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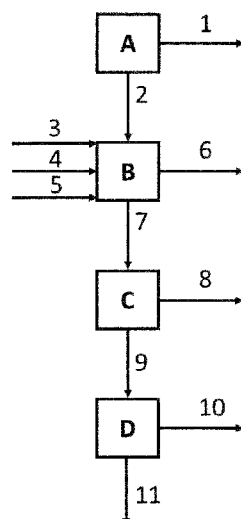
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(54) Title: AN IMPROVED PROCESS AND PLANT FOR THE PRODUCTION OF OXIMES



(57) Abstract: The present invention provides a process for the production of an oxime, the process comprising: a. converting an aldehyde or a ketone by a chemical reaction into an oxime at a temperature of 15 to 115 °C, whereby a reaction mixture comprising the formed oxime is obtained; b. recovering the formed oxime from the reaction mixture; c. producing a first aqueous phase that contains phosphate ions; d. reducing the content of phosphate ions in the first aqueous phase, whereby a second aqueous phase is formed; and e. discharging the second aqueous phase, wherein the reduction of the content of phosphate ions in the first aqueous phase is achieved by 1) forming a salt in which the molar ratio of N: Mg: P is about 1: 1: 1; and 2) separating the salt in which the molar ratio of N: Mg: P is about 1: 1: 1 from the second aqueous phase; a fertilizer product comprising magnesium ammonium phosphate hexahydrate obtained thereof; cyclohexanone oxime obtained thereof; and a chemical plant suitable for the production of an oxime.

FIG. 2

AN IMPROVED PROCESS AND PLANT FOR THE PRODUCTION OF OXIMES

Field of the invention

The present invention relates to a process and a plant for the removal
5 of phosphate from wastewater originating from the production of oximes.

Background of the invention

Oximes are usually generated by the reaction of hydroxylamine and
aldehydes or ketones. Examples of oximes are butanone oxime, cyclohexanone
oxime and cyclododecanone oxime that are made by condensation of hydroxylamine
10 and butanone, cyclohexanone, and cyclododecanone, respectively.

Butanone oxime (also called methylethyl ketone oxime) is amongst
others applied in the paint industry to suppress the formation of a skin on paint before
it is used.

Cyclododecanone oxime is mainly consumed as a precursor to
15 lauro lactam, which is a precursor of polyamide-12 (also known as nylon-12).

Cyclohexanone oxime is an intermediate in the production of, amongst
other compounds, caprolactam. This monomer is commonly used in the production of
polyamide-6 (also known as nylon-6).

A process for the production of oximes is based on the selective
20 reaction of cyclohexanone, ammonia, and hydrogen peroxide in the presence of a
catalyst. Especially, titanium silicalite based catalysts are very suitable for this so-
called ammoximation reaction. Methods for the production of such catalysts are
known in the art (see for example, US 4,410,501 and US 9,896,343). Catalytic
processes for the manufacture of cyclohexanone oxime by ammoximation in the
25 liquid phase of cyclohexanone with NH_3 and H_2O_2 are also known in the art (see for
example, US 4,794,198, EP 1 674 448 and US 7,408,080).

In the case where the cyclohexanone oxime formation is carried out by
ammoximation the occurring chemical reaction is represented as follows:

30 Reaction 1) Preparation of the cyclohexanone oxime in the
cyclohexanone formation zone:



Typically, the formed cyclohexanone oxime is purified and recovered
35 by extraction, (caustic) aqueous washing and distillation steps.

Oxime production processes based on ammoximation produce large amounts of wastewater containing significant amounts of organic and inorganic components. The main source of water is diluent water stemming from the raw materials (e.g., aqueous hydrogen peroxide) and water that is chemically formed in the ammoximation process (see e.g., Reaction 1). A typical cyclohexanone ammoximation process produces at least 2.5 tons of wastewater per ton of produced cyclohexanone oxime. Typically, this wastewater is discharged to a biochemical wastewater treatment plant.

Several patents were issued that deal with the removal of the organic components from wastewater of cyclohexanone ammoximation processes. For example, CN 103 214 044, CN 101 618 919 and CN 101 734 825 describe methods to oxidize the organic material in the wastewater of an ammoximation plant, so as to improve the biodegradability, before it is charged to a biochemical wastewater treatment plant. However, removal of phosphorus, that might be present in inorganic form, e.g., in the form of phosphate, or in organic form, e.g., in the form of trioctyl phosphate, from wastewater of an ammoximation plant has, to the knowledge of the inventors, never been disclosed in the prior art. The phosphorus that is discharged from the process with the wastewater might originate from the raw materials, e.g. aqueous hydrogen peroxide solution, and/or from auxiliary materials used in the process.

In CN 107 986 987 an alcohol, e.g., cyclohexanol, based ammoximation process has been disclosed, which is a variant of the above-mentioned aldehyde or ketone based ammoximation process. Without being bound by theory it is assumed that in this process the alcohol is first converted into an aldehyde or a ketone, which is subsequently converted into an oxime. The addition of a pre-oxidation step makes this alcohol based ammoximation process, merely an extended version of the aldehyde or ketone based ammoximation process. Although the alcohol ammoximation process is not commercial yet, the process will produce a wastewater stream that contains at least the same amount of phosphorus, because the hydrogen peroxide consumption of this alcohol ammoximation variant will be even higher than in the traditional aldehyde or ketone based ammoximation process.

In another process the oxime is prepared by reaction of a buffered hydroxylammonium phosphate solution and an aldehyde or ketone in the presence of a solvent. The hydroxylammonium phosphate solution is obtained by selective hydrogenation of nitrate ions or nitrogen oxides in an aqueous phosphoric acid containing solution. This process for the production of oximes is generally known as

the HPO[®] process and is licensed by Fibrant[®]. The HPO[®] process is mainly applied for the production of cyclohexanone oxime.

The HPO[®] cyclohexanone oxime process makes use of two recycling liquids - an inorganic liquid and an organic liquid - in which several reactions and operations take place (see e.g., H.J. Damme, J.T. van Goolen and A.H. de Rooij, Cyclohexanone oxime made without by-product (NH₄)₂SO₄, July 10, 1972, Chemical Engineering; pp 54/55 or Ullmann's Encyclopedia of Industrial Chemistry, online publication of article on "Caprolactam", pp 8-10, Version of Record online: 25 May 2018, DOI: 10.1002/14356007.a05_031, Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA (Retrieved June 04, 2018). The inorganic liquid, a phosphate-containing acidic aqueous solution, also containing ammonium, nitrate and/or nitrogen monoxide, is fed to a hydroxylamine formation zone, where hydroxylamine is produced. Hydroxylamine is formed via reduction of nitrate with hydrogen, which is catalysed by a heterogeneous catalyst, for example a palladium-containing catalyst with carbon as carrier.

In the case where the hydroxylamine formation starts from a solution of phosphoric acid and nitrate the chemical reactions occurring are represented as follows:

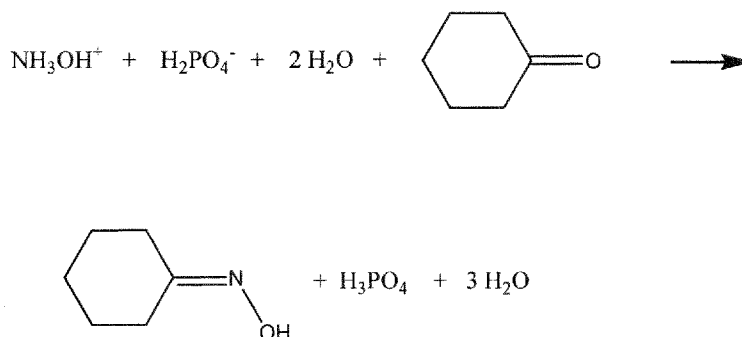
Reaction 2) Preparation of the hydroxylamine in the hydroxylamine formation zone:



The resulting mixture of the first reaction is a phosphate-containing acidic aqueous solution comprising a suspension of solid catalyst particles in a hydroxylamine solution.

In the HPO[®] cyclohexanone oxime process of Fibrant[®], the resulting hydroxylamine solution is contacted with an organic liquid containing cyclohexanone and a solvent after removal of the catalyst. Hereby cyclohexanone reacts with hydroxylamine to form cyclohexanone oxime by the following reaction:

Reaction 3) Preparation of the cyclohexanone oxime in the cyclohexanone oxime formation zone:



After separation of the organic liquid that contains the formed cyclohexanone oxime from the inorganic liquid that contains phosphoric acid, fresh
5 nitrate or nitrogen oxides are added, to the inorganic liquid that contains phosphoric acid, before it is recycled to the hydroxylamine formation zone.

The separated organic liquid that contains the formed cyclohexanone oxime is washed with water and the cyclohexanone oxime is recovered from the washed organic liquid by distillation.

