic layer was obtained that could be easily separated from the aqueous phase.

A 30 wt% NaOH solution was added to the resulting aqueous phase, until the pH was 10.5. The mixture was then transferred to a pilot scale batch crystallizer, heated to about 110°C, at a pressure of 1 bar. During crystallization, water vapor was removed from the top. After some time, NaCl crystals started to form. The resulting salt slurry was transferred to a centrifuge. During centrifugation, the salt was washed with a total wash water flow of 200 ml/kg salt. The resulting NaCl had a water content of 4 wt% and a non-purgeable organic carbon (NPOC) content of 233 ppm.

Example 2

30 l of a mixture of several aqueous waste streams from organic peroxide production processes was added to a pilot scale reactor. The mixture had a pH of about 11 and the following approximate composition:

KCl	15 wt%
Sodium neodecanoate	2 wt%
Cumyl hydroperoxide	1.5 wt%
Water	balance

The mixture was acidified to pH 2.5 by the addition of a 30 wt% HCl solution. A clear liquid organic layer was formed on top of an aqueous phase. This organic layer was separated from the aqueous phase by using a small scale oil skimmer (ex-Abanaki).

A 30 wt% KOH solution was added to the resulting aqueous phase, until the pH was 10.5. The mixture was then transferred to a pilot scale batch crystallizer, heated to about 50°C, at a pressure of 60 mbar. During crystallization, water vapor was removed from the top. After some time, KCl crystals started to form. The resulting salt slurry was transferred to a centrifuge. During centrifugation, the salt was washed with a total wash water flow of 300 ml/kg salt. The resulting KCl had a water content of 4 wt% and an NPOC content of 215 ppm. The KCl was transferred to a pilot-scale fluid bed dryer. The resulting dried salt had a water content of 0.2 wt%.

Example 3

30 l of a mixture of several aqueous waste streams from organic peroxide production processes was added to a pilot scale reactor. The mixture had the following approximate composition:

NaCl	15 wt%
Sodium benzoate	0.3 wt%
Sodium 2-ethylhexanoate	2 wt%
Tert-butyl hydroperoxide	2 wt%
Water	Balance

The mixture was acidified to pH 2.5 by the addition of a 30 wt% HCl solution and the organic layer obtained in Example 2 was added. A clear organic layer was obtained that could be easily separated from the aqueous phase.

A 30 wt% NaOH solution was added to the resulting aqueous phase, until the pH was 10.5. The mixture was then transferred to a pilot scale batch crystallizer, heated to about 110°C, at a pressure of 1 bar. During crystallization, water vapor was removed from the top. After some time, NaCl crystals started to form. The resulting salt slurry was transferred to a centrifuge. During centrifugation, the salt was washed with a total wash water flow of 400 ml/kg salt. The resulting NaCl had a water content of 4 wt% and an NPOC content of 177 ppm.

Example 4

30 l of a mixture of several aqueous waste streams from organic peroxide production processes was added to a pilot scale reactor. The mixture had the following approximate composition:

NaCl	15 wt%
KCl	3 wt%
Na_2SO_4	2 wt%
Mixed organics	4 wt%
Water	balance

The mixture was acidified to pH 2.5 by the addition of a 30 wt% HCl solution. A clear liquid organic layer was formed on top of an aqueous phase. The organic layer was separated from the water phase.

A 30 wt% NaOH solution was added to the resulting aqueous phase, until the pH was 10.5. The mixture was then transferred to a pilot scale batch crystallizer, heated to about 110°C, at a pressure of 1 bar. During crystallization, water vapor was removed from the top. After some time, salt crystals started to form. The resulting salt slurry was transferred to a centrifuge. The resulting salt mixture had a water content of 6 wt% and an NPOC content of 760 ppm.

Comparative Example 5

30 l of the mixture of waste streams used in Example 1 was transferred to a pilot scale batch crystallizer, heated to about 110°C, at a pressure of 1 bar. After some time NaCl crystals started to form. Around the same time, precipitates of sodium benzoate started to form. It was attempted to continue crystallization until a

reasonable slurry density had formed, but the sodium benzoate and other precipitates were plugging the equipment. The slurry could not be centrifuged to a water content <10% because the salt/organic mixture did not dewater well.
This experiment illustrates that the acidification step performed in Example 1 is essential for proper isolation of the salt.

Comparative example 6

30 l of the mixture of waste streams used in Example 2 was transferred to a pilot scale batch crystallizer, heated to about 50°C, at a pressure of 60 mbar. During crystallization, water vapor was removed from the top. After some time, KCl crystals started to form. The resulting salt slurry was transferred to a centrifuge. In the centrifuge, foaming was observed, which resulted in slow and incomplete centrifugation. It was attempted to wash the salt with a total wash water flow of 300 ml/kg salt. The salt was transferred to a pilot-scale fluid bed dryer. The resulting dried salt had an NPOC content of 2600 ppm.
This experiment illustrates that the acidification step performed in Example 2 is essential for obtaining a salt with sufficiently low organics content.

