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(54) **Title:** A PROCESS FOR PURIFYING ORGANIC PRODUCT SOLUTION OBTAINED FROM OXIME SYNTHESIS SECTION

(57) **Abstract:** A continuous process for purifying organic product solution comprising oxime dissolved in an organic medium comprising: (1) discharging the organic product solution from a oxime synthesis section [I] to a liquid-liquid mixing section [III]; (2) mixing the organic product solution with a water and/ or an aqueous solution and discharging the resulting mixture to liquid-liquid-separator [IV]; (3) separating organic top layer from aqueous bottom layer in liquid-liquidseparator [IV] and recovering oxime from the organic top layer in an oxime recovery section; (4) feeding the aqueous bottom layer of liquid-liquidseparator [IV] to the oxime synthesis section [I], optionally a fraction of which being fed back into the liquid- liquid mixing section [III].



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A PROCESS FOR PURIFYING ORGANIC PRODUCT SOLUTION OBTAINED
FROM OXIME SYNTHESIS SECTION

5 The present invention relates to a process for purification of the cyclohexanone oxime dissolved in an organic medium.

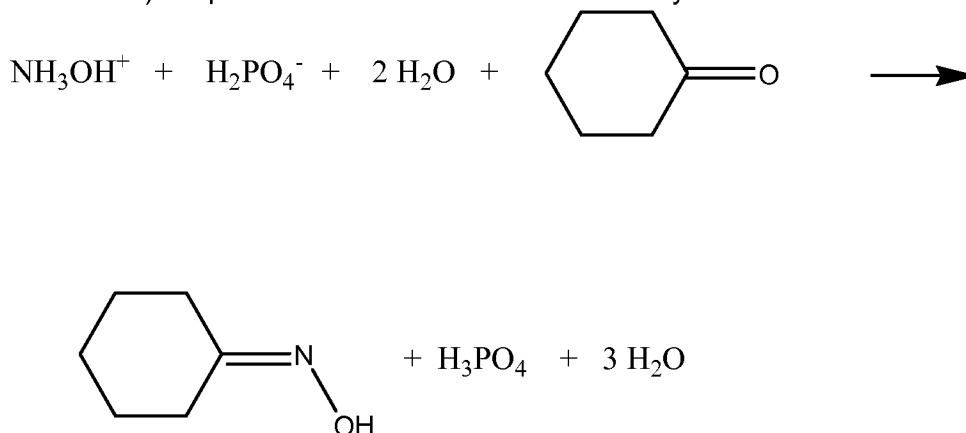
Oximes, in particular cyclohexanone oxime, can be produced in a process in which a buffered, aqueous reaction medium containing buffer acids or acidic salts, for example phosphate buffers, and buffer salts derived from these acids, is
 10 continuously recycled between a hydroxylammonium synthesis zone and an cyclohexanone oxime synthesis zone. In the hydroxylammonium synthesis zone hydroxylammonium may be formed by catalytic reduction of nitrate ions or nitric oxide with hydrogen. In the cyclohexanone oxime synthesis zone, hydroxylammonium
 15 formed in the hydroxylammonium synthesis zone may react with cyclohexanone to form cyclohexanone oxime. The cyclohexanone oxime can then be separated from the aqueous reaction medium which is recycled to the hydroxylammonium zone. In the case where the hydroxylammonium salt synthesis starts from a solution of phosphoric acid and nitrate the above-mentioned chemical reactions are represented as follows:

20

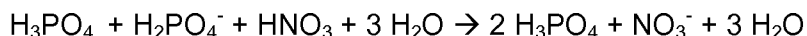
Reaction 1) Preparation of the hydroxylammonium in the hydroxylammonium salt synthesis zone:



25 Reaction 2) Preparation of the oxime in the oxime synthesis zone:



Reaction 3) Supply of HNO_3 to make up the depletion of the source of nitrate ions, after removal of the oxime formed in reaction 2):



- 5 The first reaction is catalyzed heterogeneously. Preferably, the catalyst is present as finely divided solids as a disperse phase in a liquid reaction mixture.

In the cyclohexanone oxime synthesis zone, cyclohexanone oxime may be prepared by countercurrently contacting an aqueous medium comprising
10 hydroxylammonium in water with an organic medium comprising cyclohexanone dissolved in an organic solvent, e.g. toluene or benzene. An organic solution comprising the formed cyclohexanone oxime dissolved in organic solvent may be withdrawn from the reaction zone, and distilled to recover cyclohexanone oxime.

As is clear from the reaction processes the inorganic process liquid
15 may comprise neutral species e.g. hydroxylamine or ammonia which may also be protonated e.g. hydroxylammonium or ammonium. This means that according to the present invention both hydroxylamine and hydroxylammonium may be read as hydroxylamine and/or hydroxylammonium, and that ammonia and ammonium may be read as ammonia and/or ammonium.