10 All water that is chemically formed in the HPO[®] process (see, e.g., Reaction 2) and Reaction 3)) and the water that is added to the process (e.g., water used to wash the separated organic liquid that contains the formed cyclohexanone oxime) is discharged from the process after steam stripping. A typical HPO[®]
15 cyclohexanone oxime process discharges about 1.5 tons of wastewater per ton of produced cyclohexanone oxime. This wastewater contains only traces of organic components and low amounts of inorganic components including some phosphate. Typically, this wastewater is discharged to a biochemical wastewater treatment plant.

Phosphorus is a required nutrient for plants to live and is the limiting
20 factor for plant growth in many aqueous ecosystems. An oversupply of phosphorus, e.g., due to discharge of wastewater that contains phosphate originating from cyclohexanone oxime producing processes, leads to overgrowth of plants and algae. The terms eutrophication or hypertrophication are generally used to describe this process. Already in the 70's of last century the Organization for Economic
25 Cooperation and Development (abbreviated as OECD) gave the following definition for the eutrophic process: "Eutrophication is an enrichment of water by nutrient salts that causes structural changes to the ecosystem such as: increased production of algae and aquatic plants, depletion of fish species, general deterioration of water quality and other effects that reduce and preclude use".

30 In order to avoid problems associated with eutrophication in aqueous ecosystems, all over the world, regulatory authorities tighten discharge standards.

One method applied in wastewater treatment plants to reduce phosphorus levels in discharge water is directing the phosphorus to the sewage sludge, or biosolids. This sewage sludge is often either incinerated or land applied.

Another method applied to lower the phosphorus content in wastewater before being discharged is based on the addition of sufficient calcium, e.g., in the form of lime, to react with the phosphorus in the wastewater to form precipitates of e.g., calcium hydroxyapatite, brushite or dicalcium phosphate dehydrate, which are salts with a low solubility in water.

Another method used to reduce phosphorus content in wastewater is based on the formation of slightly water soluble aluminium hydroxyphosphate. For this reason aluminium containing materials like aluminium sulphate, alum (e.g., sodium alum, potassium alum and ammonium alum) or clay are added.

Still, another phosphorus reducing method is based on precipitation of iron phosphate.

Wastewater treatment processes that apply one of the above mentioned methods (or a combination thereof) are often faced with nuisance formation of phosphate minerals in pipes, heat exchangers, and tanks due to the high levels of phosphate produced during anaerobic digestion of the solids. In addition the above mentioned methods inevitably produce large amounts of sludge due to the use of large amounts of chemicals and require complex post-treatments. Moreover, in general the produced materials do not have any economic value at all: mostly significant costs are associated with disposal or other after-treatment methods. And last but not least, the required phosphate discharge standards are often not reached by these methods.

Thus, the prior art methods for treating wastewater originating from cyclohexanone oxime production processes have been defective in that complex processes are required and they have many problems regarding performance, operation control, treatment cost and reaching required removal efficiencies.

Therefore, there is a need for the development of a method for removing phosphorus with a high efficiency, which is economically superior as well as easy and convenient to operate and which produces a phosphate containing material that has an economic value.

In view of the above, it is an object of the present invention to provide a novel dephosphorization process for wastewater originating from an oxime production process which can remove phosphorus effectively, thereby undercutting the applicable discharge standards.

It is another object of the present invention to provide a novel dephosphorization process for wastewater originating from an oxime production process that lacks problems regarding performance and operation control like nuisance formation of phosphate minerals on surfaces of applied equipment and piping.

It is another object of the present invention to provide a novel dephosphorization process for wastewater originating from an oxime production process that is more economical than existing methods.

It is another object of the present invention to provide a novel dephosphorization process for wastewater originating from an oxime production process that produces a phosphate containing material that has an economic value.

It is still another object of the present invention to provide a novel dephosphorization process for wastewater originating from an oxime production process that is more environmentally benign than processes known in the art.

Nowadays, due to severe discharge standards of phosphorus, processes for the production of an oxime that have phosphorus in their wastewater, such as processes that are either based on selective reaction of an aldehyde or a ketone, ammonia, and hydrogen peroxide in the presence of a catalyst, or those processes that are based on the reaction of a buffered hydroxylammonium phosphate solution and an aldehyde or ketone in the presence of a solvent, whereby the hydroxylammonium phosphate solution is obtained by selective hydrogenation of nitrate ions or nitrogen oxides in an aqueous phosphoric acid containing solution, require a novel dephosphorization process for their wastewater.

In addition, due to the ever increasing scarcity of phosphorus, there is a need to recover phosphorus from wastewater and reuse the recovered phosphorus.

It is advantageous for current producers of oximes that apply a process that is either based on selective reaction of an aldehyde or a ketone, ammonia, and hydrogen peroxide in the presence of a catalyst, or a process that is based on the reaction of a buffered hydroxylammonium phosphate solution and an aldehyde or ketone in the presence of a solvent, whereby the hydroxylammonium phosphate solution is obtained by selective hydrogenation of nitrate ions or nitrogen oxides in an aqueous phosphoric acid containing solution, to adapt their process for the production of an oxime. However, there arises a problem because the existing technologies are not able to fulfil the discharge requirements.

The present inventors have discovered a process that significantly improves the dephosphorization of wastewater originating from processes for the production of oximes that are either based on selective reaction of an aldehyde or a ketone, ammonia, and hydrogen peroxide in the presence of a catalyst, or on the reaction of a buffered hydroxylammonium phosphate solution and an aldehyde or ketone in the presence of a solvent, whereby the hydroxylammonium phosphate solution is obtained by selective hydrogenation of nitrate ions or nitrogen oxides in an aqueous phosphoric acid.

They have developed an improved process for the production of an oxime that is either based on selective reaction of an aldehyde or a ketone, ammonia, and hydrogen peroxide in the presence of a catalyst, or on the reaction of a buffered hydroxylammonium phosphate solution and an aldehyde or ketone in the presence of a solvent, whereby the hydroxylammonium phosphate solution is obtained by selective hydrogenation of nitrate ions or nitrogen oxides in an aqueous phosphoric acid. More specifically, the present invention provides an improved process for the production of an oxime, the process comprising:

- a. converting an aldehyde or a ketone by a chemical reaction into an oxime at a temperature of 15 to 115 °C, whereby a reaction mixture comprising the formed oxime is obtained;
 - b. recovering the formed oxime from the reaction mixture;
 - c. producing a first aqueous phase that contains phosphate ions;
 - d. reducing the content of phosphate ions in the first aqueous phase, whereby a second aqueous phase is formed; and
 - e. discharging the second aqueous phase,
- wherein the reduction of the content of phosphate ions in the first aqueous phase is achieved by
- 1) forming a salt in which the molar ratio of N: Mg: P is about 1: 1: 1; and
 - 2) separating the salt in which the molar ratio of N: Mg: P is about 1: 1: 1 from the second aqueous phase.

As defined herein a salt in which the molar ratio of N: P: Mg is about 1: 1: 1 can be ammonium magnesium phosphate and/or various hydrates thereof. Non-limiting examples of hydrates of ammonium magnesium phosphate include ammonium magnesium phosphate monohydrate (also often referred to as dittmarite), ammonium magnesium phosphate tetrahydrate (also often referred to as schertelite), and ammonium magnesium phosphate hexahydrate (also often referred to as struvite).

As used herein N, Mg and P are the symbols of the chemical elements nitrogen, magnesium and phosphorus, respectively.

According to the present invention the formed salt in which the molar ratio of N: Mg: P is about 1: 1: 1 can be amorphous or crystalline.

5 The formed salt in which the molar ratio of N: Mg: P is about 1: 1: 1 can also contain other compounds that do not have a molar ratio of N: Mg: P is about 1: 1: 1.

 The formed salt in which the molar ratio of N: Mg: P is about 1: 1: 1 can consist of large sized particles that settle, fines that do not settle and
10 combinations thereof.

 A person skilled in the art is familiar with separating a salt from an aqueous phase. Various techniques exist for the removal of both fines and larger sized particles from an aqueous phase. This includes e.g., the usage of various filtration and centrifugation techniques that can be combined with various
15 pretreatment techniques like coagulation and settling.

 Industrial wastewaters are often treated in biochemical wastewater treatment plants. To encourage the growth of bacteria and other organisms that treat the wastewater a minimal amount of phosphate is requested. Phosphate, e.g., in the form of phosphoric acid, should be added to the system in case of absence of
20 phosphate in the intake. During the biochemical process in a biochemical wastewater treatment plant, phosphorus is incorporated into biological solids, such as microorganisms. The sludge produced from biochemical wastewater treatment plants is enriched with phosphorus. After separation of the sludge from the effluent the phosphorus in the effluent from a biochemical wastewater treatment plant is reduced.
25 Although a phosphate content in the intake of a biochemical wastewater treatment plant ranging from 3 to 10 mg/l (ppm) is quite common, other biochemical wastewater treatment plants are operated outside this optimal concentration window.

