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(54) **Készülék nitrálási termékek tisztítására**

Apparatus for the purification of nitrating products

The present invention relates to the technical field of nitration, in particular the preparation of nitrated aromatic organic compounds (also referred to below as "nitroaromatics", "nitrating products" or the like) and their purification after their preparation.

In particular, the present invention relates to a device for removing impurities (such as, for example, non-reacted reactants, reaction byproducts, nitrating acid and reaction products thereof, such as nitrogen oxides or nitrous acid, etc.) in the nitration of nitratable aromatic compounds after removal of the nitrated diacetate by treatment with a scrubbing medium. In other words, the present invention thus relates to an apparatus or plant for the purification of nitrited raw products obtained during nitration of nitratable aromatic compounds after separation of the nitrating end acid.

The apparatus or plant according to the invention is particularly suitable for carrying out a corresponding process for the removal of impurities from nitrated raw products obtained during the nitration of nitratable aromatic compounds after removal of the nitrating end acid by treatment with a scrubbing medium.

Aromatic nitro compounds, such as, for example, nitrobenzene (MNB), mononitrotoluene (MNT), dinitrotoluene (DNT), trinitrotoluene (TNT), nitrochlorobenzene (MNCB), etc., which are obtained by reaction of a corresponding aromatic, such as, for example, benzene, toluene, xylene, chlorobenzene, dichlorobenzene etc., with nitric acid, directly or in the presence of sulfuric acid as catalyst and water-binding agent, must be subjected to a multi-stage scrubbing and additional purification steps before their further treatment in order to remove impurities dissolved or suspended in the raw nitroaromatics such as sulfuric acid, nitric acid, nitrose, nitrophenols, nitrocresols, etc., which may be present, for example, in the form of mono-, dinitro- and trinitro compounds, and other oxidation products, such as nitrobenzoic acids and degradation products from the decomposition of the nitrophenols, or unreacted aromatics or non-desired isomers, for example in the case of TNT production, in the raw mixture of nitroaromatics.

Usually the scrubbing of the raw nitroaromatics consists in removing the dissolved and suspended acids of the nitrating mixture, the nitrophenols and other acidic impurities which may be extracted with the scrubbing medium in three steps (see, for example, Meissner et al., Industrial and Engineering Chemistry, Vol. 46, pages. 718-724 (1954), Ullmanns Enzyklopädie der Technischen Chemie, 4th edition, vol. 17, pages 384 to 386, H. Hermann et al., "Industrial Nitration of Toluene to Dinitrotoluene", ACS Symposium Series 623 1996), pages 234 to 249, editors: L.F. Albright, R.V.C. Carr, R.J. Schmitt; US 6 288 289 B1, EP 1 816 117 B1). As a scrubbing medium, water is usually used for this purpose, wherein the scrubbing is usually carried out as liquid/liquid scrubbing (i e. at temperatures at which the nitroaromatic liquid to be scrubbed is present as a liquid).

This three-stage scrubbing typically comprises the following steps:

1. An acid scrubbing with water to remove the dissolved and suspended mineral acids, such as sulfuric acid, nitric acid, and nitrose ("acidic scrubbing").
2. A basic or alkaline scrubbing in the presence of a base ("alkali scrubbing"), such as sodium carbonate (soda), sodium bicarbonate, sodium sulfite, sodium hydrogensulfite, ammonia, sodium hydroxide solution, potassium hydroxide solution etc. (see, for example, US 4 482 769 A, US 4 597 875 A or US 6 288 289 B1), for removing the weakly acidic impurities dissolved in the raw nitroaromatics, such as nitrophenols, nitrocresols, nitrobenzoic acids, degradation products from the oxidative decomposition of the phenols or from aliphatic or

cyclic hydrocarbons, etc., such as, for example, oxalic acid, etc., or asymmetric isomers in the case of TNT ("basic scrubbing").

3. A neutral scrubbing to remove the traces of alkali and further reduce the impurities still remaining in the product ("neutral scrubbing").

The aim of these scrubbing steps is to obtain, in addition to a pure product, as little as possible of wastewater per ton of product, in which the contaminated impurities are present so that their disposal may be carried out cost-effectively.

In order to minimize the amounts of water required for this scrubbing, the scrubbing may, for example, be carried out in counter flow in such a way that the water used for the neutral scrubbing is used in the alkali scrubbing after addition of bases (cf., for example, Quakenbush et al., The Olin Dinitrotoluene (DNT) Process, Polyurethanes World Congress 1993, Publishers: Technomic Lancaster, pages 484 to 488), or that the acid scrubbing is scrubbed with a minimal amount of water so that a concentrated acid is obtained which is supplied directly or after further concentration in the nitration.

Thus, EP 0 279 312 B1, EP 0 736 514 B1 and EP 1 780 195 B1 describe processes in which the mineral acids which are still suspended and dissolved in the nitroaromatics after the nitration, such as sulfuric acid, nitric acid and nitroseads, are used in several stages, are selectively scrubbed out and returned to the nitration, so that no more wastewater from the acidic scrubbing has to be collected and disposed of.

However, methods have also been disclosed in which, in order to minimize the amount of wastewater to be treated, no acidic scrubbing is carried out, but only an alkaline and neutral scrubbing, as described, for example, in Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 17, pages 136 to 138, or in US 4 091 042 A.

In addition to the minimization of the wastewater, the goal is also to minimize the technical complexity required for the scrubbing (e.g. by specifically adapting the technology used for the scrubbing not only to the scrubbing step but to the product to be scrubbed as well).

For the scrubbing of the nitroaromatics to be purified, the so-called mixer settlers (mixer separators) (for example, EP 1 593 654 A1) are usually used as scrubbing apparatuses in which the mixing part is usually a stirrer tank (cf. for example, Ullmann's Encyclopedia of Industrial Chemistry, 5 Ed., Vol. B 3, pages 6.19 to 6.21, M Baerns et al., Technische Chemie, Verlag Wiley-VCH 2006, pages 352/352). Thus, an arrangement of mixer and separator is already described in the German patent DE 1 135 425 which makes it possible to scrub crystalline nitroaromatics at room temperature, and, for example, DNT, TNT or NCB, at elevated temperatures while minimizing the heating effort. However, centrifugal pumps and static mixers have also been used as mixers (cf. for example the publications US 3,221,064 A or EP 1 816 117 B1).

However, the use of the mixer-settler technology (mixer-separator technology) (cf., for example, Fig. 1) is complex and expensive. Due to unavoidable slippage in continuously operated stirrer tanks as a mixer, it is necessary, especially for the removal of the nitrophenols or nitrocresols when these are present in high concentrations in the raw nitroaromatics, to work in a multi-stage and, if possible, in counter flow, in order to obtain the desired low content of impurities (e.g. a content of nitrophenols of less than 10 ppm, preferably 2 to 3 ppm) for the further treatment of nitriaromatics. In addition, scrubbing in multi-stage extraction columns is technically complex and expensive and not very effective. Moreover, the production of large exchange surfaces for a two-phase mixture can not be realized in a short time for an effective mass transfer, followed by rapid chemical conversion, either in a stirrer tank or in extraction columns.

In JM Coulson, FE Warner, "A Problem in Chemical Engineering Design: The Manufacture of Mononitrotoluene", a publication of "The Institution of Chemical Engineers", 56, Victoria Street, London, SW I, 1949, pages 25/26, three-stage

scrubbing of the MNT with a scrubber of the Holley-Mott type (mixer/settler), the acidic and the alkaline scrubbing is carried out in counter flow in at least two stages in each case in order to achieve a sufficient removal of the acids and nitrocresols dissolved or suspended in the MNT.

In the Canadian patent CA 1 034 603, four-stage acid scrubbing in counter flow is proposed in order to scrub off the nitric and sulfuric acid dissolved and suspended in the raw DNT.

For the removal of all acidic components from raw nitrobenzene, such as entrained sulfuric acid and the dinitrophenols and picric acid dissolved in nitroaromatics, up to 2000 ppm, a four-stage scrubbing with soda ash in counter flow is described in US 4 091 042 in order to obtain the desired purity.

EP 1 816 117 A1 describes a four-stage neutral scrubbing in counter flow using four stirrer tanks and the corresponding separating apparatuses (so-called "mixer/settler technology") in order to determine the still too high content of nitrophenols of approximately 50 ppm after alkaline scrubbing with a residual content of about 2 ppm. However, even when the stirrer tanks are replaced by centrifugal pumps as a mixing element, three stages are still required to obtain a residual content of 3 ppm of nitrophenols in the resulting nitrobenzene.

US 4 994 242 A discloses that static mixers are not suitable alone on a technical scale as mixing elements in two-phase systems for the production of an optimum dispersion of the two immiscible phases into one another. Thus, the use of a static mixer for alkaline scrubbing is described in EP 1 816 117 B1; The nitrobenzene treated therewith still contains more than 50 ppm of nitrophenols, which must be reduced to about 2 ppm by means of complex multi-stage neutral scrubbing.

As already explained in EP 1 780 195 B1 for acidic scrubbing, the scrubbing of nitroaromatics is a complex process. In addition to generating a sufficiently large exchange surface between the organic phase and the scrubbing phase (usually water) in order to achieve an optimal transition of the impurity to be removed from the organic phase, the efficiency of a scrubbing step depends on the distribution equilibrium of the contamination between the organ phase and the scrubbing medium. The impurity extracted from the organ phase is, as such, stable in the scrubbing medium or is removed from the distribution equilibrium by a subsequent reaction.

Thus, after the transition from the organ phase into the aqueous phase, nitrose reacts with water to disperse nitric acid and NO according to equation (1):

(1) $3NO_2 (=3/2\ N_2O_4) + H_2O \rightarrow 2\ HNO_3 + NO$

Both the transition of the nitrose from the organ phase, probably as a dimer, and the reaction of the nitrose (as N_2O_4) with the water are comparatively slow reactions compared to neutralization, so that time is necessary for the removal of the nitrose from the organ phase by scrubbing with subsequent chemical reaction.

The dissociation of the acids into hydronium ions and the corresponding anions (Equation 2) or the neutralization (Equation 3) occurring in the presence of alkali is very rapid in the case of acids, such as sulfuric acid, nitric acid, or weakly acid nitrophenols. The impurities are removed from the distribution equilibrium between the nitroaromatics and scrubbing water and are in anionic form only in the scrubbing water.