20 The inorganic liquid leaving the oximation synthesis zone has to be purified thoroughly to protect the catalyst in the hydroxylammonium synthesis zone. This is done in an inorganic liquid extraction section with a solvent, e.g. toluene. Preferably, the inorganic liquid leaving the extraction section is for further purification fed to a stripping section and a carbon adsorption section.

25 WO 2004/067497 relates to a process for treating an organic solution comprising cyclohexanone oxime, cyclohexanone and an organic solvent. In one example of this application, an organic product solution comprising cyclohexanone oxime and cyclohexanone dissolved in organic solvent [toluene] is discharged from the cyclohexanone oxime synthesis zone. The organic product solution is, preferably after
30 having been washed with water or an aqueous solution, fed to a distillation column. But a specified washing process is not disclosed in this application.

The present invention provides a continuous purification process for the organic product solution by washing.
The purpose of the organic product solution washing is to recover almost all inorganic
35 process liquid (IPL) salts from the organic product solution. This washing is based on the physical property that IPL salts dissolve better in water than in the organic product solution.

Therefore, according to the present invention there is provided a continuous process for purifying organic product solution comprising oxime dissolved in an organic medium comprising:

- 5 (1) discharging the organic product solution from an oxime synthesis section [I] to a liquid-liquid mixing section [III];
- (2) mixing the organic product solution with a water and/or an aqueous solution and discharging the resulting mixture to a liquid-liquid separator [IV];
- (3) separating the resulting organic top layer from the resulting aqueous bottom layer in the liquid-liquid separator [IV] and introducing the organic top layer to
10 an oxime recovery section;
- (4) feeding the aqueous bottom layer of the liquid-liquid separator [IV] to the oxime synthesis section [I], optionally a fraction of which is fed back into the liquid-liquid mixing section [III].

15 The references are illustrated in the figures below.

Preferably, a fraction of the aqueous medium contained in the organic product solution from oxime synthesis section [I] is separated out in a liquid-liquid separator [II] before the organic product solution being introduced to the liquid-liquid mixing section [III] and the aqueous bottom layer of the liquid-liquid separator [II] is
20 introduced to the oxime synthesis section [I].

Preferably, the organic top layer obtained in the liquid-liquid separator [IV] is sent to the liquid-liquid separator [V] before the oxime is recovered therefrom in the oxime recovery section and the liquid-liquid separator [V] may be a coalescer.

Preferably, the organic top layer obtained from the liquid-liquid
25 separator [IV] is subjected to at least one rewash section before being introduced to oxime recovery section. Preferably, the organic top layer obtained from the liquid-liquid separator [IV] is subjected to two rewash sections before being introduced to the oxime recovery section.

Preferably, the organic top layer of the liquid-liquid separator [IV] is
30 introduced into a liquid-liquid separator [V] before being introduced into the rewash section.

The rewash section comprises:

- 35 (i) introducing the organic top layer of liquid-liquid separator [IV] into a liquid-liquid mixing section [III^a] and mixing the organic top layer with a water and/or an aqueous solution;
- (ii) discharging the resulting mixture from the liquid-liquid mixing section [III^a] to a liquid-liquid separator [IV^a] and separating the resulting organic top layer from the resulting aqueous bottom layer;

(iii) introducing a fraction or all of the aqueous bottom layer of the liquid-liquid separator [IV^a] into the oxime synthesis section [I] and/or into the liquid-liquid mixing section [III] and/or into the liquid-liquid mixing section [III^a] and/or being disposed off;

5 (iv) introducing the organic top layer of liquid-liquid separator [IV^a] into the oxime recovery section.

Preferably, the organic top layer obtained in the liquid-liquid separator [IV^a] is sent to a liquid-liquid separator [V^a] before the oxime is recovered in the oxime recovery section and the liquid-liquid separator [V^a] may be a coalescer.

10 Equipment for the purification of oxime comprises at least one liquid-liquid mixer and at least one liquid-liquid separator. Preferably, the liquid-liquid separator [IV] or the liquid-liquid separator [IV^a] is a gravity liquid-liquid settler. The liquid-liquid mixing section [III] or the liquid-liquid mixing section [III^a] preferably contains a stirrer and/or a static mixer, preferably a stirrer.

15 Preferably, the aqueous solution in line [7] comprises demineralized water and/or steam condensate. The aqueous solution may also contain a small amount of ammonia. The amount of the ammonia is preferably less than 30 wt%, more preferably less than 5 wt% and most preferably less than 1 wt%.

20 Preferably, the aqueous solution in line [14] comprises demineralized water and/or steam condensate. The aqueous solution in line [14] may also contain a small amount of ammonia. The amount of the ammonia is preferably less than 30 wt%, more preferably less than 5 wt% and most preferably less than 1 wt%.

25 Preferably, the aqueous solution in line [19] comprises demineralized water and/or steam condensate. The aqueous solution in line [19] may also contain a small amount of ammonia. The amount of the ammonia is preferably less than 30 wt%, more preferably less than 5 wt% and most preferably less than 1 wt%.