 The inventors realized that it is advantageous to use the second aqueous phase as phosphate source of a biochemical wastewater treatment plant
30 instead of dosing phosphate from an external source. This solution, not only leads to the saving of valuable chemical compounds like e.g., phosphoric acid, but also to an enhanced rate of dephosphorization of the second aqueous phase.

 According to a preferred embodiment of the process of the present invention, the process further comprises:

- 35 f. reducing the content of phosphate ions in the second aqueous phase, whereby a third aqueous phase is formed; and
 g. discharging the third aqueous phase,

wherein the reduction of the content of phosphate ions in the second aqueous phase is achieved by

- 1) charging the second aqueous phase to a biochemical wastewater treatment plant, and
- 5 2) discharging the third aqueous phase from the biochemical wastewater treatment plant.

The effluent from the biochemical wastewater treatment plant comprises the third aqueous phase and might further contain solid material like e.g., sludge. It is advantageous to separate this solid material to a large extent from the
10 third aqueous phase, whereby a solid material containing phase and a(n almost) clear third aqueous phase are formed.

Magnesium ammonium phosphate hexahydrate can be formed by the reaction:



According to a preferred embodiment of the process of the present invention the salt in which the molar ratio of N: Mg: P is about 1: 1: 1 is magnesium ammonium phosphate hexahydrate.

20 Preferably, the formation of magnesium ammonium phosphate hexahydrate is carried out in a pH value range from 6 to 14, more preferably from 7 to 11 and most preferably from 8 to 10. As the pH value increases, the concentrations of Mg^{2+} and NH_4^+ ions decrease, while the concentration of PO_4^{3-} increases due to the greater availability of orthophosphate at higher pH values.

25 Typically, in the process of the present invention the formation of the salt in which the molar ratio of N: Mg: P is about 1: 1: 1 can be achieved by adjusting the pH value of the first aqueous phase. Adjustment of the pH value can be achieved in various ways. Typically, the pH value of the first aqueous phase can be adjusted by addition of caustic (either as solution, solid or as a slurry), ammonia or by mixing
30 with a waste stream that provides the desired pH adjustment. The effluent stream of an incinerator, that contains sodium carbonate, sodium bicarbonate, sodium hydroxide and mixtures thereof, is very suitable for pH control. Such an effluent stream can either be a solution, solid or a slurry.

35 According to a preferred embodiment of the process of the present invention the formation of the salt is achieved by adjusting the pH value of the first aqueous phase to between about 6 and 14.

According to a preferred embodiment of the process of the present invention the formation of the salt is achieved by addition of an effluent stream of an incinerator to the first aqueous phase.

5 The formation of a salt in which the molar ratio of N: Mg: P is about 1: 1: 1, such as magnesium ammonium phosphate hexahydrate, followed by the separation of this salt is a very efficient way to dephosphorize phosphorus being present in the form of phosphate. In case phosphorus is present in organic form (organic phosphorus), e.g., in the form of trioctyl phosphate, then a pre-treatment
10 step is required that converts the organic phosphorus into phosphate. Several methods for this conversion are known. A simple and very efficient method is based on hydrolysis under alkaline conditions: For this the pH value of wastewater containing organic phosphorus is increased to e.g. a value ranging from about 10 to about 14 by addition of a base, such as e.g., NaOH. Both the temperature, ranging
15 from about ambient to boiling temperature, and the residence time of at least 15 minutes are not very critical. For instance, the hydrolysis of trioctyl phosphate to phosphate in wastewater is above 99% in case the pH value, the temperature and the residence time are at least 10.5, 40°C, and 10 hrs, respectively.

20 Typically, in the process of the present invention the formation a salt in which the molar ratio of N: Mg: P is about 1: 1: 1 requires the presence of a sufficient concentration of magnesium ions. In case the concentration of magnesium ions in the first aqueous phase is insufficient, the concentration of magnesium ions can be increased in various ways. Typically, the concentration of magnesium ions in the first
25 aqueous phase is increased by the addition of magnesium ions from an external source such as a magnesium containing salt. In fact the addition of any magnesium containing salt can meet this requirement. Especially suitable for this purpose are magnesium hydroxide, magnesium chloride and magnesium carbonate containing salts. These salts can be added either as a solution, as a solid or as a slurry.

30 Preferably, the molar ratio of magnesium ions to phosphate ions is at least 1: 1, more preferably 1.1: 1, most preferably 1.25: 1. Higher ratios are even more preferred. However, much higher ratios are not desired because of the relative high costs of magnesium salts.

 In an embodiment of the process of the present invention the
35 formation of the salt is achieved by addition of a magnesium containing salt to the first aqueous phase.

The formation of a salt in which the molar ratio of N: Mg: P is about 1: 1: 1 requires the presence of a sufficient concentration of ammonium ions. In general, ammonium ions are present in wastewaters of processes for the production of an oxime. However, it can be desired to increase the concentration of ammonium ions of the first aqueous phase in order to enhance the degree of dephosphorization by the addition of ammonium ions. In fact the addition of ammonium from any source can overcome this shortage. Especially suitable for this purpose are gaseous ammonia or aqueous ammonia solutions, such as e.g. 25 wt. % NH_3 in water.

Preferably, the molar ratio of ammonium ions to phosphate ions is at least 1: 1, more preferably at least 1.5: 1 and most preferably 2: 1. Higher ratios of a molar ratio of ammonium ions to phosphate ions above 2: 1 are even more preferred. However, much higher ratios are not desired because of restrictions regarding the content of ammonia in wastewater effluent.

In an embodiment of the process of the present invention the formation of the salt is achieved by addition of ammonium ions to the first aqueous phase.

In a preferred embodiment of the process of the present invention the formation of the salt in step e. 1) is achieved by realizing a molar ratio of magnesium ions to phosphate ions of at least 1.15: 1; and a molar ratio of ammonium ions to phosphate ions of at least 1.5: 1 in the first aqueous phase.

The addition of ammonium salts, e.g., ammonium chloride or ammonium sulphate, either as solution, in solid form or as a slurry can be very useful to increase the ammonium ion concentration of the first aqueous phase. An aqueous waste stream or a purge of an ammonium sulphate crystallization plant is extremely suitable for enhancement of the ammonium ion concentration of the first aqueous phase. Such a waste stream or a purge can also comprise other organic and inorganic impurities that e.g. originate from a caprolactam production process. The inorganic impurities include sodium ions that originate from the caprolactam purification process. The organic impurities include caprolactam and its derivatives.

In an embodiment of the process of the present invention the formation of the salt in step e. 1) is achieved by addition of a stream to the first aqueous phase that originates from an ammonium sulphate crystallization plant and comprises ammonium ions and at least one inorganic or organic impurity originating from a caprolactam production process.

The process of the present invention advantageously achieves a reduction of the phosphorous content by at least a factor of 10, preferably by a factor of 50, more preferably by a factor of 100, most preferred by a factor of 200 in the

third aqueous phase compared to the first aqueous phase. The final effluent of the process of the present invention contains less than 1.5 ppm, in particular less than 1 ppm, especially less than 0.5 ppm of phosphorous.

5 An oxime is a chemical compound belonging to the imines, with the divalent group $-C=NOH$. Oximes have the general formula $R^1R^2C=NOH$, where R^1 is an organic side-chain and R^2 may be hydrogen, forming an aldoxime, or another organic group, forming a ketoxime. Oximes can be obtained by the reaction of aldehydes or ketones and hydroxylamine.

10 According to an embodiment of the process of the present invention in the chemical reaction an aldehyde or a ketone is converted to an oxime with hydroxylamine.

According to another embodiment of the process of the present invention the process for the production of an oxime is either an ammoximation process, in which in step a. an aldehyde or a ketone, ammonia, and hydrogen
15 peroxide react in the presence of a catalyst or a process, in which first hydroxylamine is formed by selective reduction of nitrate followed by reaction of the formed hydroxylamine with the ketone cyclohexanone to form an oxime in step a.

All aldehydes or ketones can be converted with hydroxylamine to an oxime. Currently, the conversions of butanone, cyclohexanone and cyclododecanone
20 to oximes are economically most important.

According to an embodiment of the process of the present invention the ketone is selected from butanone, cyclohexanone or cyclododecanone.