(2) $H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$

(3) $NO_2Ar\text{-}OH + NaOH \rightarrow NO_2Ar\text{-}O^- Na^+ + H_2O$

By means of this rapid neutralization of substances forming anions in the alkaline scrubbing medium, it is to be expected that the extraction of these substances from the organ phase is essentially mass-transfer-controlled while the scrubbing essentially follows the same kinetic principles as a mononitiation, e.g. as the nitration of benzene to nitrobenzene.

The methods and plant known from the prior art for the purification of nitrided raw products often do not work with high efficiency or in a satisfactory manner. At times, this also involves excessively complex process sequences or work processes, and the desired purities are often not achieved, at least not at a reasonable cost.

Document DE 21 51 206 A1 relates to a method and a device for mixing liquids, wherein the mixing of liquids is carried out using jet nozzles which protrude into a mixing reactor.

Document DE 12 22 904 B relates to a process for the purification of nitrophenol-containing aromatic nitro compounds wherein the aromatic nitro compounds to be purified are subjected to scrubbing with water and are subsequently admixed either directly or after mixing with the same volume of a 0.1 to 2 wt.-% of aqueous sodium hydroxide solution, and then passed over an alkaline anion exchange resin.

Document US 3 221 064 A relates to a process for the purification of dinitrotoluenes, wherein the dinitrotoluenes are emulsified in a rotary pump with water and aqueous sodium hydroxide solution and the scrubbing medium is separated after each scrubbing step.

EP 0 279 312 A relates to a process for the separation of sulfuric acid and nitric acid from dinitrotoluene mixtures obtained during the nitration of toluene, wherein the dinitrotoluenes are mixed with water and the aqueous phase, which subsequently separates, containing sulfuric acid and nitric acid, is separated off.

US 4 597 875 A relates to a process for the removal of nitrocresol and picric acid impurities from wastewater arising during the preparation of nitroaromatics, wherein the impurities are cumulated over several scrubbing steps, acid-treated, and the precipitated organic residues are subsequently combusted.

US 4 492 860 A relates to a process for the purification of dinitrotoluene, wherein the dinitrotoluene is scrubbed with an aqueous basic phase to remove the dinitroorthocresol compounds while leaving the dinitroorthocresol in the organic phase.

The present invention is therefore based on the object of providing an apparatus or plant for removing impurities from nitrided raw products obtained during the nitration of nitratable aromatic compounds after removal of the nitrating end acid, wherein the above-described problems and disadvantages occurring in connection with the prior art are at least largely avoided or at least mitigated.

In particular, it is an object of the present invention to provide an apparatus or plant suitable for carrying out a corresponding process, by means of which efficient purification of the nitrided raw products, as obtained from the nitration of nitratable aromatic compounds after separation of the so-called nitrating end acids.

Furthermore, it is an object of the present invention to provide the scrubbing of the raw nitroaromatics resulting after separation of the nitrating end acid in which there are significant amounts of impurities, such as, for example, entrained nitrating end acid, dissolved sulfuric acid, nitric acid, nitrose, nitrophenols, nitrobenzoic acids, degradation products from the oxidative decomposition of nitrophenols, etc., so that in each scrubbing step the nitrophenol content is as low as possible in the scrubbed nitroaromatic compound (e.g. nitrobenzene from an adiabatic nitration with originally about 2000 ppm di- and trinitrophenols of the content of nitrophenols after alkaline scrubbing is less than 50 ppm, preferably less than 10 ppm, and less than 2 ppm after neutral scrubbing), while the effort and cost thereof are clearly lower than in prior art methods and apparatuses.

The above-described object is achieved according to the invention by an apparatus or plant according to claim 1, further, advantageous developments and embodiments of this aspect of the invention are the subject matter of the subclaims.

It goes without saying that embodiments, developments, advantages or the like, which are only implemented subsequently for the purpose of avoiding unnecessary repetitions, that apply to one aspect of the invention, also correspondingly apply to the other aspects of the invention.

Furthermore, it goes without saying that, in the case of subsequent statements of values, numbers and ranges, the relevant values, numbers and ranges are not to be understood as limiting; it is self-evident to the person skilled in the art that, depending on the particular case or application, the specified ranges or specifications may be deviated from without departing from the scope of the present invention.

In addition, all the values or parameter data or the like mentioned below may be determined, or determined in principle, using standardized or explicitly specified determination methods, or with determination methods which are known per se to a person skilled in the art.

The present invention will be described in more detail below.

With the apparatus or plant according to the invention, it is thus possible to carry out processes for removing impurities from nitrided raw products obtained during the nitration of nitratable aromatic compounds after removal of the nitrating end acid by treatment with a scrubbing medium, wherein the process comprises the following process steps:

- in a first process step (a), the nitrided raw products are first brought into contact with a scrubbing medium, while the nitrided raw products and the scrubbing medium are distributed into each other in such a way that a dispersion, in particular emulsion, results (i.e. in this first process step (a), a dispersion or emulsion of nitrided raw products, on the one hand, and scrubbing medium, on the other hand, are produced), while,
- in a second process step (b), the resulting dispersion, in particular the emulsion, is fed into a tube reactor so that, during the passage of the emulsion through the tube reactor, the impurities initially present in the nitrided raw products are removed and/or so that during the passage of the emulsion through the tube reactor, the impurities initially present in the nitrided raw products are converted into the scrubbing medium or are neutralized thereby.

The above process is therefore outstandingly suitable for the purification of nitrided raw products obtained during the nitration of nitratable aromatic compounds after removal of the nitrating end acid.

The principle of the above process therefore consists in contacting the raw nitroaromatics, which are derived from the nitration and still contain significant quantities of impurities, after first separating the nitrating end acid (e.g. in a separator) with a scrubbing medium and converting the resulting emulsion or dispersion in a tube reactor so that the impurities initially present in the nitroaromatics to be purified are transferred into the scrubbing medium or neutralized thereby, and in this way a purified nitroaromatic compound is obtained.

As the applicant has found in a completely surprising manner, the use of a tube reactor - in combination with an upstream dispersing or emulsifying device - leads to a particularly good mixing and very thorough and fine distribution of scrubbing medium, on the one hand, and nitroaromatics to be purified, on the other hand, so that in this way the impurities

may, so to speak, be completely or at least substantially completely removed in a single process step (namely within the scope of the tube reactor treatment).

In contrast to the prior art, therefore, advanced complex process steps for the purification of the raw nitroaromatic compound are efficiently avoided without impairing quality in the purification of the raw nitroaromatic compound.

Surprisingly, the tubular reactor used according to the invention for the treatment of the raw nitroaromatic compound with the scrubbing medium ensures such a thorough and fine distribution of raw nitroaromatics, on the one hand, and scrubbing medium, on the other hand, that all, or substantially all, impurities are introduced into the scrubbing medium within the scope of the tube reactor treatment according to process step (b), or are thereby neutralized, so that they may subsequently be separated off together with the scrubbing medium from the then purified nitroaromatic compound (i.e. after completion of the process step (b)).

Surprisingly, it has been found that it is possible within the scope of the present invention to carry out a scrubbing of nitroaromatics successfully in a one-stage manner, even with a high load of impurities such as nitrating acid, nitrophenols and nitrocresols, by means of a simple and inexpensive method, but also other dispersing organs, such as, for example, centrifugal pumps, with additional devices, such as static mixers, diaphragms, etc., in tube reactors alone or in combination with stirrer tanks, which allow a precisely defined mixing energy to be mixed into the mixture in mutually miscible phases. The resulting emulsions from the organ phase to be purified in the scrubbing medium (O/W type) or the scrubbing medium in the organ phase (W/O type) provide the interface between the nitroaromatic and the scrubbing medium required for an effective and optimal mass transfer.

As far as the preparation of the emulsion or dispersion in process step (a) is concerned, this is generally effected by means of a suitable dispersing or emulsifying device, in particular by means of a suitable mixing element.

Within the scope of the present invention, a mixing vessel, a jet mixer (or jet mixing device) or a pump, for example, may be used as a dispersing or emulsifying device (i.e. in particular as a first dispersing or emulsifying device), in particular a centrifugal pump may be used.

According to one embodiment, a pump, in particular a centrifugal pump, is used as a dispersing or emulsifying device, in particular as a mixing element, in the course of process step (a).

According to an alternative preferred embodiment, a so-called jet mixer (synonymously also referred to as a jet-mixing device) is used as a dispersing or emulsifying device, in particular as a mixing element, in process step (a). The jet mixer according to the invention is, in particular, a device which generates a (central) driving jet with a medium (e.g. ring beam) surrounding the (central) driving jet.

All types of jet mixers may be used as jet mixers, which allow the nitroaromatics to be scrubbed or the scrubbing medium to be scrubbed at a high relative speed by means of the central jet stream as a free jet, which may consist of both the scrubbing medium and the nitroaromatics to be scrubbed, wherein the nitroaromatic to be scrubbed in the scrubbing medium or the scrubbing medium to be scrubbed in the nitroaromatics is distributed as an emulsion with a large boundary surface. Such devices are described, for example, in Ullmann's Encyclopedia of Industrial Chemistry, 2003, Ed., Vol. B 4, pages 87/88 and 565-571, or in Perry's Chemical Engineers' Handbook, McGraw-Hill Book Company, 1984, 6th edition, pages 5-21 to 5-23, or in the German patent application DE 2 151 206.

In this case, the (central) jet stream in the jet mixer may be the scrubbing medium, while the surrounding medium is the nitrated raw aromatic to be purified; Alternatively, however, the (central) jet stream may also be formed by the

scrubbing medium which is to be purified, while the medium surrounding the (central) jet stream is the scrubbing medium. Both alternative embodiments result in the desired result.

Particularly good results with regard to the purification of the raw aromatics to be purified are obtained (irrespective of whether the central jet is formed by the scrubbing medium or else by the purified nitrided raw product), if the ratio of the speeds between the central driving jet, on the one hand, and the medium surrounding the central jet (e.g. ring jet) in the jet mixer is adjusted in the range of from 1 : 5 to 30 : 1, preferably in the range from 1 : 2 to 20 : 1, particularly preferably in the range from 1 : 1 to 10 : 1. In this way, a particularly thorough and fine distribution of the scrubbing medium, on the one hand, and the raw product, on the other hand, and consequently a particularly efficient purification, is achieved.