Preferably, the aqueous bottom layer of liquid-liquid separator [IV] is fed to the oxime synthesis section [I]; optionally a fraction of which is fed back into the liquid-liquid mixing section [III].

30 More preferably, a fraction of the aqueous bottom layer of liquid-liquid separator [IV] is introduced into the liquid-liquid mixing section [III] and the remainder is sent to the oxime synthesis section [I]. Preferably, the amount of the aqueous bottom layer being introduced to the liquid-liquid mixing section [III] is more than 80 wt%, more preferably more than 90 wt% and most preferably more than 95 wt%.

35 Preferably, a fraction or all of the aqueous bottom layer of liquid-liquid separator [IV^a] is fed into oxime synthesis section [I] and/or into the liquid-liquid mixing section [III] and/or into liquid-liquid mixing section [III^a].

More preferably, a fraction of the aqueous bottom layer of liquid-liquid separator [IV^a] is introduced to the liquid-liquid mixing section [III^a] and the remainder is sent into the liquid-liquid mixing section [III] and/or is disposed off. Preferably, the amount of the aqueous bottom layer being introduced to the liquid-liquid mixing section [III^a] is more than 80 wt%, more preferably more than 90 wt% and most preferably more than 95 wt%.

Preferably, the organic top layer obtained from the liquid-liquid separator [IV] is subjected to two or more rewash sections before being introduced to oxime recovery section. Preferably, a fraction or all of aqueous bottom layer of the liquid-liquid separator of each rewash process can be introduced into the oxime synthesis section [I] and/or any one or more previous liquid-liquid mixing sections and/or be disposed off.

Preferably, the organic top layer obtained from each rewash process can be introduced into a liquid-liquid separator before being introduced into next rewash process. Preferably, the liquid-liquid separator is a coalescer. Preferably, a fraction or all of the aqueous bottom layer obtained in the liquid-liquid separator is introduced into the oxime synthesis section [I] and/or any one or more previous liquid-liquid mixing section and the remainder is disposed off.

Preferably, the oxime is cyclohexanone oxime.

Preferably, the organic solution is toluene.

Preferably, the temperature in the liquid-liquid mixing section [III] is in the range of from 30°C to 90 °C, more preferably in the range of from 40°C to 80 °C and most preferably in the range of from 50°C to 70 °C.

Preferably, the temperature in the liquid-liquid mixing section [III^a] is in the range of from 30°C to 90 °C, more preferably in the range of from 40°C to 80 °C and most preferably in the range of from 50°C to 70 °C.

By subjecting the organic product solution to the washing process, more IPL (inorganic process liquid) salts are recovered and as a result, the loss of IPL salts is reduced.

Another advantage is that less fouling will occur in the oxime recovery section.

Additionally it was found that more pure caprolactam is produced.

BRIEF DESCRIPTION OF THE DRAWING

Figures 1-4 represents a schematic overview of a process for purifying cyclohexanone oxime dissolved in an organic medium.

Figure 1

A preferred embodiment of the process according to the invention is schematically illustrated in figure 1.

In this embodiment, cyclohexanone oxime is produced in the
5 cyclohexanone oxime synthesis section [I]. In the cyclohexanone oxime synthesis section [I] an aqueous medium containing hydroxylammonium and inorganic ions in water is contacted with an organic medium comprising cyclohexanone and organic solvent, preferably toluene. In the cyclohexanone oxime synthesis section [I], hydroxylammonium reacts with cyclohexanone to form cyclohexanone oxime. The
10 aqueous medium and the organic medium are supplied to the cyclohexanone oxime synthesis section [I] via lines [1] and [2], respectively. The resulting aqueous layer is discharged from the cyclohexanone oxime synthesis section [I] via line [3].

An organic product solution comprising cyclohexanone oxime and cyclohexanone dissolved in organic solvent (toluene) is discharged from the
15 cyclohexanone oxime section [I] via line [4] at a discharge level for an organic product solution. This organic product solution, which contains some water, hydroxylammonium and inorganic ions, is supplied via line [4] to liquid-liquid mixing section [III]. The liquid-liquid mixing section [III] might contain a stirrer and/or a static mixer, preferably a stirrer. Water or an aqueous solution, is supplied to the liquid-liquid mixing section [III]
20 via line [7]. A mixture of an aqueous medium and an organic medium is discharged from the liquid-liquid mixing section [III] via line [8] and is supplied to the liquid-liquid separator [IV]. In liquid-liquid separator [IV] an organic top layer and an aqueous bottom layer are formed. The aqueous bottom layer is discharged from the liquid-liquid separator [IV] via line [9]. Optionally, a fraction of the aqueous bottom layer discharged
25 from the liquid-liquid separator [IV] is supplied to liquid-liquid mixing section [III] via line [9A], while the remainder is discharged via line [9B] to the cyclohexanone oxime synthesis section [I]. The organic top layer is discharged via line [10]. This organic top layer, which contains some remaining water, hydroxylammonium and inorganic ions, can be directly discharged to the cyclohexanone oxime recovery section in which a
30 product comprising mainly cyclohexanone oxime is obtained.