The oximes that are obtained by the conversion of butanone, cyclohexanone and cyclododecanone with hydroxylamine are butanone oxime, cyclohexanone oxime and cyclododecanone oxime, respectively.
25

According to an embodiment of the process of the invention the formed oxime is selected from butanone oxime, cyclohexanone oxime or cyclododecanone oxime. According to a preferred embodiment of the process of the invention the ketone is cyclohexanone and the formed oxime is cyclohexanone
30 oxime. Thereafter, the obtained cyclohexanone oxime can be further reacted by Beckmann rearrangement to form caprolactam. The Beckmann rearrangement can be performed both in the liquid and in the gas phase. The formed caprolactam can be used as raw material for the production of polyamide-6.

According to another preferred embodiment of the process of the invention the ketone is cyclodecanone and the formed oxime is cyclodecanone
35 oxime. Thereafter, the obtained cyclodecanone oxime can be further reacted by

Beckmann rearrangement to form laurolactam. The formed laurolactam can be used as raw material for the production of polyamide-12.

A chemical plant is all apparatus necessary to manufacture or otherwise process the desired chemicals. This includes units for one or multiple
5 chemical or physical operations, for example, heating up, cooling down, mixing, distillation, extraction and reaction. It further typically includes all auxiliary equipment, for example reflux units, coolant supply, pumps, heat exchangers and pipework. The exact structure of the chemical plant depends amongst others on the type and purity of the starting material(s) and the desired end product(s), but also on the scale and
10 type of the process carried out. In case the processes carried out produce wastewater the chemical plant also includes all apparatus parts necessary to convert the wastewater into an effluent that can be discharged into e.g., a sea, a river or a canal.

As used herein a continuous process is a process operating 24 hours
15 per day, seven days per week with the exception of infrequent interruptions due to e.g., a process disturbance, a maintenance activity or for economic reasons. In other words a continuous process for the production of an oxime as used herein is a process in which an aldehyde or a ketone are fed without interrupting the process and whereby an oxime is withdrawn without interrupting the process. The continuous
20 process for the production of an oxime can be carried out at a constant rate or its rate can fluctuate over time.

The chemical plant for carrying out the process of the invention is preferably of industrial scale. As used herein industrial scale means an oxime production rate of at least 1,000 kg of oxime per hour, more preferably at least 2,000
25 kg of oxime per hour, even more preferably at least 4,000 kg of oxime per hour, most preferably at least 6,000 kg of oxime per hour.

Converting an aldehyde or a ketone by a chemical reaction as used herein means that an aldehyde or a ketone is partly or completely transformed whereby an oxime is formed as product. Preferably, at least 50 mole % of the
30 aldehyde or the ketone is converted into an oxime, more preferably at least 80 mole %, even more preferably at least 96 mole %, and most preferably at least 99 mole %.

In a further embodiment of the invention there is provided a chemical plant suitable for the production of an oxime comprising:

- 35
- a. a chemical reaction section wherein the oxime is formed;
 - b. an oxime purification and recovery section wherein the formed oxime is purified and recovered;

- c. a section in which an aqueous phase containing phosphate is formed;
and
- d. a dephosphorization section wherein solid magnesium ammonium phosphate hexahydrate is formed and separated from an aqueous phase.

5

Typically, the chemical reaction section wherein the oxime is formed can comprise:

- charging of the aldehyde or ketone;
- charging (batch-wise or in a continuous mode) of a phosphorus containing compound, like e.g., aqueous hydrogen peroxide containing phosphorus compounds, or phosphoric acid.
- optionally, charging of a solvent, like e.g., toluene or t-butanol; and
- contacting of the aldehyde or ketone with (in-situ formed) hydroxylamine.

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Typically, the oxime purification and recovery section wherein the formed oxime is purified and recovered can comprise:

- a washing unit, in which an oxime comprising phase is washed with water and/or an aqueous solution (e.g., aqueous caustic); and
- a distillation unit, in which the oxime is separated from other components (e.g., solvent like toluene, unconverted aldehyde or ketone).

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Typically, the section in which an aqueous phase containing phosphate is formed can comprise:

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- a unit in which an aqueous phase containing phosphorus compounds is separated from process liquid originating from the chemical reaction section, like e.g., a liquid-liquid separator or a stripper;
- optionally, a unit in which an aqueous phase containing phosphorus compounds is separated from an oxime containing organic phase process that has been washed with water and/or an aqueous solution (e.g., aqueous caustic), like e.g., a liquid-liquid separator;
- optionally, a stripping unit, in which volatile organic compounds are (e.g., steam) stripped from an aqueous phase; and
- optionally, a unit in which organic phosphorus is converted into phosphate;

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Typically, the dephosphorization section wherein solid magnesium ammonium phosphate hexahydrate is formed and separated from an aqueous phase can comprise:

- 5 - optionally, a unit in which organic phosphorus is converted into phosphate;
- charging of optionally pH adjustment chemicals, a source of magnesium ions and/or a source of ammonium ions.
- a magnesium ammonium phosphate hexahydrate separation unit (e.g., a filter).

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In an embodiment of the chemical plant of the present invention the chemical plant further comprises:

- e. a biochemical wastewater treatment section.

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Typically, the biochemical wastewater treatment section can comprise:

- a sedimentation section, in which solids are removed from wastewater by gravity;
- a filtration section, in which colloidal suspensions of fine solids can be removed from wastewater by filtration;
- 20 - an oxidation section, in which the biochemical oxygen demand of wastewater is reduced by biochemical oxidation and optionally also by chemical oxidation; and
- a pH adjustment section, in which the pH value of the wastewater following the oxidation is adjusted to reduce its chemical reactivity.

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According to an embodiment of the chemical plant of the present invention the chemical plant further comprises:

- f. a polishing section to filter wastewater, which is discharged from the biochemical wastewater treatment section.

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The polishing section to filter wastewater, which is discharged from the biochemical wastewater treatment section can comprise a filtration through a sand bed, in which mainly solid contaminants are removed.

In a preferred embodiment of the chemical plant of the present invention the filtration section comprises a sand bed.

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Preferably, in a chemical plant of the present invention the ketone is cyclohexanone or cyclododecanone and the resulting cyclohexanone oxime or cyclododecanone oxime is further reacted by Beckmann rearrangement to form caprolactam or lauro lactam, respectively.

5 Most preferred in a chemical plant of the present invention the oxime is cyclohexanone oxime.

 Magnesium ammonium phosphate hexahydrate is a unique fertilizer because it provides three essential nutrients to plants: magnesium, nitrogen, and
10 phosphorus. Besides its unique composition magnesium ammonium phosphate hexahydrate has slow release properties. Slow release properties as used herein mean that the magnesium ammonium phosphate releases its nutrients not (almost) instantaneously but over a course of time.

 In another aspect of the invention, there is provided a fertilizer product
15 comprising magnesium ammonium phosphate hexahydrate, obtainable by the process of the invention for the production of an oxime.

 The process of the invention for the production of an oxime is much more ecologically beneficial than processes known in the art. As a result of that the product of such a process is also much more ecologically beneficial than products
20 that are produced via other processes. The special character of such a much more ecologically beneficial product can be guaranteed by e.g., certification.

 In still a further aspect of the invention, there is provided a fertilizer product comprising magnesium ammonium phosphate hexahydrate, obtainable by the process of the invention for the production of an oxime.

25 As used herein, cyclohexanone oxime, obtainable by the process of the invention is the product resulting from the conversion of cyclohexanone.

 Preferably, the obtained cyclohexanone oxime has a content of the chemical compound cyclohexanone oxime that is at least 92 wt.%; more preferably at least 97 wt.%; even more preferably, it is at least 99 wt.%; still preferably at least 99.5
30 wt.%; most preferably at least 99.9 wt.%. As impurities cyclohexanone, toluene and water can be present.

 FIG. 1 schematically shows a conventional state of the art plant for the production of cyclohexanone oxime and wastewater treatment.

35 FIG. 2 shows a plant according to the present invention, for the production of cyclohexanone oxime and wastewater treatment.

FIG. 3 schematically shows a cyclohexanone oxime production section based on HPO[®] technology, which is an example of a cyclohexanone oxime production section [A] that is depicted in both FIG. 1 and FIG. 4.

5 Fig. 4 schematically shows a cyclohexanone oxime production section based on cyclohexanone ammoximation technology, which is an example of a cyclohexanone oxime production section [A] that is depicted in both FIG. 1 and FIG. 4.

10 FIG. 1 schematically shows a conventional state of the art plant for the production of cyclohexanone oxime and wastewater treatment that comprises a cyclohexanone oxime production section [A], a wastewater treatment plant [C] and a filtration section [D].

Cyclohexanone oxime production section [A] comprises a reaction section wherein cyclohexanone oxime is formed, and a cyclohexanone oxime
15 separation and purification section. The purified cyclohexanone oxime is discharged from cyclohexanone oxime production section [A] through line [1]. Wastewater that contains phosphorus is discharged from cyclohexanone oxime production section [A] through line [2].