The flow rate of the scrubbing emulsion after the jet mixer in the downstream tube reactor is, in particular, in the range from 0.1 to 15.0 m/s, preferably in the range from 0.5 to 10 m/s.

According to an embodiment of the present invention, it may be provided that the dispersing device used in process step (a), in particular the mixing element, is connected upstream of the tube reactor, in particular directly upstream. According to a particular variant of this embodiment, it may be provided that the dispersing or emulsifying device, in particular the mixing element, merges into the tube reactor.

Likewise, however, it is also possible that the dispersing device, in particular the mixing element, is integrated into the tube reactor or is a component of the tube reactor. For this purpose, for example, the dispersing device may be arranged in the upper or upstream part of the tube reactor. Such an embodiment is possible, in particular, when the dispersing device, in particular the mixing element, is designed as a so-called jet mixer.

According to a particularly preferred embodiment, it may be provided that the tube reactor is equipped with mixing elements for carrying out process step (b), in particular for the input of additional mixing energy; in this way, particularly good purification results may be achieved because the additional mixing elements achieve a still further improved, particularly thorough, distribution of the scrubbing medium, on the one hand, and the raw aromatics to be purified, on the other hand. The mixing elements may be, in particular, plates, in particular impact or deflection plates, diaphragms, static mixers, flow dividers or the like. According to the invention, it is preferred if 1 to 15, in particular 2 to 15, preferably 2 to 10, particularly preferably 2 to 5, mixing elements are present in the tube reactor.

According to this embodiment, it is preferred if the mixing energy provided by the mixing element in the tube reactor is a mixing energy (i.e. a volume-related mixing energy) of a total of 10 to 1,000 joules/l, preferably 10 to 500 joules/l, more preferably 20 to 200 joules/l. In other words, according to this embodiment, a mixing energy (i.e. a volume-related mixing energy) of 10 to 1,000 joules/l, preferably 10 to 500 joules/l, more preferably 20 to 200 joules/l.

Particularly good results are obtained, in particular, when the mixing elements are designed in such a way that the pressure drop per mixing element is 0.1 bar to 3.0 bar, preferably 0.3 to 1.5 bar, particularly preferably 0.3 to 0.8 Bar.

As far as the residence time of the emulsion of scrubbing medium, on the one hand, and raw aromatics, on the other hand, in the tube reactor in the context of process step (b) is concerned, this may vary within wide limits. It is particularly preferred if the residence time in the tube reactor is 0.1 to 120 seconds, preferably 0.1 to 60 seconds, particularly preferably 1 to 30 seconds. In this way, particularly good scrubbing results are achieved, since this ensures, on the one hand, a sufficient minimum residence time, but on the other hand also an economical throughput.

The mass and phase ratio between purified nitrided raw products, on the one hand, and scrubbing medium, on the other hand, are also important in the course of the purification and may vary widely in each case.

Particularly good results are obtained when the mass ratio between nitrided raw products to be purified, on the one hand, and the scrubbing medium (i.e. freshly dosed scrubbing medium), on the other hand, is in the range from 200 : 1 to 1 :10, preferably in the range from 100 : 1 to 1 : 5, particularly preferably in the range from 10 : 1 to 1 : 2.

Likewise, particularly good results are obtained when the phase ratio (i.e. in particular the phase ratio in the scrubbing apparatus) between purified nitrided raw products, on the one hand, and scrubbing medium, on the other hand, is in the range from 25 : 1 to 1 : 5, in particular in the range from 10 : 1 to 1, preferably in the range from 5 : 1 to 1 : 1. The adjustment of the phase ratio may be achieved, in particular, by a circulation of the scrubbing medium after phase separation. On the one hand, this ensures an optimal exchange surface between the organ phase and the scrubbing medium and, on the other hand, the shortest possible time for phase separation in the phase separating apparatus.

The scrubbing of the nitroaromatics is usually carried out as a liquid/liquid scrubbing (i.e. at temperatures at which the nitroaromatic to be scrubbed or purified, as well as the scrubbing medium, is present as a liquid).

With regard to the scrubbing medium used, this is in the form of liquid under process conditions, in particular at temperatures above 5 °C, in particular at temperatures above 25 °C, and at atmospheric pressure.

An aqueous-based scrubbing medium, preferably water, is preferably used.

Depending on the phase ratio in the scrubbing apparatus, the nitroaromatic to be scrubbed is dispersed in the scrubbing medium as an oil-in-water emulsion (O/W emulsion), or the scrubbing medium in the aromatics to be scrubbed as water-in-oil emulsion (W/O emulsion).

The efficiency of the scrubbing medium may be further increased by the fact that at least one base may be added to the scrubbing medium. The base may be selected, in particular, from the group of inorganic hydroxides, carbonates, hydrogencarbonates, sulfites, hydrogensulfites and ammonia, as well as their mixtures or combinations, preferably from the group of sodium hydroxide solution, potassium hydroxide solution, sodium carbonate, potassium carbonate, sodium hydrogencarbonate, potassium hydrogen-carbonate, ammonia, ammonium carbonate, sodium sulfite, and sodium hydrogensulfite, as well as mixtures or combinations thereof.

The quantity of alkali used in an alkaline scrubbing should, in particular, be such that not only all acids may be converted quantitatively to their salts, but an excess of base should, in particular, be used so that the pH value in the scrubbing liquor is so high that even weak acids such as mononitrophenols may be quantitatively scrubbed out.

The content of alkali may be, in particular, from 0.01 mol to 0.4 mol/l, preferably from 0.02 mol/l to 0.2 mol/l, but at least twice the amount required for the neutralization of all nitrophenols.

Particularly good results are obtained when the content of base in the scrubbing medium is from 0.01 to 0.4 mol/l, preferably from 0.02 to 0.2 mol/l.

In particular, the content of base in the scrubbing medium should be at least twice the theoretically required alkali quantities for the neutralization of all nitrophenols contained as impurities.

As previously stated, the phase ratio of nitroaromatic and freshly dosed scrubbing medium should advantageously be from 200 : 1 to 1 : 10, preferably from 100 : 1 to 1 : 5, particularly preferably from 10 : 1 to 1 : 2. By means of circulation of the scrubbing medium after phase separation, a phase ratio between 25 : 1 to 1 : 5, particularly 10 : 1 to 1: 2, particularly preferably 5 : 1 to 1 : 1, may be adjusted between the nitroaromatic and scrubbing medium to be scrubbed, in order to produce an optimal exchange surface between the organ phase and the scrubbing medium and, on the other hand, to keep the time for the phase separation in the phase separation apparatus as short as possible.

Depending on the phase ratio in the scrubbing apparatus, the nitroaromatic to be scrubbed is dispersed as an oil-in-water emulsion (O/W emulsion) in the scrubbing medium, or the scrubbing medium in the aromatics to be scrubbed as water-in-oil emulsion (W/O emulsion) (cf. the above embodiment).

Depending on the selected phase ratio, either the aromatics or the scrubbing medium to be scrubbed is used as the driving jet, in order to adjust the desired emulsion type.

The flow rate of the scrubbing emulsion after the jet mixer in the following tube reactor may be, in particular, in the range from 0.1 to 15.0 m/s, preferably from 0.5 to 10 m/s.

As mentioned above, the ratio of the velocity between the central jet and the surrounding medium moves between 1 : 5 to 30 : 1, preferably 1 : 2 to 20 : 1, and particularly preferably between 1 : 1 to 10 : 1.

In order to prevent the coalescence of the scrubbing emulsion after a short time and thus not to completely remove the impurity to be removed from the nitroaromatic compound to be purified, it is advantageous to keep the scrubbing emulsion stable by adding additional mixing energy until all impurities are scrubbed out of the nitroaromatic compound, and may be prevented by further reactions in the scrubbing medium in the re-extraction in the nitroaromatics to be scrubbed. This additional mixing energy may be introduced into the mixture of the two immiscible phases by feeding into a reactor with additional mixing elements, preferably into a tube reactor without backmixing, wherein additional mixing elements are distributed in the tube reactor, such as diaphragms, baffle plates, flow dividers, static mixers or other static mixing elements, to maintain the O/W or W/O type emulsion. Preferably, from 1 to 15, in particular from 2 to 15, more preferably from 2 to 10, and particularly preferably from 2 to 5, mixing elements may be present in the tube reactor, wherein the jet mixer also counts as a mixing element.

The total volume-related mixing energy to be introduced should be 10 to 1000 J/l, preferably 10 to 500 J/l and particularly preferably 20 to 200 J/l.

The pressure loss per mixing element should be 0.1 to 3.0 bar, preferably 0.2 to 1.5 bar and particularly preferably 0.2 to 0.8 bar, so that the number of additional mixing elements required in the tube reactor is as low as possible, while keeping the residence time in the phase separation device as short as possible.

The residence time in the tube reactor for the separation of acids followed by a rapid further reaction such as, for example, a neutralization, from the nitroaromatics to be scrubbed, such as nitric acid, sulfuric acid, mono-, di- and trinitrophenols and cresols, nitrobenzoic acids, etc. in the case of a scrubbing with alkali, such as sodium hydroxide solution, soda, bicarbonate, ammonia, potassium hydroxide solution, etc., should not be more than 0.1 to 120 seconds, preferably 0.1 to 60 seconds, more preferably 1 to 30 seconds.

The residence time in the following reactor should be adapted to these ratios in order to remove impurities from the nitroaromatics to be scrubbed with high distribution coefficients in favor of the nitroaromatic compound to be scrubbed, high mass transfer resistances in the organ phase and slow further reaction of the extracted impurity in the scrubbing medium, e.g. nitrose or nitrogen dioxide (such as, for example, by a combination of the means described above for producing an optimal scrubbing emulsion with stirrers to produce the necessary residence time). According to a particular embodiment of the above process, this is achieved, in particular, by a combination of the above-described means for producing an optimal scrubbing emulsion with stirrers in order to ensure the necessary residence time for the phase transfer and the subsequent reaction.

As mentioned above, the amount of alkali used in an alkaline scrubbing should be sufficiently high so that not only may all acids be converted quantitatively to their salts, but an excess of base should be used to keep the pH in the scrubbing liquor sufficiently high so that weak acids, such as mononitrophenols, may also be quantitatively scrubbed out. As mentioned above, the content of alkali in this case should in particular be from 0.01 mol/l to 0.4 mol/l, preferably from 0.02 mol/l to 0.2 mol/l, but at least twice as the amount required for the neutralization of all nitrophenols.