Figure 2

A preferred embodiment of the process according to the invention is schematically illustrated in figure 2.

35 In this embodiment, cyclohexanone oxime is produced in the cyclohexanone oxime synthesis section [I]. In the cyclohexanone oxime synthesis section [I] an aqueous medium containing hydroxylammonium and inorganic ions in water is contacted with an organic medium comprising cyclohexanone and organic

solvent, preferably toluene. In the cyclohexanone oxime synthesis section [I], hydroxylammonium reacts with cyclohexanone to form cyclohexanone oxime. The aqueous medium and the organic medium are supplied to the cyclohexanone oxime synthesis section [I] via line [1] and [2], respectively. The resulting aqueous layer is discharged from the cyclohexanone oxime synthesis section [I] via line [3].

An organic product solution comprising cyclohexanone oxime and cyclohexanone dissolved in organic solvent (toluene) is discharged from the cyclohexanone oxime section [I] via line [4] at a discharge level for an organic product solution. This organic product solution, which contains some water, hydroxylammonium and inorganic ions, is via line [4B] supplied to a liquid-liquid separator [II], and/or via line [4A] supplied to liquid-liquid mixing section [III]. In liquid-liquid separator [II] an organic top layer and an aqueous bottom layer are formed. The aqueous bottom layer is discharged from the liquid-liquid separator [II] via line [5]. Preferably, this aqueous bottom layer is supplied to the cyclohexanone oxime synthesis section [I]. The organic top layer is discharged via line [6] and is supplied to liquid-liquid mixing section [III].

The liquid-liquid mixing section [III] might contain a stirrer and/or a static mixer, preferably a stirrer. Water or an aqueous solution, preferably demineralized water or an aqueous NH_3 solution, is supplied to the liquid-liquid mixing section [III] via line [7]. A mixture of an aqueous medium and an organic medium is discharged from the liquid-liquid mixing section [III] via line [8] and is supplied to the liquid-liquid separator [IV]. In liquid-liquid separator [IV] an organic top layer and an aqueous bottom layer are formed. The aqueous bottom layer is discharged from the liquid-liquid separator [IV] via line [9]. Optionally, a fraction of the aqueous bottom layer discharged from the liquid-liquid separator [IV] is supplied to liquid-liquid mixing section [III] via line [9A], while the remainder is discharged via line [9B] to the cyclohexanone oxime synthesis section [I].

The organic top layer is discharged via line [10]. This organic top layer, which contains some remaining water, hydroxylammonium and inorganic ions, can be directly discharged to the cyclohexanone oxime recovery section via line [10A] in which a product comprising mainly cyclohexanone oxime is obtained or can be fed into a liquid-liquid separator [V] via line [10B] before being introduced into the cyclohexanone oxime recovery section. In liquid-liquid separator [V] an organic top layer and an aqueous bottom layer are formed. The aqueous bottom layer is discharged from the liquid-liquid separator [V] via line [12]. Preferably, this aqueous bottom layer is supplied to the cyclohexanone oxime synthesis section [I].

Figure 3 (see also figure 1 and 2)

Rewash process

The organic top layer from liquid-liquid separator [IV] is fed into a liquid-liquid mixing section [III^a] via line [10]. Water or an aqueous solution is fed into the liquid-liquid mixing section [III^a] via line [14]. Optionally an aqueous solution originating from liquid-liquid separator [IV^a] and/or an aqueous solution originating from liquid-liquid separator [V^a] are fed into the liquid-liquid mixing section [III^a] via lines [13A] and [17A], respectively. The water and/or aqueous solution is mixed with the organic top layer in the liquid-liquid mixing section [III^a] and the obtained mixture is introduced into a liquid-liquid separator [IV^a] via line [15]. The organic top layer is separated from the aqueous bottom layer in the liquid-liquid separator [IV^a] and the aqueous bottom layer is discharged from liquid-liquid separator [IV^a] via line [13]. A fraction of the aqueous bottom layer is fed back into the liquid-liquid mixing section [III^a] via line [13A] and the remainder is introduced into the liquid-liquid mixing section [III] via line [13B] and/or is introduced into oxime synthesis section [I] via line [13C] and/or disposed off via line [13D]. The organic top layer of the liquid-liquid separator [IV^a] can be discharged via line [16] and can be introduced into the cyclohexanone oxime recovery section directly via line [16A]. The organic top layer of the liquid-liquid separator [IV^a] can also be introduced into a liquid-liquid separator [V^a] via line [16B] to separate the water or aqueous solution contained in the organic top layer. The aqueous bottom layer of the liquid-liquid separator [V^a] is introduced into cyclohexanone oxime synthesis section [I] via line [17C] and/or the liquid-liquid mixing section [III] via line [17B] (figure 1) and/or liquid-liquid mixing section [III^a] via line [17A] and/or disposed off via line [17D]. The organic top layer of the liquid-liquid separator [V^a] is directly introduced into the cyclohexanone oxime recovery section via line [18] in which a product comprising mainly cyclohexanone oxime is obtained.