In wastewater treatment plant [C] organic compounds are removed to
20 a large extent from wastewater that is charged through line [2]. Optionally, wastewater from other plants is charged to the same wastewater treatment plant [C] (not shown in the Figure). Preferably, the removal of organic compounds is done by biochemical oxidation. The hereby formed sludge, that contains a part of the phosphorus that is charged to the wastewater treatment plant [C], is discharged
25 through line [8]. The treated wastewater, that contains less organic compounds than the wastewater that is charged to the wastewater treatment plant [C], is discharged through line [9].

In filtration section [D] particulate solids are removed from the waste water that is charged through line [9]. Filtration section [D] might contain one or more
30 sand bed filters and/or membrane filtration units. The solids removed in filtration section [D] are discharged through line [10]. The obtained treated wastewater from filtration section [D] is discharged into e.g., a sea, a river or a canal through line [11].

FIG. 2 shows a plant according to the present invention, for the
35 production of cyclohexanone oxime and wastewater treatment that comprises a cyclohexanone oxime production section [A], a dephosphorization section [B], wastewater treatment plant [C] and a filtration section [D].

Cyclohexanone oxime production section [A] comprises a reaction section wherein cyclohexanone oxime is formed, and a cyclohexanone oxime separation and purification section. The purified cyclohexanone oxime is discharged from cyclohexanone oxime production section [A] through line [1]. Wastewater that contains phosphorus is discharged from cyclohexanone oxime production section [A] through line [2].

In dephosphorization section [B] magnesium ammonium phosphate hexahydrate is formed and separated from the wastewater that is charged through line [2]. Optionally, wastewater from other plants is charged to the same dephosphorization section [B] (not shown in the Figure). Optionally, pH adjustment chemicals are charged through line [3]. Optionally, a source of magnesium ions is charged through line [4]. Optionally, a source of ammonium ions is charged through line [5]. The formed magnesium ammonium phosphate hexahydrate is discharged through line [6]. Optionally, the formed magnesium ammonium phosphate hexahydrate is further treated, e.g., dried or blended with other compounds, before being applied as fertilizer (not shown in the Figure). The dephosphorized wastewater is discharged from dephosphorization section [B] through line [7]. Optionally, the wastewater from cyclohexanone oxime production section [A] is first treated to convert organic phosphorus into phosphate before being charged to dephosphorization section [B] (not shown in the Figure).

In wastewater treatment plant [C] organic compounds are removed to a large extent from wastewater that is charged through line [7]. Optionally, wastewater from other plants is charged to the same wastewater treatment plant [C] (not shown in Figure). Preferably, the removal of organic compounds is done by biochemical oxidation. The hereby formed sludge, that contains a part of the phosphorus that is charged to the wastewater treatment plant [B], is discharged through line [8]. The treated wastewater, that contains less organic compounds than the wastewater that is charged to the wastewater treatment plant [C], is discharged through line [9].

In filtration section [D] particulate solids are removed from the wastewater that is charged through line [9]. Filtration section [D] might contain one or more sand bed filters and/or membrane filtration units. The solids removed in filtration section [D] are discharged through line [10]. The obtained treated wastewater from filtration section [D] is discharged in e.g., a sea, a river or a canal through line [11].

FIG. 3 schematically shows a cyclohexanone oxime production section based on HPO[®] technology, which is an example of a cyclohexanone oxime production section [A] that is depicted in both FIG. 1 and FIG. 2.

Gaseous ammonia charged through line [a] is combusted with air charged through line [b] to an ammonia combustion unit, whereby NO_x gases are formed. These NO_x gases are absorbed in an aqueous phosphate containing solution, whereby nitrate is formed. This nitrate loaded aqueous phosphate containing solution is charged to a hydroxylamine formation section, in which nitrate is catalytically reduced with hydrogen gas charged through line [c] to form hydroxylamine. The hereby formed aqueous phosphate and hydroxylamine containing solution is contacted with an organic solution that contains fresh added cyclohexanone charged through line [d] and recycled cyclohexanone and solvent toluene, in the cyclohexanone oxime formation zone, whereby cyclohexanone oxime is formed. An aqueous phosphate containing solution with low hydroxylamine content is discharged from the cyclohexanone oxime formation zone and is recycled via an NO_x absorption unit to the hydroxylamine formation section.

A solution of cyclohexanone oxime in toluene that contains small amounts of phosphate is removed from the cyclohexanone oxime formation zone and is washed in the cyclohexanone oxime washing section with washing water charged through line [e], whereby a washed solution of cyclohexanone oxime in toluene and water phase that contains phosphate is obtained. The water phase that contains phosphate is separated from the solution of cyclohexanone oxime in toluene and is partly discharged as first water phase that contains phosphate and partly recycled into the process. In the cyclohexanone oxime distillation section the washed solution of cyclohexanone oxime in toluene is distilled, whereby toluene and cyclohexanone are obtained that are recycled and cyclohexanone oxime that is discharged through line [1].

In the cyclohexanone oxime production section water is formed due to the formation of NO_x in the combustion unit, due to the formation of the hydroxylamine in the hydroxylamine formation section (: Reaction 2), and due to the formation of cyclohexanone oxime in the cyclohexanone oxime formation zone (: Reaction 3). This formed water has the tendency to accumulate in the aqueous phosphate solution. Steam stripping of the aqueous phosphate solution is applied in order to balance the amount of water in the process, whereby a second water phase that contains phosphate is obtained.

Both the first water phase that contains phosphate and the second water phase that contains phosphate are treated in a stripping unit in which volatile

organic compounds are removed. The hereby obtained stripped aqueous phase is the phosphorus containing wastewater that is discharged from the cyclohexanone oxime production section [A] through line [2].

5 FIG. 4 schematically shows a cyclohexanone oxime production section based on cyclohexanone amroximation technology, which is an example of a cyclohexanone oxime production section [A] that is depicted in both FIG. 1 and FIG. 2.

 Gaseous or aqueous ammonia is charged through line [f], aqueous
10 hydrogen peroxide that contains phosphorus compounds is charged through line [g], and cyclohexanone is charged through line [h] to the cyclohexanone oxime formation zone. Typically, also recycled or fresh amroximation catalyst and recycled or fresh solvent t-butanol are charged to the cyclohexanone oxime formation zone. The resulting reaction mixture is after removal of the catalyst distilled whereby amongst
15 others solvent t-butanol and excess ammonia are going overhead and an aqueous cyclohexanone oxime and phosphorus compounds containing phase is obtained as bottom flow.

 This aqueous cyclohexanone oxime and phosphorus compounds containing phase is extracted with toluene whereby an organic cyclohexanone oxime containing toluene phase and a first phosphorus compounds and organics containing
20 wastewater stream are obtained. The organic cyclohexanone oxime containing toluene phase is washed with (optionally caustic) washing water that is charged through line [i], whereby a washed solution of cyclohexanone oxime in toluene and a second phosphorus compounds and organics containing wastewater stream are
25 obtained. The second phosphorus compounds and organics containing wastewater stream is separated from the solution of cyclohexanone oxime in toluene and is discharged. In a distillation unit the washed solution of cyclohexanone oxime in toluene is distilled, whereby toluene and cyclohexanone are obtained that are (optionally) recycled and cyclohexanone oxime that is discharged through line [1].

30 Both the first phosphorus compounds and organics containing wastewater stream and the second phosphorus compounds and organics containing wastewater stream are combined and are discharged from cyclohexanone oxime production section [A] through line [2].

 It is also possible to charge cyclohexanol instead of cyclohexanone
35 through line [h]. In such a case, cyclohexanol is first converted into cyclohexanone through the action of hydrogen peroxide and then the cyclohexanone is converted into cyclohexanone oxime.

The present invention is illustrated by, but not intended to be limited to, the following examples.

5 COMPARATIVE EXPERIMENT A

- A continuous HPO[®] process for the production of cyclohexanone oxime, in which first hydroxylamine is formed by selective reduction of nitrate followed by reaction of the formed hydroxylamine with cyclohexanone to form cyclohexanone oxime at about 70 °C, where after the formed cyclohexanone oxime
- 10 is separated from the reaction mixture and whereby the generated wastewater is treated in a biochemical wastewater treatment plant was performed in a chemical plant, comprising:
- a NH₃ combustion unit;
 - a NO_x absorption unit;

15 - a hydroxylamine formation section;

 - a cyclohexanone oxime formation zone;
 - a cyclohexanone oxime washing section;
 - a cyclohexanone oxime distillation section;
 - a steam stripper for the removal of water from the aqueous phosphate

20 solution;

 - a stripping unit in which organic compounds are removed from the first water phase that contains phosphate and the second water phase that contains phosphate;
 - a biochemical wastewater treatment plant with sludge removal;

25 - a filtration section for removal of solids that is located downstream of the biochemical wastewater treatment plant; and

 - a discharge of the treated wastewater from the filtration section

as described above and substantially as depicted in FIG. 1 and FIG. 3 was operated for some period of time.