The emulsion present at the end of the mixing section may, for example, be separated again into the individual phases in a phase separation apparatus (e.g. separator or settler). The scrubbing medium with the impurities contained therein may be fed either as wastewater for wastewater treatment, or introduced into the upstream scrubbing stage in counter flow.

The scrubbed nitroaromatic may be fed either into the subsequent scrubbing step or transferred directly to the end of the scrubbing process for further treatment or to an intermediate storage.

All types of static separators may be used as a phase separator, as well as dynamic separators such as centrifugal separators. The separation time of the emulsion nitroaromatic/scrubbing medium depends, in addition on the emulsion type (W/O or O/W) and the mixing energy introduced, as well as on the excess of base in the scrubbing medium which is not required for neutralization. When the same mixing energy is introduced, the separation time drops significantly with increasing base concentration in the scrubbing medium. To accelerate the phase separation, however, it is also possible to use surface-active agents or else mechanical separation aids, such as packings, separating plates, etc. The phase separation may also be accelerated by means of a space between the individual mixing elements which is matched to the nitroaromatics and emulsion type.

As regards the nitrided raw products to be purified, these are generally liquid under process conditions, in particular at temperatures above 5 °C, particularly at temperatures above 25 °C, and atmospheric pressure. In particular, the nitrided raw products to be purified are derived from the nitration of mono- or poly-nuclear aromatics, in particular from the nitration of benzene, toluene, xylene or halogenated aromatics, such as, in particular, chlorinated benzenes.

The nitrided raw products to be purified are, in particular, halogenated mono-, di- and trinitroaromatics, such as nitrobenzene (MNB), mononitrotoluene (MNT), dinitrotoluene (DNT), trinitrotoluene (TNT), nitrochlorobenzene (MNCB) or the like.

In general, the process step (b) is followed by separation of the nitrided products freed from the impurities from the scrubbing medium. This separation is generally carried out by means of a suitable separating device (separator or settler).

Furthermore, according to a particular embodiment of the above process, it is possible for the mixture of purified nitrided products and scrubbing medium emerging from the tube reactor, in particular still before separation of the nitrided products from the scrubbing medium freed from the impurities, to be initially transferred into a stirrer tank. In this way, the contact and/or residence time between nitriding products to be purified, on the one hand, and scrubbing medium, on the other hand, is extended in an efficient manner so that, if necessary, impurities which have not yet been scrubbed out, are transferred into the scrubbing medium or neutralized thereby.

According to an advantageous embodiment of the above method, it is provided that the scrubbing medium is recycled, in particular after separation of the nitrided products from the scrubbing medium, which is freed from the impurities. In this way, efficient scrubbing or circulation is enabled and the amount of scrubbing medium is reduced to a minimum.

If appropriate, residual amounts or traces of water, in particular suspended and/or dissolved water, which are still present, may be removed after scrubbing or after separation of the scrubbing medium (for example after separation of the scrubbing emulsion in a static separator or by a centrifugal separator) though drying of the purified nitroaromatics.

The above process is suitable for carrying out the acidic scrubbing and/or the basic scrubbing and/or the neutral scrubbing of the nitrided raw products. The above process may thus be used in all three aforementioned scrubbing steps. Likewise, however, it is also possible to use the above process only for one or two scrubbing steps, for example only for the acidic scrubbing or only for the basic scrubbing or only for the neutral scrubbing. In this respect, the above method is flexible in use.

As described above, the above process is associated with a variety of advantages and peculiarities, some of which will be set forth below, but not by way of limitation or in a non-limiting manner.

In particular, the above process permits an efficient purification of nitrided raw products obtained during the nitration of nitratable aromatic compounds after separation of the nitrating end acid with only low complexity and great process economy as a result of process efficiency.

The tube reactor used according to the invention enables an efficient and thorough distribution of the scrubbing medium, on the one hand, and nitrided raw aromatics, on the other hand, so that no further scrubbing steps or other treatment steps are necessary. The scrubbing or treatment efficiency may be further increased by the fact that additional mixing elements are provided in the tube reactor, as described above, which improve the mixing further.

The tube reactor which is used according to the invention for the purification may likewise be used as a reaction vessel during the preceding nitration, so that no additional apparatus needs to be used for the purification of the nitrided raw products.

The tube reactor which is used according to the invention for the purification of the raw nitration products permits the generation of large exchange surfaces for a two-phase mixture of scrubbing medium, on the one hand, and nitrided raw aromatics, on the other hand, so that in this way an effective mass transfer and a rapid transfer of the impurities into the scrubbing medium or, in the case of acidic compounds, rapid neutralization, is ensured.

Furthermore, the above procedure allows a rapid and, as it were, efficient elimination of the impurities from the nitrided raw products from the nitration, wherein the scrubbing medium is easily recycled or circulated after the treatment of the nitrided raw aromatics.

The invention relates to an apparatus for the removal of impurities from nitrated raw products obtained during the nitration of nitratable aromatic compounds after removal of the nitrating end acid by treatment with a scrubbing medium, wherein the apparatus according to the invention is particularly suitable for carrying out a process as described above. The apparatus comprises the following means:

(a) at least one dispersing device, in particular at least one mixing element, for contacting and emulsifying nitrided raw products to be purified, on the one hand, and scrubbing medium, on the other hand;

(b) downstream of the dispersing device is arranged a tube reactor for feeding the emulsion of nitrided raw products to be purified in the dispersing device, on the one hand, and scrubbing medium, on the other hand, wherein the tube reactor is designed in such a way that during the passage of the emulsion through the tube reactor, removal of the nitrided raw products takes place while, during the passage of the emulsion through

the tube reactor, the impurities originally present in the nitrided raw products are transferred into the scrubbing medium and are thereby neutralized; and

(c) downstream of the tube reactor is arranged a separating device (separator) for separating the nitrided products from the scrubbing medium which are freed from the impurities.

As described above in connection with the above method, the dispersing device, in particular the mixing element, may be a stirrer tank, a jet mixer or a pump, in particular a centrifugal pump, preferably a pump, in particular a centrifugal pump, or a jet mixer, in particular a jet mixer.

As described above in connection with the above method, the dispersing device, in particular the mixing element, may be connected upstream of the reactor, in particular directly upstream. In particular, it may be provided in this context that the dispersing device, in particular the mixing element, merges into the tube reactor.

According to an alternative embodiment, the dispersing device, in particular the mixing element, may be integrated into the tube reactor and/or be a component of the tube reactor. In this regard, reference may be made to the above statements in connection with the above method.

As explained above in the description of the above method, the tube reactor may be equipped with mixing elements, in particular for the input of additional mixing energy. As described above, the mixing elements may be designed as plates, in particular impact or deflection plates, as diaphragms, as static mixers or as flow dividers.

Within the scope of the apparatus according to the invention, it is possible to carry out a one-, two- or three-stage scrubbing of the raw nitration product (i.e. acidic scrubbing and/or basic scrubbing and neutral scrubbing).

Furthermore, according to the invention, a separation device, namely a separating device (separator or settler and/or dynamic separator or centrifugal separator), is arranged for the separation of the nitrided products freed from the impurities from the scrubbing medium.

Furthermore, within the scope of the apparatus according to the invention, there is the possibility that a stirred tank and/or stirrer reactor is arranged downstream of the tube reactor and upstream of the separating device (i.e. in other words between the tube reactor and the separating device). In particular, the contact and/or residence time between nitrided products, on the one hand, and the scrubbing medium, on the other hand, is extended in this way.

For further details on the apparatus or plant according to the invention, reference may be made to the above statements on the above-described method which apply correspondingly with respect to the apparatus or plant according to the invention.

The apparatus according to the invention may be used in a production plant for the nitration of nitratable aromatic compounds with subsequent purification of the nitrided raw products formed during nitration, wherein the production plant comprises the following units:

(a) a nitrating unit for the nitration of aromatic compounds, in particular with one or more corresponding reaction vessels for carrying out the nitrating reaction(s);

(b) optionally, in the production line downstream from the nitrating unit, at least one separation device, in particular a separating device (separator), for separating the nitrating acid from the nitrided raw products;

(c) at least one scrubbing device for carrying out a scrubbing of the nitrided raw products arranged downstream of the nitration unit and the optionally present separating device in the production line, wherein the scrubbing device comprises:

- at least one dispersing device, in particular at least one mixing element, for contacting and emulsifying the nitrided raw products to be purified, on the one hand, and the scrubbing medium, on the other hand, and
- downstream from the dispersing device is arranged a tube reactor for the feeding of the emulsion produced in the dispersing device from the nitrated raw products to be purified, on the one hand, and the scrubbing medium, on the other hand, wherein the tube reactor is so designed that, during the passage of the emulsion through the tube reactor, removal of the impurities initially present in the nitrided raw products is made possible and/or that during the passage of the emulsion through the tube reactor, the impurities present initially in the nitrided raw products are transferred into the scrubbing medium and thereby neutralized;

(d) optionally, in the production line downstream of the scrubbing device, a stirrer tank, in particular for increasing the contact and/or residence time between nitrided products, on the one hand, and scrubbing medium, on the other hand;

(e) in the production line downstream of the scrubbing unit and the stirrer tank, if any, is arranged a separation device, namely a separating device (separator), for separating the nitrided products, which are freed from the impurities, from the scrubbing medium.

In other words, in the above production plant, the above-described apparatus or plant for the purification, i.e. the removal of impurities, is part of this production plant, namely in the form of the scrubbing unit or scrubbing device (c), the optional scrubbing device (d) as well as the separating device e).

As described above, the dispersing device, in particular the mixing element, a stirrer tank, a jet mixer or a pump, in particular a centrifugal pump, preferably a pump, in particular a centrifugal pump, or a jet mixer, particularly preferably a jet mixer.

According to a particular embodiment of the above production plant, the dispersing device, in particular the mixing element, may be connected upstream of the reactor, in particular directly upstream, as described above. In particular in this embodiment, the dispersing device, in particular the mixing element, may merge into the tube reactor.

Likewise, it may be provided according to the invention that the dispersing device, in particular the mixing element, is integrated into the tube reactor and is part of the tube reactor. With regard to this embodiment, it is possible to refer to the above explanations to avoid unnecessary repetitions.