Figure 4 represents a schematic overview of a process for purifying cyclohexanone oxime dissolved in an organic medium comprising two rewashing steps. For details please refer to Example 3.

The invention will be further elucidated by means of the following examples without being limited thereto.

Example 1 (see figure 1)

Continuous cyclohexanone oxime production by reaction of cyclohexanone dissolved in toluene with hydroxylammonium dissolved in an aqueous phosphoric acid containing solution was carried out in a plant that was utilising DSM HPO[®] technology. The obtained organic product solution (toluene/cyclohexanone oxime flow) leaving the top of the cyclohexanone oxime synthesis section [I] was sent

to the washing section which consisted of a liquid-liquid mixing section [III], liquid-liquid separator [IV], and a liquid-liquid separator [V]. The liquid-liquid mixing section [III] consisted of a cylindrical mixing box and was equipped with a turbine stirrer. The organic product solution (toluene/cyclohexanone oxime mixture), fresh demineralized water and an aqueous recycle stream were fed to the liquid-liquid mixing section [III]. The liquid-liquid mixing section [III] was operated with the organic phase as the continuous phase. The liquid-liquid separator [IV] consisted of a gravity settler and was equipped with 4 baffles. The obtained aqueous bottom layer was divided into a fraction that was sent to the cyclohexanone oxime synthesis section [I] and a fraction that was returned to the liquid-liquid mixing section [III]. The obtained organic top layer was sent to a liquid-liquid coalescer [V] with glass fiber as coalescing media. The aqueous bottom layer recovered in the coalescer [V] was sent to the cyclohexanone oxime synthesis section [I].

Conditions (averaged values of a 24 hr period of stable cyclohexanone oxime production) of the purification section of cyclohexanone oxime dissolved in toluene were:

Average temperature:	in the range of from 50 to 60 °C
Flow rate toluene/cyclohexanone oxime mixture:	ca. 43.2 m ³ /hr
Flow rate demineralised water:	ca. 0.26 m ³ /hr
Cyclohexanone oxime content:	ca. 43.3 wt%
Flow rate aqueous recycle:	ca. 45 m ³ /hr

The aqueous phase that was returned to the cyclohexanone oxime reactor contained:

phosphate	12.2 wt%
nitrate	2.8 wt%
ammonia	1.5 wt %

The recovery yield of phosphate: 61 wt%.

Example 2 (see figure 2)

Continuous cyclohexanone oxime production by reaction of cyclohexanone dissolved in toluene with hydroxylammonium dissolved in an aqueous phosphoric acid containing solution was carried out in a plant that was utilising DSM HPO[®] technology. The obtained organic product solution (toluene/cyclohexanone oxime flow) leaving the top of the cyclohexanone oxime synthesis section [I] was sent to the washing section which consisted of a liquid-liquid mixing section [III], liquid-liquid separator [IV], and a liquid-liquid separator [V]. The liquid-liquid mixing section [III] consisted of a cylindrical mixing box and was equipped with a turbine stirrer. The organic product solution (toluene/cyclohexanone oxime mixture), fresh demineralized

water, aqueous phase recovered in liquid-liquid separator [IV] and aqueous phase recovered in the coalescer [V] were fed to the liquid-liquid mixing section [III]. The liquid-liquid mixing section [III] was operated with the organic phase as the continuous phase. The liquid-liquid separator section [IV] consisted of a gravity settler and was equipped with 4 baffles. The obtained aqueous bottom layer was divided into a fraction that was sent to the cyclohexanone oxime synthesis section [I] and a fraction that was returned to the liquid-liquid mixing section [III]. The obtained organic phase was sent to a liquid-liquid coalescer [V] with glass fiber as coalescing media. The aqueous phase recovered in the coalescer [V] was sent to the liquid-liquid mixing section [III].

Conditions (averaged values of a 24 hr period of stable cyclohexanone oxime production) of the purification section of cyclohexanone oxime dissolved in toluene were:

Average temperature:	in the range of from 50 to 60 °C
Flow rate toluene/cyclohexanone oxime mixture:	ca. 43 m ³ /hr
Flow rate demiwater:	ca. 0.30 m ³ /hr
Cyclohexanone oxime content:	ca. 42.8 wt%
Flow rate aqueous recycle:	ca. 40 m ³ /hr

The phosphate concentration in the toluene/cyclohexanone oxime flow leaving the top of the cyclohexanone oxime reactor was ca. 828 ppm (wt/wt). The obtained purified toluene/cyclohexanone oxime flow that was recovered in the coalescer did contain ca. 284 ppm (wt/wt) phosphate. Due to this purification of the toluene/cyclohexanone oxime approx. 20 kg phosphate per hour could be recovered.