- 30 This commercial chemical plant had on average an hourly output of about 25 t/h of cyclohexanone oxime, which is equivalent to an annual plant output of approximately 200 kta of cyclohexanone oxime (assuming 8000 effective production hours per year). The main raw materials that were charged to the cyclohexanone oxime production section of this chemical plant were ammonia, air, hydrogen gas,
- 35 and cyclohexanone. In addition small amounts of phosphoric acid and toluene were charged to compensate for losses and washing water was charged to the cyclohexanone oxime washing section.

The wastewater that is discharged from the cyclohexanone oxime production section is mixed with wastewaters from other chemical plants on the caprolactam production site. These other chemical plants include a chemical plant for cyclohexanone production by oxidation of cyclohexane, a chemical plant for caprolactam production by liquid phase Beckmann rearrangement of cyclohexanone oxime followed by neutralization with ammonia, a chemical plant for caprolactam purification and a chemical plant for ammonium sulphate crystallization.

The total amount of wastewaters that are charged to the biochemical wastewater treatment plant is about 150 m³/h and contains on average about 120 ppm phosphorus (in the form of phosphate). The treated wastewater that is discharged from the filtration section for removal of solids that is located downstream of the biochemical wastewater treatment plant contains on average about 110 ppm phosphorus (in the form of phosphate).

In Example 1 (according to the invention), the cyclohexanone oxime production section, the biochemical wastewater treatment plant with sludge removal, and the filtration section located downstream of the biochemical wastewater treatment plant for removal of solids were the same as the cyclohexanone oxime production section, the biochemical wastewater treatment plant with sludge removal, and the filtration section located downstream of the biochemical wastewater treatment plant for removal of solids in Comparative Experiment A. In addition the chemical plant in Example 1 is provided with a dephosphorization section.

EXAMPLE 1

A continuous HPO[®] process for the production of cyclohexanone oxime, in which first hydroxylamine is formed by selective reduction of nitrate followed by reaction of the formed hydroxylamine with cyclohexanone to form cyclohexanone oxime at about 70 °C, where after the formed cyclohexanone oxime is separated from the reaction mixture and whereby the generated wastewater is treated in a dephosphorization section and consequently in a biochemical wastewater treatment plant was performed in a chemical plant, comprising:

- a NH₃ combustion unit;
- a NO_x absorption unit;
- a hydroxylamine formation section;
- a cyclohexanone oxime formation zone;
- a cyclohexanone oxime washing section;
- a cyclohexanone oxime distillation section;

- a steam stripper for the removal of water from the aqueous phosphate solution;
- a stripping unit in which organic compounds are removed from the first water phase that contains phosphate and the second water phase that contains phosphate;
- dephosphorization section, in which magnesium ammonium phosphate hexahydrate is formed and discharged;
- a biochemical wastewater treatment plant with sludge removal;
- a filtration section for removal of solids that is located downstream of the biochemical wastewater treatment plant; and
- a discharge of the treated wastewater from the filtration section

as described above and substantially as depicted in FIG. 2 and FIG. 3 was operated for some period of time.

This commercial chemical plant had on average an hourly output of about 25 t/h of cyclohexanone oxime, which is equivalent to an annual plant output of approximately 200 kta of cyclohexanone oxime (assuming 8000 effective production hours per year). The main raw materials that were charged to the cyclohexanone oxime production section of this chemical plant were ammonia, air, hydrogen gas, and cyclohexanone. In addition small amounts of phosphoric acid and toluene were charged to compensate for losses and washing water was charged to the cyclohexanone oxime washing section.

The wastewater that is discharged from the cyclohexanone oxime production section is mixed with wastewaters from other chemical plants on the caprolactam production site. These other chemical plants include a chemical plant for cyclohexanone production by oxidation of cyclohexane, a chemical plant for caprolactam production by liquid phase Beckmann rearrangement of cyclohexanone oxime followed by neutralization with ammonia, a chemical plant for caprolactam purification and a chemical plant for ammonium sulphate crystallization.

The total amount of wastewaters that are charged to the dephosphorization section is about 150 m³/h and contains on average about 120 ppm phosphorus (in the form of phosphate). In the dephosphorization section, the pH value is maintained at about 9 by addition of caustic. In the dephosphorization section, the molar ratio of P: Mg: N is maintained at about 1: 1.2: 2 by addition of MgCl₂ and ammonium sulphate containing purge liquid from the ammonium sulphate crystallization plant. The hereby formed magnesium ammonium phosphate hexahydrate is separated from the wastewater and is discharged. The discharged magnesium ammonium phosphate hexahydrate is after drying applied as fertilizer.

The wastewater that is discharged from the dephosphorization section contains about 5 ppm phosphorus (in the form of phosphate) is charged to the biochemical wastewater treatment plant with sludge removal. The treated wastewater that is discharged from the filtration section for removal of solids that is located downstream of the biochemical wastewater treatment plant contains less than 0.5 ppm phosphorus (in the form of phosphate).

Comparison of Comparative Experiment A and Example 1 shows that, for a process for the production of cyclohexanone based on $\text{HPO}^\circledast$ technology, due to the addition of the dephosphorization section, in which magnesium ammonium phosphate hexahydrate is formed and discharged, the treated wastewater that is discharged from the filtration section for removal of solids that is located downstream of the biochemical wastewater treatment plant is reduced from about 110 ppm phosphorus (in the form of phosphate) to less than 0.5 ppm phosphorus (in the form of phosphate). In addition discharged magnesium ammonium phosphate hexahydrate is obtained that can be used as fertilizer.

COMPARATIVE EXPERIMENT B

A continuous process for the production of cyclohexanone oxime, in which cyclohexanone, ammonia, and hydrogen peroxide react in the presence of a TS-1 catalyst and t-butanol as solvent at about 85 °C and whereby the formed cyclohexanone oxime is separated from the reaction mixture by extraction in toluene, washed with an aqueous caustic solution and then separated by distillation and whereby the generated wastewaters are treated in a biochemical wastewater treatment plant was performed in a chemical plant, comprising:

- a cyclohexanone oxime formation zone;
- a catalyst filtration section to recover TS-1 catalyst;
- a distillation column, wherein solvent t-butanol and excess ammonia are going overhead and an aqueous cyclohexanone oxime and phosphorus compounds containing phase is obtained as bottom flow;
- an extraction section, wherein organic cyclohexanone oxime containing toluene phase and a first phosphorus compounds and organics containing wastewater stream are obtained;
- a washing section, wherein the organic cyclohexanone oxime containing toluene phase is washed with caustic washing water, whereby a washed solution of cyclohexanone oxime in toluene and a second phosphorus compounds and organics containing wastewater stream are obtained;

- a cyclohexanone oxime distillation section;
- a biochemical wastewater treatment plant with sludge removal;
- a filtration section for removal of solids that is located downstream of the biochemical wastewater treatment plant; and

5 - a discharge of the treated wastewater from the filtration section

as described above and substantially as depicted in FIG. 1 and FIG. 4 was simulated.

This chemical plant had on average an hourly output of about 12.5 t/h of cyclohexanone oxime, which is equivalent to an annual plant output of approximately 100 kta of cyclohexanone oxime (assuming 8000 effective production
10 hours per year). The main raw materials that were charged to the cyclohexanone oxime production section of this chemical plant were ammonia, 27 wt.% aqueous hydrogen peroxide, and cyclohexanone. The used 27 wt.% aqueous hydrogen peroxide is produced in a hydrogen peroxide plant that is based on the well-known anthraquinone technology. The phosphorus content of 27 wt.% aqueous hydrogen
15 peroxide is about 0.5 kg trioctyl phosphate per ton of 27 wt.% aqueous H₂O₂ and about 1 kg phosphoric acid per ton of 27 wt.% aqueous H₂O₂. In addition small amounts of t-butanol and toluene were charged to the cyclohexanone oxime production section of this chemical plant to compensate for losses and caustic washing water was charged to the cyclohexanone oxime washing section.

20 All wastewaters, including the first phosphorus compounds and organics containing wastewater stream and the second phosphorus compounds and organics containing wastewater stream that are discharged from cyclohexanone oxime production section are combined and are charged to the biochemical wastewater treatment plant with sludge removal. The treated wastewater that is
25 discharged from the filtration section for removal of solids that is located downstream of the biochemical wastewater treatment plant contains on average about 150 ppm phosphorus (partly in the form of phosphate and partly in the form of organic phosphorus).