As described above in connection with the above method and in connection with the apparatus or plant according to the invention for purification, the tube reactor may be equipped with mixing elements, in particular for the input of additional mixing energy. In particular, in this embodiment, the mixing elements may be designed as plates, in particular impact or deflection plates, as diaphragms, as static mixers or as flow dividers.

The above process is particularly suitable for carrying out an acidic scrubbing and/or a basic scrubbing and/or neutral scrubbing of nitrided raw products. The above process may thus be used in all three aforementioned scrubbing steps of a scrubbing device. Likewise, however, it is also possible to use the above process for only one or two scrubbing steps, for example only for an acid scrubbing or only for a basic scrubbing or only for a neutral scrubbing. In this respect, the above method is flexible in use.

For further details on the above production plant, reference may be made to the above discussion of the above method and to the apparatus or plant according to the invention, which apply correspondingly with respect to the above production plant.

The above process and the apparatus or the plant according to the invention for the purification, as well as the above production plant for the nitration, are exemplified and illustrated by way of non-limiting illustrations in the accompanying figures.

Further advantages, features, aspects and characteristics of the present invention will become apparent from the following description of preferred embodiments according to the invention shown in the drawings:

Fig. 1 shows a schematic representation of a scrubbing of prior art nitroaromatics using mixer-settler technology for the usual three scrubbing stages of nitroaromatic scrubbing;

Fig. 2 shows a schematic representation of a one-stage scrubbing for nitroaromatics according to the above method and with the apparatus or plant according to the invention;

Fig. 3 shows a schematic representation of a sequence of the above method and a schematic representation of the device according to the invention according to a preferred exemplary embodiment of the invention for the usual three scrubbing stages of the scrubbing of nitroaromatics;

Fig. 4 shows a schematic representation of a production plant for the nitration of nitratable aromatic compounds with subsequent scrubbing of the nitroaromatics obtained according to a preferred embodiment of the invention.

Fig. 1 shows an example of the scrubbing of nitroaromatics in three steps according to the prior art.

a) In step 1, the sulfuric and nitric acid suspended and dissolved in the raw nitroaromatic compounds (NA 10) are scrubbed out by scrubbing with fresh water (WW 10) in a multi-stage continuous acidic scrubbing (WS). The nitroaromatic (NA 10) and the scrubbing water (WW 10) to be scrubbed are introduced into a mixing element, usually a stirrer tank, with a residence time of approximately 10 minutes. The scrubbing emulsion formed is then separated in a separator (S). For the complete removal of the dissolved and suspended mineral acids, up to 4 mixer-settler units (n = 3) may be used, wherein the scrubbing medium and the nitroaromatic to be scrubbed are fed in counter flow. After the separation of the phases, the scrubbing medium is either completely discharged as wastewater (WW 11) or a partial quantity is additionally circulated in order to set a predetermined phase ratio and thus a defined emulsion type and to minimize the time for separating the phases. The nitroaromatic (NA 11) freed from mineral acids is fed into scrubbing stage 2, the alkaline scrubbing (WA).

b) In step 2, all dissolved nitrophenols, nitrobenzoic acids and other acidic substances from the oxidative degradation of impurities and isomeric nitroaromatics are removed from the nitroaromatic compound (e.g. TNT) in a multi-stage continuous alkaline scrubbing (WA). The nitroaromatic mixture (NA 11) to be scrubbed and the scrubbing water (WW 10 or WW 13), together with a base, are introduced into a stirrer tank with a residence time of about 10 minutes. The scrubbing emulsion formed is then separated in a separator (S). For the complete removal of the nitrophenols, nitrobenzoic acids and other acidic substances dissolved in the nitroaromatic compound from the oxidative degradation of impurities and isomeric nitroaromatics, up to 4 mixer-settler units (n = 3) may be used. The scrubbing medium and the nitroaromatic to be scrubbed are fed countercurrently. After separation of the phases, the scrubbing medium is either immediately and completely discharged as a wastewater (WW 12), or a partial quantity is additionally circulated in order to set a predetermined phase relationship and thus a defined emulsion type and to minimize the time to separate the phases. The nitroaromatic compound (NA 12) liberated from the oxidative degradation of impurities and isomeric nitroaromatics from mineral acids, nitrophenols, nitrobenzoic acids and other acidic substances is fed into scrubbing stage 3, the neutral scrubbing (WN).

c) In step 3, the entrained traces of scrubbing medium are removed from the alkaline scrubbing (WA) in a multi-stage neutral scrubbing (WN). The nitroaromatic (NA 12) and the scrubbing water (WW 10) to be scrubbed are placed in a stirrer tank with a residence time of about 10 minutes. The scrubbing emulsion formed is then separated in a separator (S). For the complete removal of the traces of base, suspended or dissolved in the nitroaromatic compound, up to 4 mixer-settler units (n = 3) may be used, wherein the scrubbing medium and the nitroaromatic to be scrubbed are fed in counter flow. The aqueous phase is either immediately introduced into the alkaline scrubbing (WA) as a scrubbing medium (WW 13), or a partial quantity is additionally circulated in order to set a predetermined phase ratio and thus a defined emulsion type and to minimize the time for separation of the phases.

The nitroaromatic (NA 13), which is now freed of mineral acids, nitrophenols, nitrobenzoic acids and other acidic substances from the oxidative degradation of impurities, isomeric nitroaromatics and residual trace alkali, is delivered directly for further processing or into an intermediate storage.

Fig. 2 shows an embodiment for a scrubbing stage according to the above method or with the apparatus or plant according to the invention for scrubbing nitroaromatics with the scrubbing medium as the driving jet.

The nitroaromatic acid to be scrubbed, after removal of the nitric acid (NA1 (n-1) where n = 1), or after removal of the nitric acid present in nitroaromatics as a microemulsion, or of the sulfuric acid, nitric acid and nitrose, dissolved in nitroaromatics, in an acidic scrubbing (WS where n = 2) or after removal of all nitrophenols, nitrobenzoic acids and other acidic substances dissolved in the nitroaromatics from the oxidative decomposition of impurities and isomeric nitroaromatics from the nitroaromatic compound (e.g. TNT) in the presence of bases in an alkaline scrubbing (WA with n = 3) is brought together in a jet mixer (SM) with the scrubbing medium WW1 (n-1), which serves as a driving jet in the illustrated case, and is introduced directly into a tube reactor (e) of the additional mixing elements (Mm).

In order to allow a prolonged residence time for slow-running conversions of the impurities to be scrubbed out in the scrubbing medium, such as nitrose, the scrubbing emulsion may be fed from the tube reactor into a residence time container, such as, for example, one or several stirrer tanks (R). The scrubbing emulsion from the tube reactor is separated into the phases directly or after a prolonged residence time in the stirrer tank in a separating device.

The scrubbed nitroaromatic (NA1 n where n = 1 to 3) is delivered either to the subsequent scrubbing stage or as a finished product (NA13) for further processing. The laden scrubbing medium (WW1 n where n = 1 to 3) is either discharged directly as wastewater or recycled as a partial flow for setting a defined phase ratio between nitroaromatic and scrubbing medium. This recycled partial stream may be fed either directly into the tube reactor together with the newly added scrubbing water as a jet or as a circulating flow.

Fig. 3 shows an example of the above process in three steps for the separate removal of the mineral acids by means of acidic scrubbing (WS), the removal of all dissolved nitrophenols, nitrobenzoic acids and other acidic substances from the oxidative degradation of impurities and isomeric nitroaromatics in the presence of bases in the alkaline range by means of alkaline scrubbing (WA) and a neutral scrubbing (WN).

a) In Step 1, the sulfuric and nitric acids suspended and dissolved in the raw nitroaromatic compounds (NA 10) are removed by scrubbing with fresh water (WW 10) in a one-stage acidic scrubbing (WS). The nitroaromatic (NA 10) and the scrubbing water (WW 10) to be scrubbed are fed by means of pumps (P) via a jet mixer or directly into a tube reactor which contains additional mixing elements (Mn). After passing through the tube reactor, the

emulsion formed is separated in a separator (S). The scrubbing medium is either directly discharged as wastewater (WW 11) after phase separation, or a partial quantity is additionally circulated for setting a predetermined phase ratio and thus a defined emulsion type and to minimize the time for separating the phases. The nitroaromatic (NA 11) freed from mineral acids is fed into scrubbing step 2, the alkaline scrubbing (WA).

b) In step 2, all dissolved nitrophenols, nitrobenzoic acids and other acidic substances from the oxidative degradation of impurities and isomeric nitroaromatics are removed from the nitroaromatic compound in a single-stage alkaline scrubbing (WA). The nitroaromatic (NA 11) to be scrubbed after the acidic scrubbing (WS) and the scrubbing water (WW 10 or WW13 from the neutral scrubbing) and a base are fed by means of pumps (P) via a jet mixer or directly into a tube reactor with additional mixing elements (Mn). After passing through the tube reactor, the emulsion formed is separated in a separator. The scrubbing medium, which contains all dissolved nitrophenols, nitrobenzoic acids and other acidic substances from the oxidative decomposition of impurities and extracted isomeric nitroaromatics (dissolved as a salt), is either directly discharged as effluent (WW 12) after phase separation or a partial quantity is circulated for setting a predetermined phase ratio and thus a defined emulsion type, and to minimize the time for separating the phases. The nitroaromatic (NA 12) liberated from the oxidative degradation of impurities and isomeric nitroaromatics from mineral acids, nitrophenols, nitrobenzoic acids and other acidic substances is fed into scrubbing stage 3, the neutral scrubbing (WN).

c) In step 3, the entrained traces of scrubbing medium are removed from the alkaline scrubbing in a single-stage neutral scrubbing (WN). The nitroaromatic (NA 12) and the scrubbing water (WW 10) to be scrubbed are fed by means of pumps (P) via a jet mixer or directly into a tube reactor which contains additional mixing elements (Mn). After passing through the tube reactor, the emulsion formed is separated in a separator (S). The scrubbing medium, which contains the residual traces of alkali and impurities, is introduced either directly into the scrubbing stage 2 (WA) as wastewater (WW 13), or a partial quantity is additionally circulated in order to set a predetermined phase ratio and thus a defined emulsion type for the time to separate the phases. The nitroaromatic compound (NA 13), which has now been freed from the oxidative degradation of impurities, isomeric nitroaromatics and residual traces of alkali, from mineral acids, nitrophenols, nitrobenzoic acids and other acidic substances, is delivered directly for further processing or into an intermediate storage.