Example 3 (refer to figure 4)

The cyclohexanone oxime in the purified toluene/cyclohexanone oxime flow that was recovered in the coalescer [V] (See Example 2) was further purified by rewashing. This rewashing consisted of a liquid-liquid mixing section [III^a], a liquid-liquid separator [IV^a], a liquid-liquid mixing section [III^b], a liquid-liquid separator [IV^b], and a coalescer [V^b].

The liquid-liquid mixing section [III^a] consisted of a cylindrical mixing box and was equipped with a turbine stirrer. The organic phase recovered in the coalescer [V] (toluene/cyclohexanone oxime mixture), an aqueous bottom layer of the liquid-liquid separator [IV^b], an aqueous bottom layer recovered in the coalescer [V^b], and aqueous bottom layer recovered in the liquid-liquid separator [IV^a] were fed to the liquid-liquid mixing section [III^a] via lines [11], [21B], [23] and [13A]. Both the liquid-liquid separator [IV^a] and [IV^b] consisted of gravity settlers. The aqueous bottom layer obtained in the liquid-liquid separator [IV^a] was divided into a fraction that was returned to the liquid-liquid section [III^a] via line [13A] and a fraction that was disposed off via line

[13B]. The obtained organic top layer in the liquid-liquid separator [IV^a] was sent to the liquid-liquid mixing section [III^b] via line [16]. The liquid-liquid mixing section [III^b] consisted of a series of in-line static mixers. In this section the organic phase was mixed with fresh demineralized water via line [19] and an aqueous recycle stream. The
5 obtained mixture was fed to the liquid-liquid separator [IV^b] via line [20]. The aqueous bottom layer obtained in the liquid-liquid separator [IV^b] was divided into a fraction that was sent to the liquid-liquid mixing section [III^a] via line [21B] and a fraction that was returned to the liquid-liquid mixing section [III^b] via line [21A]. The obtained organic top layer was sent to a coalescer [V^b] via line [22] with glass fiber as coalescing media. The
10 purified toluene/cyclohexanone oxime flow that was recovered in coalescer [V^b] was sent to a distillation section via line [24] in order to separate cyclohexanone oxime from toluene. The obtained cyclohexanone oxime was used for the production of ϵ -caprolactam.

Conditions (averaged values of a 24 hr period of stable
15 cyclohexanone oxime production) of the purification section of cyclohexanone oxime dissolved in toluene were:

Average temperature: in the range of from 50 to 60 °C

Flow rate toluene/cyclohexanone oxime mixture: ca. 43 m³/hr

Flow rate demineralized water: ca. 6.5 m³/hr

20 Due to this purification of the toluene/cyclohexanone oxime flow approx. 7 kg phosphate per hour could be recovered. And as a result the obtained purified toluene/cyclohexanone oxime flow that was fed to the distillation section was almost free of phosphate

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CLAIMS

1. A continuous process for purifying an organic product solution comprising oxime dissolved in an organic medium comprising:
 - 5 (1) discharging the organic product solution from an oxime synthesis section [I] to a liquid-liquid mixing section [III];
 - (2) mixing the organic product solution with a water and/or an aqueous solution and discharging the resulting mixture to a liquid-liquid separator [IV];
 - 10 (3) separating the resulting organic top layer from the resulting aqueous bottom layer in the liquid-liquid separator [IV] and introducing the organic top layer to an oxime recovery section;
 - (4) feeding the aqueous bottom layer of the liquid-liquid separator [IV] to the oxime synthesis section [I], optionally a fraction of which is fed back into the liquid-liquid mixing section [III].
- 15 2. A process according to claim 1 wherein in step (4), a fraction of the aqueous bottom layer is introduced to the liquid-liquid mixing section [III] and the remainder is sent to the oxime synthesis section [I].
3. A process according to claim 2 wherein at least 80 wt% of the aqueous bottom layer is introduced to the liquid-liquid mixing section [III].
- 20 4. A process according to any of preceding claims, wherein a fraction of the aqueous medium contained in the organic product solution is separated out in a liquid-liquid separator [II] before the organic product solution being introduced to the liquid-liquid mixing section [III].
- 25 5. A process according to any preceding claim, wherein the organic top layer obtained from step (3) is introduced into a liquid-liquid separator [V] before being introduced to the oxime recovery section.
6. A process according to any of preceding claims, wherein the organic top layer obtained from step (3) is subjected to at least one rewash process before being introduced to the oxime recovery section.
- 30 7. A process according to claim 6 wherein the organic top layer obtained from step (3) is subjected to two rewash processes in sequence before being introduced to the oxime recovery section.
8. A process according to claim 6 or 7, wherein the rewash process comprises:
 - 35 (i) introducing the organic top layer of liquid-liquid separator [IV] into a liquid-liquid mixing section [III^a] and mixing the organic top layer with a water and/or an aqueous solution;