30 In Example 2 (according to the invention), the cyclohexanone oxime production section, the biochemical wastewater treatment plant with sludge removal, and the filtration section located downstream of the biochemical wastewater treatment plant for removal of solids were the same as the cyclohexanone oxime production section, the biochemical wastewater treatment plant with sludge removal,
35 and the filtration section located downstream of the biochemical wastewater treatment plant for removal of solids in Comparative Experiment B. In addition the chemical plant in Example 2 is provided with a dephosphorization section.

EXAMPLE 2

A continuous process for the production of cyclohexanone oxime, in which cyclohexanone, ammonia, and hydrogen peroxide react in the presence of a TS-1 catalyst and t-butanol as solvent at about 85 °C and whereby the formed cyclohexanone oxime is separated from the reaction mixture by extraction in toluene, washed with an aqueous caustic solution and then separated by distillation and whereby the generated wastewaters are treated in a biochemical wastewater treatment plant was performed in a chemical plant, comprising:

- a cyclohexanone oxime formation zone;
- a catalyst filtration section to recover TS-1 catalyst;
- a distillation column, wherein solvent t-butanol and excess ammonia are going overhead and an aqueous cyclohexanone oxime and phosphorus compounds containing phase is obtained as bottom flow;
- an extraction section, wherein organic cyclohexanone oxime containing toluene phase and a first phosphorus compounds and organics containing wastewater stream are obtained;
- a washing section, wherein the organic cyclohexanone oxime containing toluene phase is washed with caustic washing water, whereby a washed solution of cyclohexanone oxime in toluene and a second phosphorus compounds and organics containing wastewater stream are obtained;
- a cyclohexanone oxime distillation section;
- an organic phosphorus conversion unit;
- a dephosphorization section, in which magnesium ammonium phosphate hexahydrate is formed and discharged;
- a biochemical wastewater treatment plant with sludge removal;
- a filtration section for removal of solids that is located downstream of the biochemical wastewater treatment plant; and
- a discharge of the treated wastewater from the filtration section

as described above and substantially as depicted in FIG. 2 and FIG. 4 was simulated.

This chemical plant had on average an hourly output of about 12.5 t/h of cyclohexanone oxime, which is equivalent to an annual plant output of approximately 100 kta of cyclohexanone oxime (assuming 8000 effective production hours per year). The main raw materials that were charged to the cyclohexanone oxime production section of this chemical plant were ammonia, 27 wt.% aqueous hydrogen peroxide, and cyclohexanone. The used 27 wt.% aqueous hydrogen peroxide is produced in a hydrogen peroxide plant that is based on the well-known anthraquinone technology. The phosphorus content of 27 wt.% aqueous hydrogen

peroxide is about 0.5 kg trioctyl phosphate per ton of 27 wt.% aqueous H_2O_2 and about 1 kg phosphoric acid per ton of 27 wt.% aqueous H_2O_2 . In addition small amounts of t-butanol and toluene were charged to the cyclohexanone oxime production section of this chemical plant to compensate for losses and caustic washing water was charged to the cyclohexanone oxime washing section.

All wastewaters, including the first phosphorus compounds and organics containing wastewater stream and the second phosphorus compounds and organics containing wastewater stream that are discharged from cyclohexanone oxime production section are combined and are charged to the organic phosphorus conversion unit. In this unit organic phosphorus conversion organic phosphorus compounds, like e.g., trioctyl phosphate, are almost completely hydrolyzed under alkaline conditions. The pH value, temperature and residence time in this unit are maintained at about 11, 50°C, and 8 hrs, respectively. The pH value is adjusted by dosing of NaOH.

The treated wastewater that is discharged from the organic phosphorus conversion unit is charged to the dephosphorization section. In the dephosphorization section, the pH value is maintained at about 9. In the dephosphorization section, the molar ratio of P: Mg: N is maintained at about 1: 1.2: 2 by addition of $MgCl_2$ and ammonium sulphate containing purge liquid from an ammonium sulphate crystallization plant. The hereby formed magnesium ammonium phosphate hexahydrate is separated from the wastewater and is discharged. The discharged magnesium ammonium phosphate hexahydrate is after drying applied as fertilizer.

The wastewater that is discharged from the dephosphorization section is charged to the biochemical wastewater treatment plant with sludge removal. The treated wastewater that is discharged from the filtration section for removal of solids that is located downstream of the biochemical wastewater treatment plant contains less than 0.5 ppm phosphorus (in the form of phosphate).

Comparison of Comparative Experiment B and Example 2 shows that, for a process for the production of cyclohexanone based on ammoximation, due to the addition of the organic phosphorus conversion unit and the dephosphorization section, in which magnesium ammonium phosphate hexahydrate is formed and discharged, the treated wastewater that is discharged from the filtration section for removal of solids that is located downstream of the biochemical wastewater treatment plant is reduced from about 110 ppm phosphorus (in the form of

phosphate) to less than 0.5 ppm phosphorus (in the form of phosphate). In addition discharged magnesium ammonium phosphate hexahydrate is obtained that can be used as fertilizer.

CLAIMS

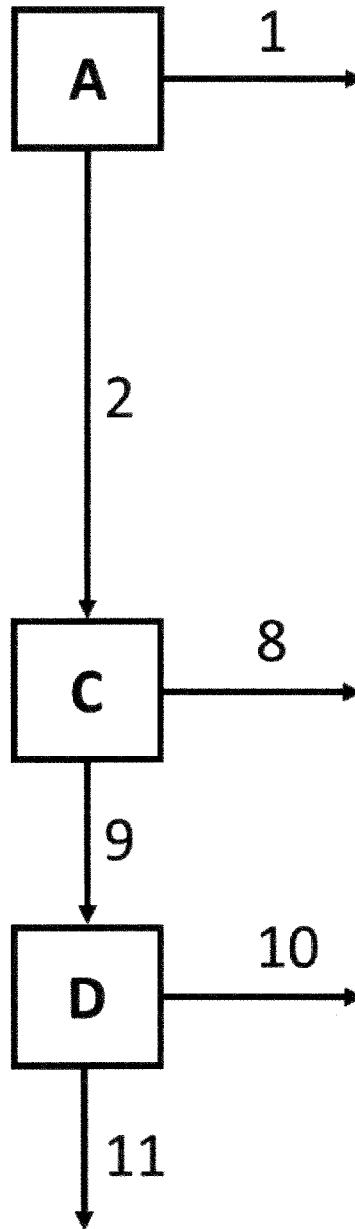
1. A process for the production of an oxime, the process comprising:
 - a. converting an aldehyde or a ketone by a chemical reaction into an oxime
5 at a temperature of 15 to 115 °C, whereby a reaction mixture comprising the formed oxime is obtained;
 - b. recovering the formed oxime from the reaction mixture;
 - c. producing a first aqueous phase that contains phosphate ions;
 - d. reducing the content of phosphate ions in the first aqueous phase,
10 whereby a second aqueous phase is formed; and
 - e. discharging the second aqueous phase,
wherein the reduction of the content of phosphate ions in the first aqueous phase is achieved by
 - 1) forming a salt in which the molar ratio of N: Mg: P is about 1: 1: 1; and
15 2) separating the salt in which the molar ratio of N: Mg: P is about 1: 1: 1 from the second aqueous phase.
2. A process according to claim 1, wherein the process further comprises:
 - f. reducing the content of phosphate ions in the second aqueous phase,
20 whereby a third aqueous phase is formed; and
 - g. discharging the third aqueous phase,
wherein the reduction of the content of phosphate ions in the second aqueous phase is achieved by
 - 1) charging the second aqueous phase to a biochemical wastewater
25 treatment plant, and
 - 2) discharging the third aqueous phase from the biochemical wastewater treatment plant.
3. The process according to claim 1 or 2, whereby the salt in which the molar
30 ratio of N: Mg: P is about 1: 1: 1 is magnesium ammonium phosphate hexahydrate.
4. The process according to any one of claims 1 to 3, wherein the formation of
35 the salt is achieved by addition of an effluent stream of an incinerator to the first aqueous phase.