Fig. 4 shows an example of a production plant for the production of nitroaromatics with integrated inventive scrubbing of the raw nitroaromatics from an isothermal or adiabatic nitration. The raw nitroaromatic compound (NA 10) formed in the nitration unit (N) by reacting the aromatic with nitric acid in the presence of sulfuric acid (NA 10) is treated with water (WW 10) in the separator according to the invention after removal of the nitrating acid in the separator (S) through scrubbing. After separation of the phases, the resulting wastewater (WW 11), which contains all the sulfur and nitric acid extracted, together with the nitric acid (WNA) obtained from the exhaust gas treatment of the nitriding plant in an adsorber system (A), either directly or after concentration in an SAC plant (SAC), together with the end acid (AS), is returned to the nitration or discharged as wastewater to be treated.

The nitroaromatic (NA 11) freed from the mineral acids is scrubbed in the scrubbing step 2 (alkaline scrubbing WA) in the presence of bases by the quasi-single stage in the above process. After separation of the phases, the waste from the alkaline scrubbing (WW12) with a pH value in the range from 8.0 to 13, which contains all nitrophenols, nitrobenzoic acids and

other acidic substances from the oxidative degradation of impurities and isomeric nitroaromatics (e.g. TNT) is supplied for additional treatment, such as a thermolysis, before being discharged into a receiving water.

The nitroaromatic (NA 12) from the alkaline scrubbing (WA) is fed into the neutral scrubbing (WN) and scrubbed with water (WW 10) by a quasi-stage. After separation of the phases, the wastewater (WW 13) from the neutral scrubbing (WN) is fed into the scrubbing stage 2 (WA) together with the base. The scrubbed nitroaromatic (NA 13) is is released into the further processing, such as an isomer separation, the reduction to the corresponding amine or into an intermediate storage.

Further refinements, modifications, variations of the present invention will be readily apparent to the person skilled in the art upon reading the description without departing from the scope of the present invention.

The present invention is illustrated by the following embodiments without, however, limiting the present invention thereto.

Although the above process or apparatus according to the invention is illustrated with nitrobenzene as nitroaromatic compounds to be purified, the process or the apparatus according to the present invention is in no way limited to this, but is also limited to any other nitroaromatics, for example from the nitration of toluene, chlorobenzenes, xylenes, nitrobenzenes, etc., and any bases other than sodium hydroxide solution.

Exemplary embodiments

Example 1 Single-stage alkaline scrubbing (comparative example)

12 kg/h of a nitrobenzene from an adiabatic nitration scrubbed with water (acidic scrubbing) and still containing a total of 1,910 ppm of nitrophenols (0.8 ppm of 2-nitrophenol (2-NP), 1,346 ppm of 2,4-di-phenol (2, 4-DNP) and 203 ppm of 2,6-dinitrophenol (2,6-DNP) and 360 ppm of picric acid (2,4,6-TNP)) was added together with a scrubbing liquor containing 0.8 g of NaOH/l (two-fold excess, based on all nitrophenols), in a weight ratio of 1 : 1, into a stirrer tank at 60 °C. The stirrer speed was adjusted so that an O/W emulsion with the metered phase ratio was present in the stirrer tank. The residence time in the stirrer tank was 6 minutes. After phase separation (about 40 minutes), the pH in the scrubbing liquor containing 1,850 ppm of nitrophenols was approximately 11.7. In the scrubbed nitrobenzene, 60 ppm of nitrophenols were found. When a scrubbing liquor containing 4 g/l sodium hydroxide solution was used under otherwise identical conditions, the separation time could be shortened by a factor of about 4 to about 15 minutes.

Example 2: Single-stage alkaline scrubbing (according to the invention)

12 kg/h of a nitrobenzene from an adiabatic nitration scrubbed with water (acidic scrubbing) containing a total of 1,910 ppm of nitrophenols (0.8 ppm of 2-nitrophenol (2-NP), 1,346 ppm of 2,4-di-phenol (2, 4-DNP) and 203 ppm of 2,6-dinitrophenol (2,6-DNP) and 360 ppm of picric acid (2,4,6-TNP)) was treated with a scrubbing liquor containing 0.8 g of NaOH/l (two-fold excess, based on all nitrophenols) in a weight ratio of 1 : 1 by means of a jet mixer with the scrubbing medium as the central jet at 60 °C into a tube reactor which additionally contained 5 static mixing elements. The relative speed between the central jet and the nitrobenzene to be scrubbed was 8 : 1. The residence time in the tube reactor was not more than 5 seconds. The pressure drop over the entire tube reactor length was 1.6 bar. After the separation of the O/W emulsion (about 40 minutes), the pH value in the scrubbing liquor containing 1,908 ppm of nitrophenols was approximately 11.6. In the scrubbed nitrobenzene, 2 ppm nitrophenols were found. When a scrubbing liquor was used with 4 g/l sodium hydroxide solution under otherwise identical conditions, the separation time could be shortened by a factor of four to about 10 minutes. The same results were obtained with the nitroaromatic compound to be scrubbed as a central jet in the jet mixer.

Example 3: Single-stage neutral scrubbing (according to the invention)

12 kg/h of a nitrobenzene from an adiabatic nitration, which after a scrubbing with alkali (see, for example, Example 2, alkaline scrubbing) and still containing a total of 2 to 5 ppm of nitrophenols, was mixed in a weight ratio of 1 : 1 by means of a jet mixer with water as a central jet at 60 °C into a tube reactor which additionally contained 2 static mixing elements. The relative speed between the central jet and the nitrobenzene to be scrubbed was 8 : 1. The residence time in the tube reactor was about 5 seconds. The pressure drop over the entire tube reactor length was 0.6 bar. After pH separation (about 25 minutes), the pH in the scrubbing water was from about 9.0 to about 1.5 to 4.5 ppm of nitrophenols. In the scrubbed nitrobenzene, 0.5 ppm nitrophenols were still found. The same results were obtained with the nitroaromatics to be scrubbed as the central jet in the jet mixer.

Example 4 Single-stage alkaline scrubbing (according to the invention)

20 kg/h kg of a nitrobenzene from an adiabatic nitration which was pre-scrubbed with water (acid scrubbing) and still contained a total of 1,910 ppm of nitrophenols (0.8 ppm of 2-nitrophenol (2-NP), 1,346 ppm of 2,4-dinitrophenol (2,4-DNP) and 203 ppm of 2,6-dinitrophenol (2,6-DNP) and 360 ppm of picric acid (2,4,6-TNP)) was treated with 4 kg/h scrubbing liquor with 4 g of NaOH/l (two-fold excess, based on all nitrophenols), and scrubbed directly according to a weight ratio of nitroaromatic to scrubbing liquor of 5 : 1, with the scrubbing medium being fed into a tube reactor at 60 ° by means of a jet mixer and the nitroaromatics to be scrubbed, which additionally contained 5 static mixing elements. The relative speed between the central jet and the nitrobenzene to be scrubbed was 8 : 1. The residence time in the tube reactor was not more than 5 seconds. The pressure drop over the entire tube reactor length was 1.6 bar. After phase separation of the W/O type emulsion (about 5 minutes), the pH in the scrubbing liquor containing 9,552 ppm of nitrophenols was about 12.3. In the scrubbed, still turbid nitrobenzene, approximately 8 ppm nitrophenols were found.

Example 5 Single-stage neutral scrubbing (according to the invention)

20 kg/h of a nitrobenzene from an adiabatic nitration, which after scrubbing with alkali (see Example 2, alkaline scrubbing) contained a total of 5 to 8 ppm of nitrophenols, was added in the weight ratio 5 : 1 by means of a jet mixer with water as the central jet at 60 ° into a tube reactor which additionally contained two static mixing elements. The relative speed between the central jet and the nitrobenzene to be scrubbed was 8 : 1. The residence time in the tube reactor was about 5 seconds. The pressure drop over the entire tube reactor length was 0.6 bar. After phase separation (about 20 minutes), the pH value in the scrubbing water was from about 9.0 to about 1.5 to 4.5 ppm of nitrophenols. In the scrubbed nitrobenzene, 0.5 ppm nitrophenols were still found. The same results were obtained with the nitroaromatics to be scrubbed as the central jet in the jet mixer.

KÉSZÜLÉK NITRÁLÁSI TERMÉKEK TISZTÍTÁSÁRA

SZABADALMI IGÉNYPONTOK

1. Berendezés (apparatus) [üzem (plant)] tisztátalanságok (impurity) eltávolítására olyan nitridált nyerstermékekből, amelyek nitrálható aromás vegyületek nitrálása során kapunk a nitráló végsav (end acid) elkülönítése után kezelés révén egy kimosó (scrubbing) közeggel, ahol a berendezés a következő készülékeket (device) tartalmazza:

a) legalább egy diszpergáló készülék, elsősorban legalább egy keverő készülék, hogy érintkezésbe hozzuk és emulgeáljuk egyrészt a tisztítandó nitridált nyerstermékeket, másrészt a kimosó közeget;

b) egy csőreaktor van elrendezve áramlásirányban (downsream) a diszpergáló készüléktől, hogy betápláljuk (feed) egyrészt a tisztítandó nitridált nyerstermékeket, másrészt a kimosó közeg emulzióját, ahol a csőreaktor úgy van tervezve, hogy az emulzió áthaladása (passage) során a csöreaktoron keresztül lehetővé váljék a nitridált nyerstermékekben eredetileg jelen levő tisztátalanságok eltávolítása, és a nitridált nyerstermékekben eredetileg jelen levő tisztátalanságok átvitele (transfer) a kimosó közegbe és/vagy semlegesítése (neutralize); és

c) egy elkülönítő készülék (szeparátor) van elrendezve áramlásirányban (downsream) a csőreaktortól, hogy elkülönítse a tisztátalanságoktól megszabadított nitridált termékeket a kimosó közegből.

2. Az 1. igénypont szerinti berendezés, **azzal jellemezve, hogy** a diszpergáló készülék, elsősorban a keverő készülék, keverő tartály (stirrer tank), jet (folyadéksugaras) keverő vagy szivattyú (pump), különösen centrifugális szivattyú, előnyösen szivattyú, különösen centrifugális szivattyú vagy jet keverő, különösen előnyösen jet keverő (jet mixer).