- (ii) discharging the resulting mixture from the liquid-liquid mixing section [III^a] to a liquid-liquid separator [IV^a] and separating the resulting organic top layer from the resulting aqueous bottom layer;
- (iii) introducing a fraction or all of the aqueous bottom layer of the liquid-liquid separator [IV^a] into the oxime synthesis section [I] and/or into the liquid-liquid mixing section [III] and/or into the liquid-liquid mixing section [III^a] and/or being disposed of;
- (iv) introducing the organic top layer of liquid-liquid separator [IV^a] into the oxime recovery section.
- 5
- 10 9. A process according to claim 8, wherein a fraction of the aqueous bottom layer of liquid-liquid separator [IV^a] is introduced back into the liquid-liquid mixing section [III^a].
10. A process according to claim 6, wherein a fraction or all of the aqueous bottom layer of the liquid-liquid separator of each rewash process is introduced into the oxime synthesis section [I] and/or any one or more previous liquid-liquid mixing section and the remainder is disposed of.
- 15
11. A process according to claim 6, wherein the organic top layer obtained from each rewash process can be introduced into a liquid-liquid separator before being introduced into next rewash process.
- 20 12. A process according to claim 11, wherein the liquid-liquid separator is a coalescer.
13. A process according to claim 11, wherein a fraction or all of aqueous bottom layer obtained in the liquid-liquid separator is introduced into the oxime synthesis section [I] and/or any one or more previous liquid-liquid mixing section and the remainder is disposed off.
- 25
14. A process according to claim 8, wherein more than 80 wt% of the aqueous bottom layer of the liquid-liquid separator [IV^a] is fed into the liquid-liquid mixing section [III^a].
15. A process according to claim 8 wherein the organic top layer liquid-liquid separator [IV^a] is sent to the liquid-liquid separator [V] before being introduced to oxime recovery section.
- 30
16. A process according to claim 5 wherein the liquid-liquid separator [V] is a coalescer.
17. A process according to claim 1 wherein the aqueous solution comprises demineralized water and/or steam condensate.
- 35
18. A process according to claim 1, wherein the liquid-liquid separator [IV] is a gravity liquid-liquid settler.
19. A process according to claim 1 wherein the oxime is cyclohexanone oxime.

20. A process according to claim 1 wherein the temperature in the liquid-liquid mixing section [III] is in the range of from 30 to 90 °C.
21. A process according to claim 1 wherein the organic medium is toluene.