Example 7

Dibenzoyl peroxide was made with benzoyl chloride, H_2O_2-30%, NaOH-25% and a surfactant. The reaction mixture was filtered to separate the product and the water layer. The water layer had the following composition:

NaCl	7 wt%
Sodium benzoate	0,6 wt%
Sodium perbenzoate	0.03 wt%
Water	balance

To 100.4 g of the water layer with a pH of > 6, as measured with a Knick pH meter and a Mettler Toledo Inlab pH electrode, 8.04g dimethyl phthalate (DMP) was added. The combined mixture was acidified under stirring at 20-25°C to pH 2.3 by the addition of a 0.84g 18 wt% HCl solution. After continuing stirring for 5 more minutes the layers were allowed to separate. The lower DMP layer was separated from the water layer. The obtained water phase with a benzoic acid

content of 0,07% was neutralized with 30 wt% NaOH solution to a pH > 7. The mixture was then transferred to a batch crystallizer, heated to about 110°C, at a pressure of 1 bar. During crystallization, water vapor was removed from the top. After some time, salt crystals started to form. The resulting salt slurry was transferred to a centrifuge. The obtained salt had a water content of 6 wt% and an NPOC content of 620 ppm. The DMP layer was washed with a 3% NaOH solution until pH > 7 and was reused in the extraction of benzoic acid.

Comparative example 8

77,3 g of the water layer of the benzoyl peroxide process as in Example 7 was acidified under stirring at 20-25°C to pH 2.3 by the addition of a 0.64g 18 wt% HCl solution. A white precipitate was formed in the aqueous phase. After continuing stirring for 5 more minutes the solid was filtered. The obtained clear water phase with a benzoic acid content of 0,17% was neutralized with 30 wt% NaOH solution to a pH > 7. The mixture was then transferred to a batch crystallizer, heated to about 110°C, at a pressure of 1 bar. During crystallization, water vapor was removed from the top. After some time, salt crystals started to form. The resulting salt slurry was transferred to a centrifuge. The obtained salt had a water content of 6 wt% and an NPOC content of 1490 ppm.

This experiment illustrates that the addition of a solvent in the acidification step performed in Example 7, and the following liquid-liquid separation are essential for obtaining a salt with sufficiently low organics content.

CLAIMS

1. Process for producing a salt comprising NaCl and/or KCl from the aqueous effluents from one or more organic peroxide production processes, said process comprising the following steps:
   a) ensuring the pH of the aqueous effluents to be in the range 1-5,
   b) separating the effluents in a liquid organic layer and an aqueous layer,
   c) removing the organic layer,
   d) raising the pH of the aqueous layer to a value in the range 6-14,
   e) crystallizing the salt from the aqueous layer having a pH in the range 6-14.

2. Process according to claim 1 wherein step a) involves acidification of the effluents to a pH in the range 1-4.

3. Process according to claim 2 wherein HCl is used for the acidification.

4. Process according to any one of the preceding claims wherein, prior to step d), the aqueous layer is subjected to steam stripping in order to remove volatile organic compounds.

5. Process according to claim 4 wherein the volatile organic compounds comprise isobutyric acid, n-butyric acid, pivalic acid, tert-amyl hydroperoxide, and/or tert-butyl hydroperoxide.

6. Process according to any one of the preceding claims wherein an organic solvent is added before or during step b).

7. Process according to claim 6 wherein the organic layer collected in step c) is recycled and reused as the organic solvent, optionally after it has been washed with an alkaline aqueous solution.

8. Process according to any one of the preceding claims wherein step c) involves the use of an oil skimmer.

9. Process according to any one of the preceding claims wherein step e) involves subjecting the aqueous phase to evaporation, thereby crystallizing the salt to form a salt slurry.

10. Process according to any one of the preceding claims wherein the salt obtained in step e) is dried to a moisture content below 0.5 wt%.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2020/052039

A. CLASSIFICATION OF SUBJECT MATTER

INV.	C02F1/66	C02F9/00			
ADD.	C02F1/20	C02F1/52	C02F1/40	C02F1/04	C02F103/36
	C02F101/34	C02F101/12	B01D9/00	C02F1/24	C02F1/26

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)

C02F B01D

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	CN 108 423 908 A (CHANGSHU BINJIANG CHEMICAL CO LTD) 21 August 2018 (2018-08-21) paragraphs [0002] - [0004], [0006] - [0007], [0014], [0015], [0025], [0028], [0052], [0057]; claims 1,10 -----	1-10
A	US 2013/313199 A1 (MARCIN MARK A [US] ET AL) 28 November 2013 (2013-11-28) paragraphs [0114], [0121] - [0122]; figure 1C -----	1-10
A	CN 103 787 442 A (CHINA PETROCHEMICAL CORP) 14 May 2014 (2014-05-14) abstract paragraphs [0011] - [0013] -----	1-10

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search 25 February 2020	Date of mailing of the international search report 05/03/2020
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 Fiocchi, Nicola

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2020/052039

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 108423908 A	21-08-2018	NONE	
US 2013313199 A1	28-11-2013	NONE	
CN 103787442 A	14-05-2014	NONE	