3. Az 1. vagy 2. igénypont szerinti berendezés, **azzal jellemezve, hogy** a diszpergáló készülék, elsősorban a keverő készülék, a csőreaktortól felfelé (upstream) kapcsolódik, elsősorban közvetlenül felfelé, különösen ott, ahol a diszpergáló készülék, elsősorban a keverő készülék, bekapcsolódik (merge) a csőreaktorba.

4. Az 1. vagy 2. igénypont szerinti berendezés, **azzal jellemezve, hogy** a diszpergáló készülék, elsősorban a keverő készülék, integrálva van a csöreaktorba, és/vagy ez alkotórésze a csöreaktornak.

5. A 2. igénypont szerinti berendezés, **azzal jellemezve, hogy** a jet keverő generál egy előnyösen központi hajtású jetet (central drive jet) és egy olyan közeget, amely körülveszi a hajtott jetet, előnyösen egy gyürüs jet (ring jet) formájában.

6. Az 1-5. igénypontok bármelyike szerinti berendezés, **azzal jellemezve, hogy** a csőreaktor fel van szerelve keverő készülékekkel, elsősorban további keverési energia beépéséhez (input), elsősorban ott, ahol a keverő készülékek lemezek (plate), főleg terelőlemezek (baffle plate) vagy eltérítő lemezek (deflection plate), diafragmák, statikus keverők vagy áramláselosztók (flow divider) formájában vannak.

7. A 6. igénypont szerinti berendezés, **azzal jellemezve, hogy** a nyomásesés keverő készülékekként a 0,1 bar és 3,0 bar közötti tartományban, előnyösen a 0,3 bar és 1,5 bar közötti tartományban, különösen előnyösen a 0,3 bar és 0,8 bar közötti tartományban van, és/vagy 10 és 1000 joule/liter közötti, előnyösen 10 és 500 joule/liter közötti, különösen előnyösen 20 és 200 joule/liter közötti keverési energia van bevezetve a keverő készüléken keresztül.

8. Az 1-7. igénypontok bármelyike szerinti berendezés, **azzal jellemezve, hogy** egy keverő tartály van elrendezve a csőreaktortól lefelé (downstream) és az elkülönítő készüléktől felfelé (upstream) és/vagy a csőreaktor és az elkülönítő készülék között, különösen az érintkezési idő és/vagy a tartózkodási idő megnövelésére egyrészt a nitridált termékek, másrészt a kimosó közeg között.

9. Alkalmazása egy, az 1-8. igénypontok bármelyike szerinti berendezésnek egy eljárás kivitelezésére tisztátalanságok eltávolítására olyan nitridált nyerstermékekből, amelyek nitrálható aromás vegyületek nitrálása során kapunk a nitráló végsav eltávolítása után kezelés révén egy kimosó közeggel, ahol

a) először a nitridált nyerstermékeket érintkezésbe hozzuk egy kimosó közeggel , és a nitridált nyerstermékeket és a kimosó közeget elosztjuk egymásba úgy, hogy emulzió keletkezzék,

b) ezt követően a keletkező emulziót bevezetjük egy csőreaktorba úgy, hogy a kiinduláskor a nitridált

nyerstermékekben jelen levő tisztátalanságok eltávolítódjanak az emulzió átjutása (passage) során a csőreaktoron keresztül, és/vagy úgy, hogy az emulzió átjutása során a csőreaktoron keresztül a nyerstermékben kiinduláskor jelen levő tisztátalanságok átszállítódjanak (transfer) a kimosó közegbe és/vagy ezáltal semlegesítődjenek (neutralize),

c) a (b) lépés után a tisztátalanságoktól megszabadított nitridált termékeket a kimosó közegből elkülönítjük egy elkülönítő készülékben (szeparátor).

10. A 9. igénypont szerinti alkalmazás, **azzal jellemezve, hogy** egy jet keverőt alkalmazunk diszpergáló készülékként, elsősorban keverő készülékként, ahol a jet keverő generál egy előnyösen központi hajtású jetet (central drive jet) és egy olyan közeget, amely körülveszi a hajtott jetet, előnyösen egy gyűrűs jet (ring jet) formájában.

11. A 10. igénypont szerinti alkalmazás, **azzal jellemezve, hogy** a hajtott jet a jet keverőben a kimosó közeg vagy a tisztítandó nitridált nyerstermék, és vagy a sebességek hányadosát (ratio) a központi hajtású jet és a központi jet áramlatot (stream) körülvevő közeg, elsősorban egy gyűrűs jet, között úgy állítjuk be, hogy az 1:5 és 30:1 közötti tartományban, előnyösen az 1:2 és 20:1 közötti tartományban, különösen előnyösen az 1:1 és 10:1 közötti tartományban legyen.

12. Az 1-11. igénypontok bármelyike szerinti alkalmazás, **azzal jellemezve, hogy** a tartózkodási idő a csőreaktorban a 0,1 és 120 másodperc közötti tartományban, előnyösen a 0,1 és 60 másodperc közötti tartományban, különösen előnyösen az 1 és 30 másodperc közötti tartományban van.

13. Az 1-12. igénypontok bármelyike szerinti alkalmazás, **azzal jellemezve, hogy** a hányados egyrészt a tisztítandó nitridált nyerstermékek, másrészt a kimosó közeg között a 200:1 és 1:10 közötti tartományban, előnyösen a 100:1 és 1:5 közötti tartományban, különösen előnyösen a 10:1 és 1:2 közötti tartományban van, és a fázis hányados (phase ratio) egyrészt a tisztítandó nitridált nyerstermékek, másrészt a kimosó közeg között a 25:1 és 1:5 közötti tartományban, elsősorban a 10:1 és 1:2 közötti tartományban, előnyösen a 10:1 és 1:2 közötti tartományban, különösen előnyösen az 5:1 és 1:1 közötti tartományban van.

14. Az 1-13. igénypontok bármelyike szerinti alkalmazás, **azzal jellemezve, hogy** a kimosó közeg folyadék állapotú az eljárási körülmények között, elsősorban 5°C fölötti hőmérsékletnél és atmoszferikus nyomásnál, és a közeg előnyösen víz-alapú, előnyösen víz, és/vagy a tisztítandó nitridált nyerstermékek folyadék állapotúak az eljárási körülmények között, elsősorban 5°C fölötti, elsősorban 25°C fölötti hőmérsékletnél és atmoszferikus nyomásnál, és/vagy a tisztítandó nitridált nyerstermékek a következők nitrálása közül választhatók ki: mono- vagy poliaromás aromások, elsősorban benzol, toluol, xilol vagy halogénezett aromások, elsősorban klórozott benzolok, és/vagy a tisztítandó nitridált nyerstermékek, ha alkalmasak, lehetnek halogénezett mono-, di- és trinitro-aromások.