Figure 1

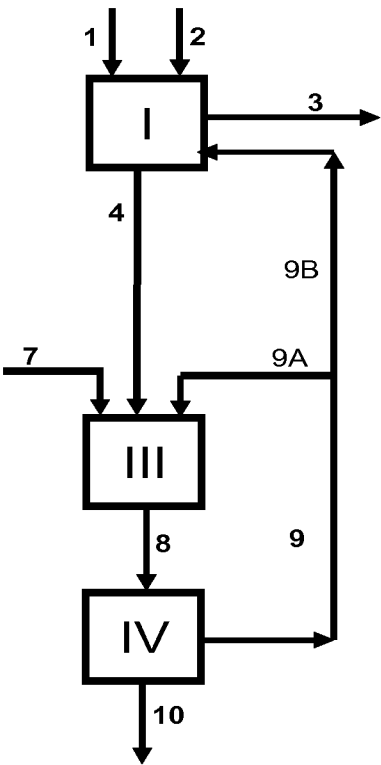


Figure 2

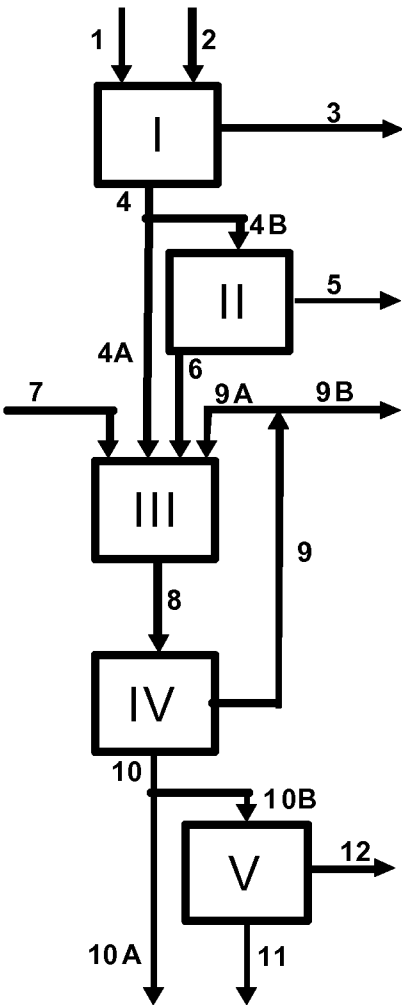


Figure 3

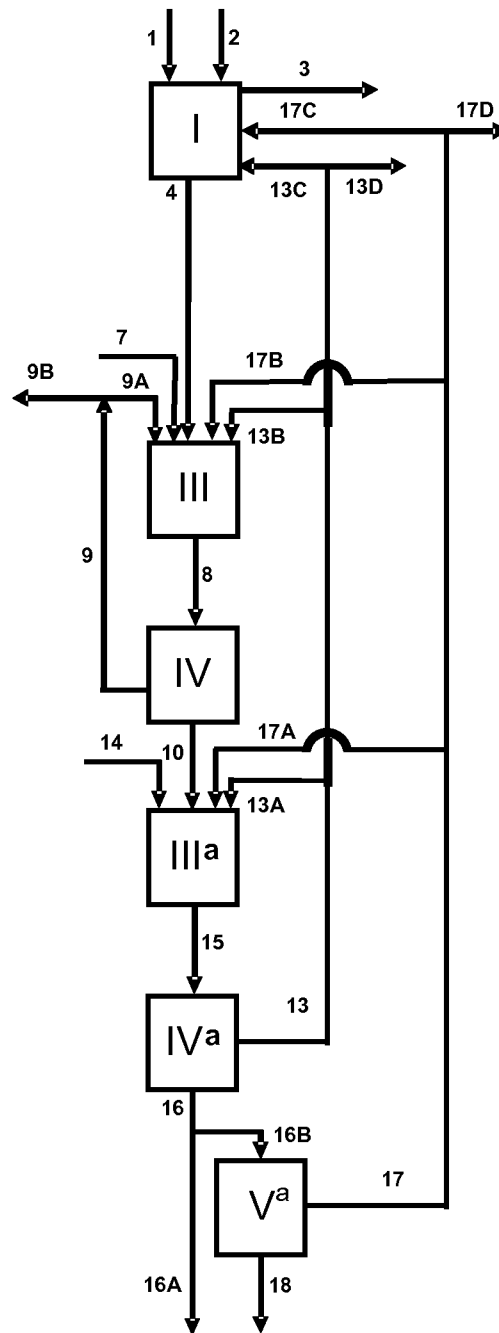
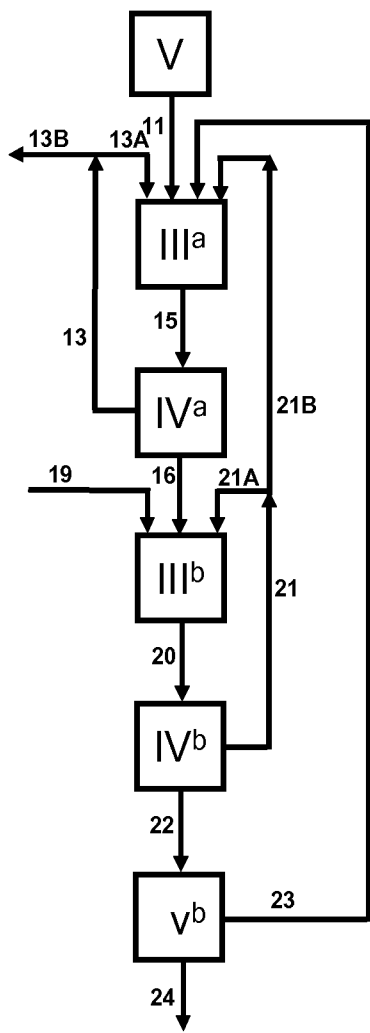


Figure 4

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/059067A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C249/14
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)
C07C

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	EP 1 700 846 A1 (SUMITOMO CHEMICAL CO [JP]) 13 September 2006 (2006-09-13) the whole document	1,19-21
X	EP 1 270 548 A1 (ENICHEM SPA [IT] SYNDIAL S P A [IT]) 2 January 2003 (2003-01-02) the whole document	1-21



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/059067

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
EP 1700846	A1	13-09-2006	CN	1827592 A		06-09-2006
			EP	1700846 A1		13-09-2006
			JP	4635644 B2		23-02-2011
			JP	2006232774 A		07-09-2006
			KR	20060095476 A		31-08-2006
			SG	125242 A1		29-09-2006
			TW	1363747 B		11-05-2012
			US	2006205939 A1		14-09-2006

EP 1270548	A1	02-01-2003	CA	2391715 A1		28-12-2002
			CZ	20022254 A3		18-02-2004
			EP	1270548 A1		02-01-2003
			ES	2336193 T3		09-04-2010
			IT	MI20011361 A1		30-12-2002
			JP	4425524 B2		03-03-2010
			JP	2003034674 A		07-02-2003
			TW	1260317 B		21-08-2006
			US	2003013916 A1		16-01-2003