5. The process according to any one of claims 1 to 4, wherein the formation of the salt is achieved by addition of a stream to the first aqueous phase that originates from an ammonium sulphate crystallization plant and comprises ammonium ions and at least one inorganic or organic impurity originating from a caprolactam production process.
6. The process according to any one of claims 1 to 5, whereby in the chemical reaction an aldehyde or a ketone is converted to an oxime with hydroxylamine.
7. The process according to any one of claims 1 to 6, wherein the process for the production of an oxime is either an amoximation process, in which in step a. an aldehyde or a ketone, ammonia, and hydrogen peroxide react in the presence of a catalyst, or a process, in which first hydroxylamine is formed by selective reduction of nitrate followed by reaction of the formed hydroxylamine with cyclohexanone to form an oxime in step a.
8. The process according to any one of claims 1 to 7, wherein the ketone is selected from butanone, cyclohexanone or cyclododecanone.
9. The process according to any one of claims 1 to 8, wherein the formed oxime is selected from butanone oxime, cyclohexanone oxime or cyclododecanone oxime.
10. The process according to any one of claims 1 to 9 wherein the ketone is cyclohexanone and the formed oxime is cyclohexanone oxime.
11. A chemical plant suitable for the production of an oxime comprising:
- a chemical reaction section wherein the oxime is formed;
 - an oxime purification and recovery section wherein the formed oxime is purified and recovered;
 - a section in which an aqueous phase containing phosphate is formed;
 - a dephosphorization section wherein a salt in which the molar ratio of N: Mg: P is about 1: 1: 1 is formed and separated from the aqueous phase.
12. The chemical plant according to claim 11, wherein the salt in which the molar ratio of N: Mg: P is about 1: 1: 1 is magnesium ammonium phosphate hexahydrate.

13. The chemical plant according to claim 11 or 12, wherein the ketone is cyclohexanone or cyclododecanone and the resulting oxime is cyclohexanone oxime or cyclododecanone.
- 5
14. A fertilizer product comprising magnesium ammonium phosphate hexahydrate, obtainable by the process according to any one of claims 1 to 10.
- 10 15. Cyclohexanone oxime, obtainable by an improved process according to any one of claims 1 to 10.

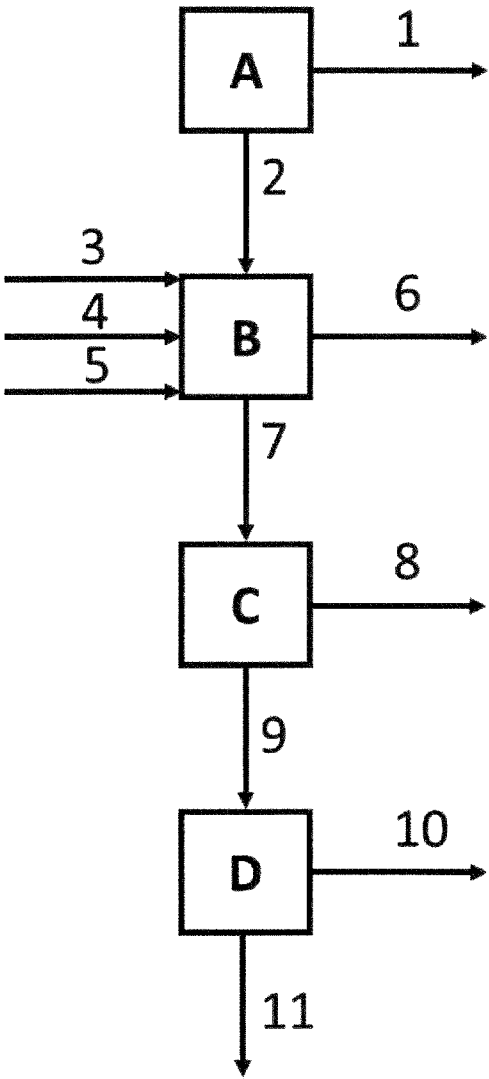
DRAWINGS

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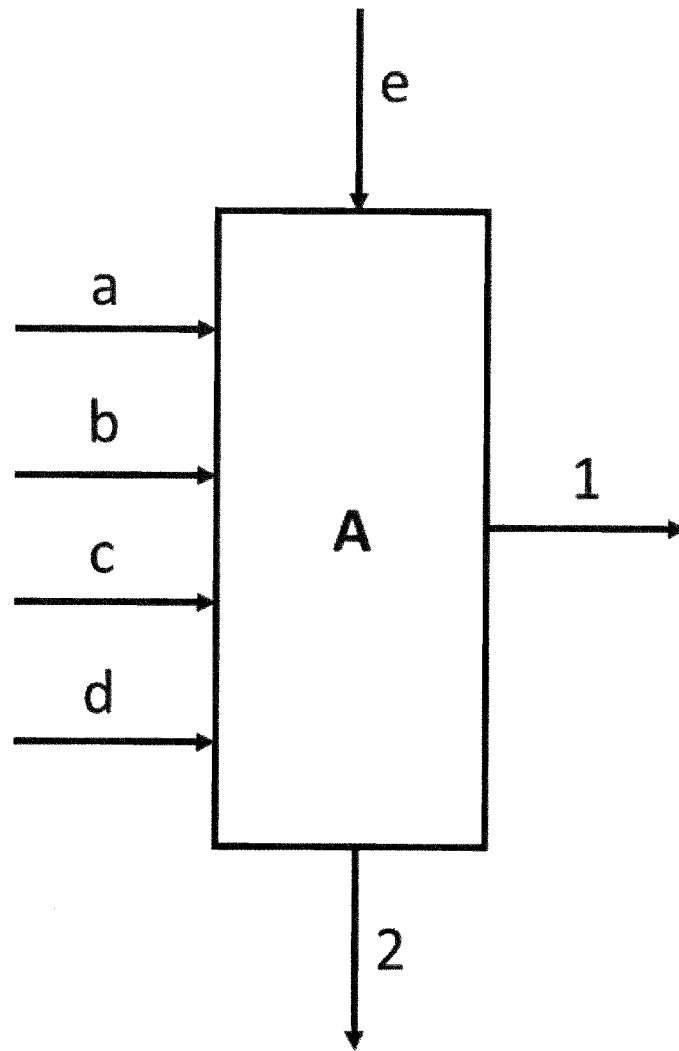
FIG. 1



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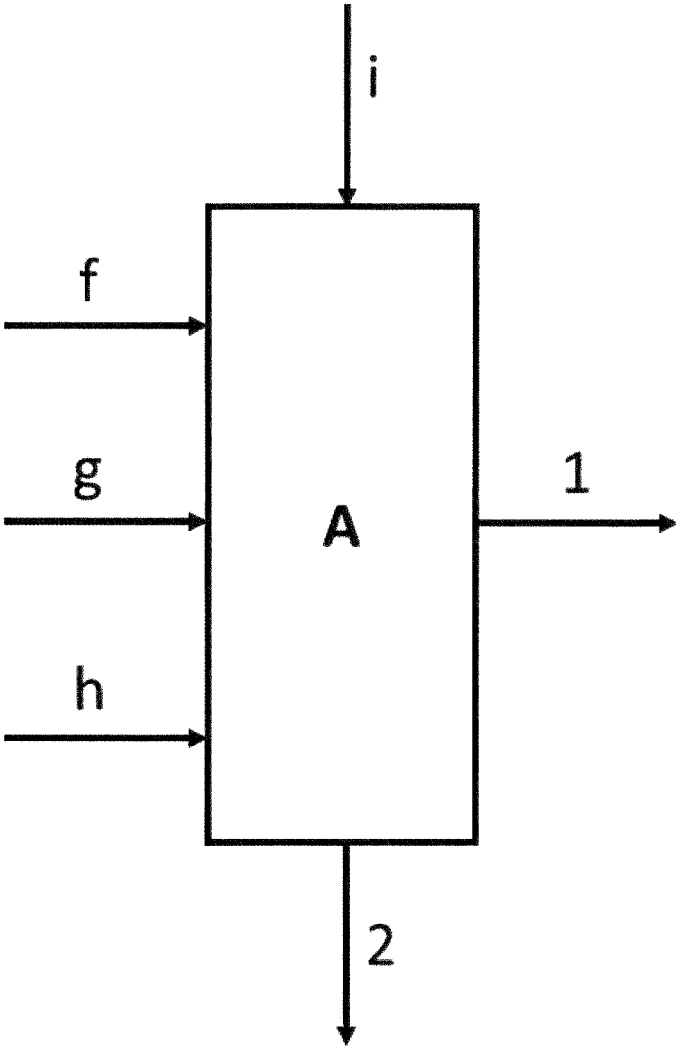
FIG. 2



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FIG. 3



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FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/077744

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J3/00 C07C249/08 C07C251/44
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)
B01J 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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2014/102106 A1 (DSM IP ASSETS BV [NL]) 3 July 2014 (2014-07-03)	11-13,15
Y	See claim 1	1-10
X	WO 02/096861 A2 (DSM NV [NL]; BENNEKER ARNO [NL]; OEVERING HENK [NL]; BROUWERS JOHANNES) 5 December 2002 (2002-12-05)	11-13,15
Y	See claim 1	1-10
X	US 2005/023220 A1 (BARAK PHILLIP W [US] ET AL) 3 February 2005 (2005-02-03)	14
Y	See claim 1	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search

8 January 2020

Date of mailing of the international search report

15/01/2020

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/077744

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