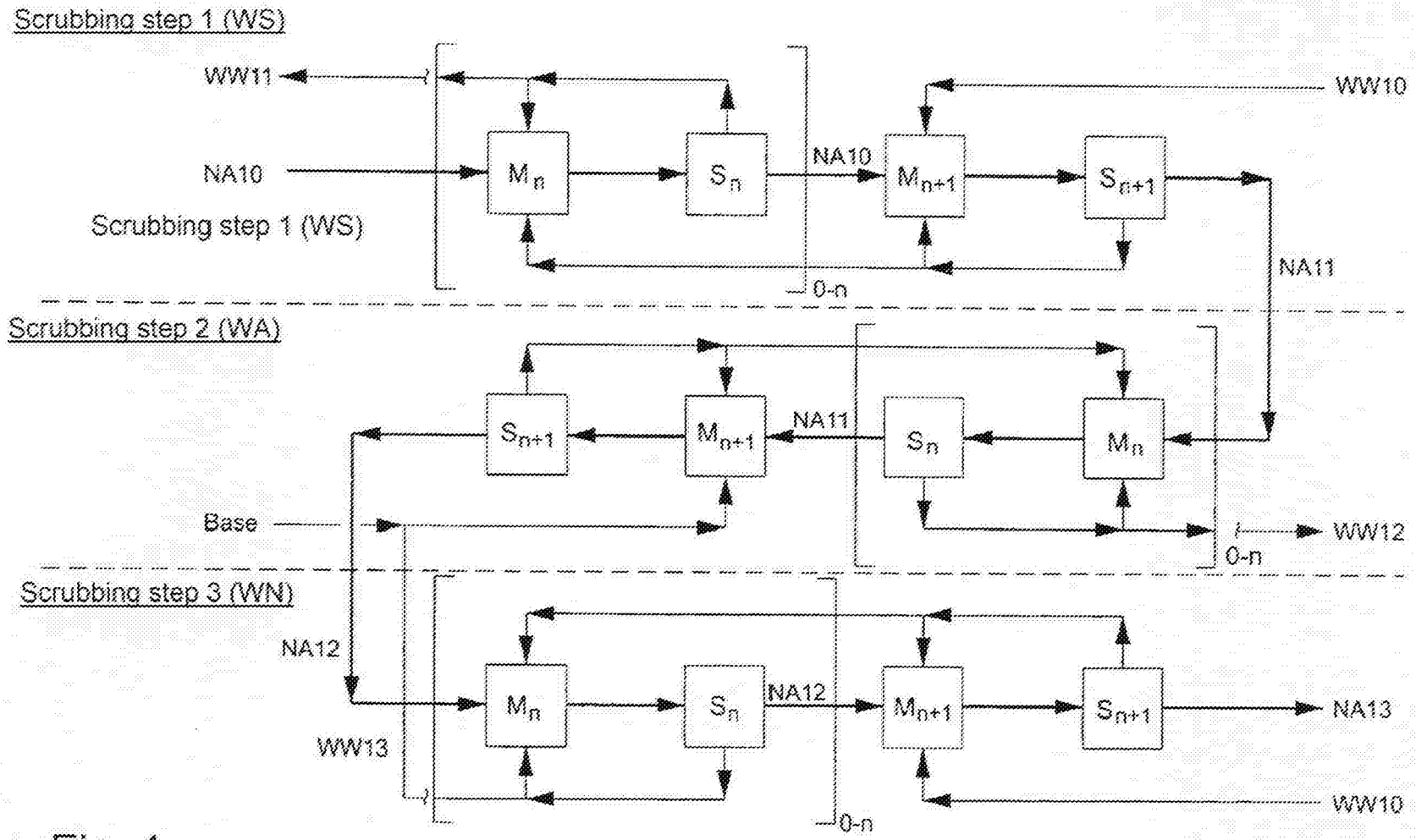

Fig. 1

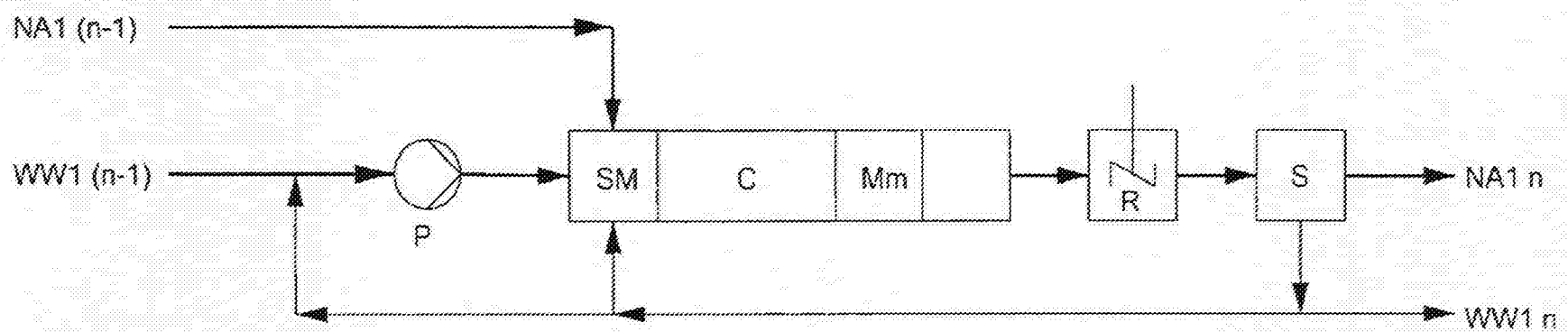

Fig. 2

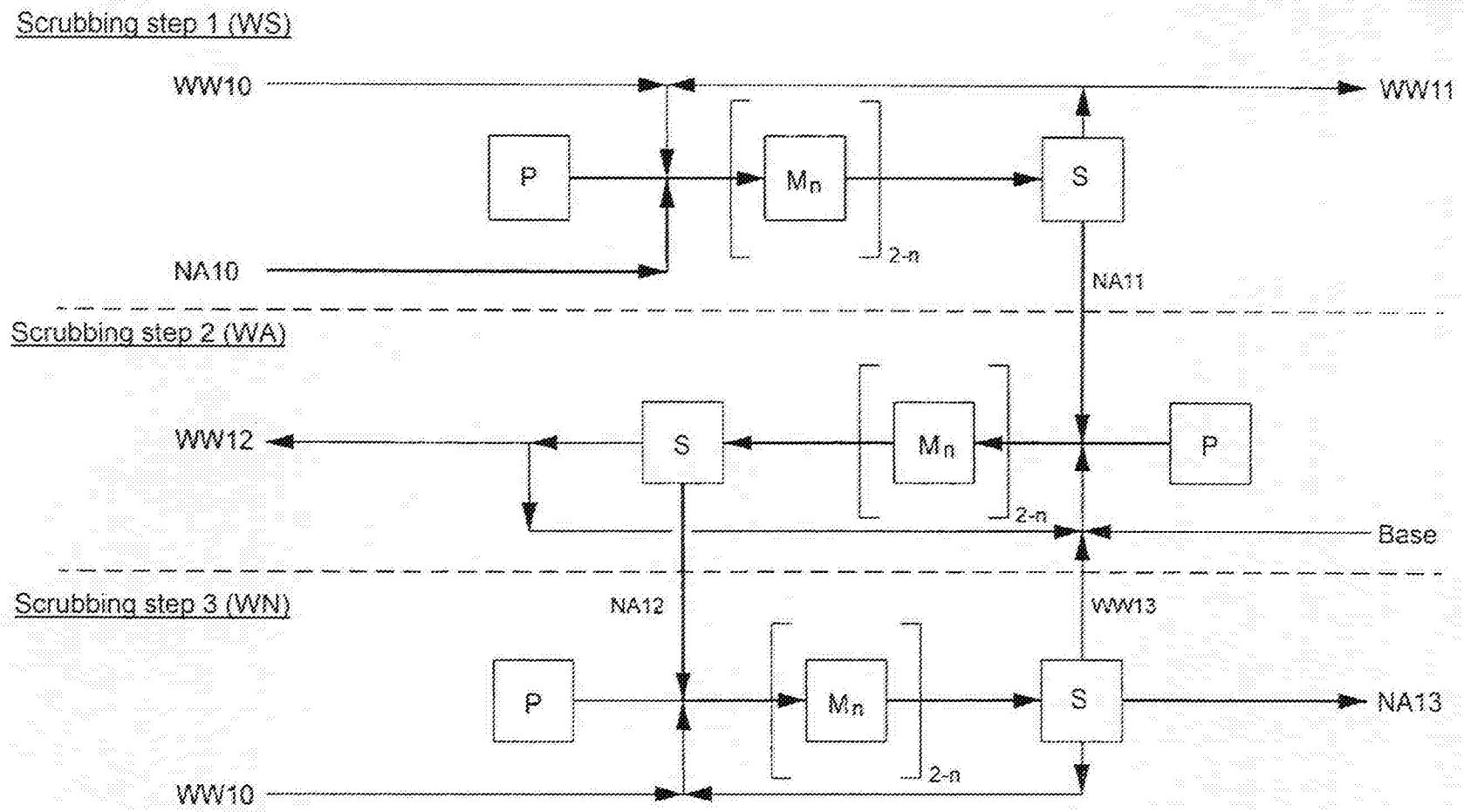
Scrubbing step 1 (WS)
WW10
WW11
P
Mn
S
2-n
NA10
NA11
Scrubbing step 2 (WA)
WW12
S
Mn
P
2-n
Base
Scrubbing step 3 (WN)
NA12
WW13
P
Mn
S
NA13
2-n
WW10

Fig. 3

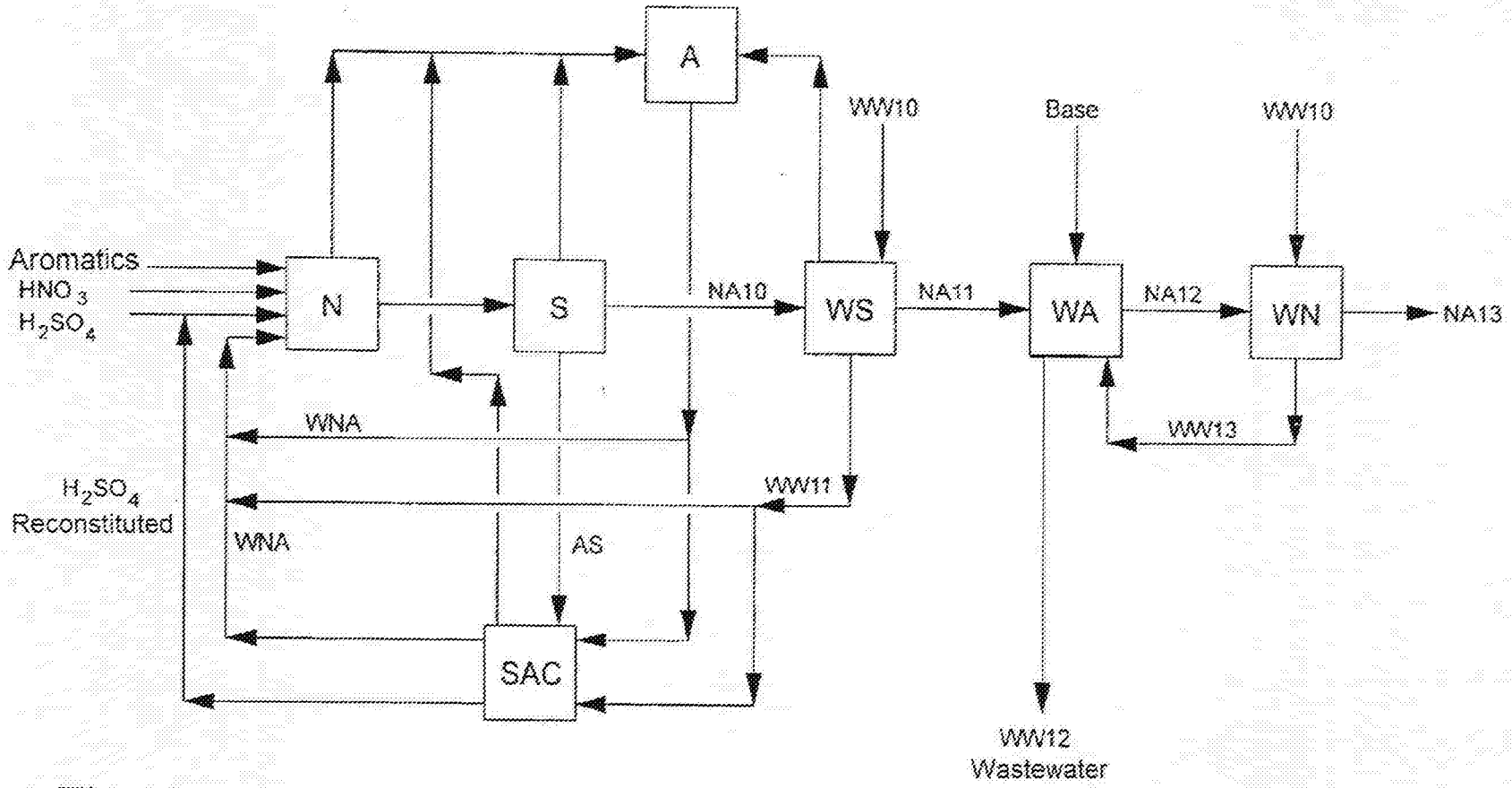
A
WW10
Base
WW10
Aromatics
HNO3
H2SO4
N
S
NA10
WS
NA11
WA
NA12
WN
NA13
WNA
WW13
H2SO4
Reconstituted
WW11
WNA
AS
SAC
WW12
Wastewater

Fig. 4