

Process and absorbent for dehumidifying moist gas mixtures

The invention relates to a process for dehumidifying a moist gas mixture in which the moist gas mixtures are brought into contact with an absorbent comprising dialkylimidazolium salts and trialkyl phosphate. In addition, the invention also relates to an absorption heat pump comprising the absorbent according to the invention and to the absorbent according to the invention itself.

Background of the invention

Dehumidification of moist gas mixtures is necessary in a multitude of technical fields.

For instance, ventilation and air conditioning of buildings or vehicles generally necessitates not only cooling but also dehumidification of the air since the air to be cooled is often so humid that during cooling to the desired temperature the temperature falls below the dew point temperature. Hence in conventional air conditioning systems dehumidification of the air accounts for a large part of the electricity consumption.

The electricity consumption of air conditioning systems for buildings is reduced by dehumidifying the air by adsorption or absorption of water with a drying medium and subsequently regenerating the water-laden drying medium by heating to a temperature at which the water is desorbed again. Compared to adsorption on a solid adsorbent, the advantage of absorption in a liquid absorption medium is that air dehumidification can be carried out with reduced equipment complexity and with less drying medium and that regeneration of the water-laden drying medium is easier to carry out using solar heat.

A further technical field where dehumidification of moist gas mixtures is employed is the field of absorption chillers (principle described in WO 2014/079675 A1; "absorption chiller" is used synonymously with "absorption heat pump" according to the invention). Here, the moist gas mixture is formed during evaporation of water under low pressure. The water vapour thus formed needs to be removed from the moist gas mixture so that said mixture may then be returned to the water evaporation to pass through a new cycle. Here too, absorption in a liquid absorption medium is favoured over adsorption on a solid adsorption medium.

In addition to use in absorption chillers, there is still a further area in which the drying of gas streams is necessary. This is natural gas refinement, which applies other requirements on the ionic liquids to be used therefor.

To absorb moisture with the aid of ionic liquids, the prior art proposes a series of ionic liquids. Thus, DE 10 2010 004 779 A1 mentions 1-ethyl-3-methylimidazolium ethylsulphate, 1-ethyl-3-

methylimidazolium methylsulphate, 1-ethyl-3-methylimidazolium diethylphosphate, 1-ethyl-3-methylimidazolium methylsulphonate, 1-butyl-3-methylimidazolium bistrifluoromethanesulphonimide, 1-butyl-3-ethylimidazolium chloride for example.

- 5 CN 102335545 A describes a series of ionic liquids based on alkyl phosphates, namely inter alia 1,3-dimethylimidazolium dimethylphosphate, 1-ethyl-3-methylimidazolium dimethylphosphate and 1-butyl-3-methylimidazolium dimethylphosphate.

Y. Luo et al., Appl. Thermal Eng. 31 (2011) 2772-2777 proposes using the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate in place of aqueous solutions of lithium bromide for air dehumidification. However, this ionic liquid has the disadvantage of only poor absorption capability.

- 10 Y. Luo et al., Solar Energy 86 (2012) 2718-2724 proposes the ionic liquid 1,3-dimethylimidazolium acetate as an alternative to 1-ethyl-3-methylimidazolium tetrafluoroborate for air dehumidification. The acetates are also discussed by M. Kanakubo et al., J. Mol. Liq. 217 (2016) 112-119.

US 2011/0247494 A1 proposes a further ionic liquid for this purpose, namely 1-ethyl-3-methylimidazolium acetate.

- 15 The application of these ionic liquids in absorption chillers is also discussed in WO 2013/050242 A1.

While these ionic liquids described in the prior art are very well-suited for dehumidification, the ionic liquids, which include dialkylimidazolium ions, exhibit the disadvantage that, especially on contact with gas mixtures, chemicals are given off which lead to olfactory contamination of the ambient air.

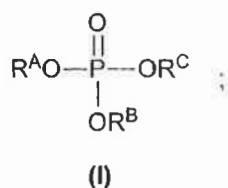
- 20 This is especially the case on dehumidification of indoor air and is undesirable in the case of absorption chillers such as refrigerators. Therefore, an absorbent is sought with which this contamination can be minimized.

For this reason, the object of the present invention consisted of providing an absorbent in which the tendency to give off badly odorous substances therefrom is particularly low.

- 25 An absorption medium which achieves this object has now surprisingly been found.

Detailed description of the invention

- 30 Accordingly, the present invention relates to a process for dehumidifying a moist gas mixture G_1 , wherein the moist gas mixture G_1 is contacted with a liquid absorption medium A_1 , which comprises a mixture of at least one trialkyl phosphate of structure (I)



and at least one salt **S** selected from the group consisting of Q^+A^- , $\text{Q}^+(\text{R}^1\text{O})_2\text{PO}_2^-$, $(\text{Q}^+)_2\text{R}^2\text{OPO}_3^{2-}$, $\text{Q}^+\text{M}^+\text{R}^3\text{OPO}_3^{2-}$, to obtain a gas mixture **G**₂ which has a lower water content compared to the moist gas mixture **G**₁ and a liquid absorption medium **A**₂ which has an elevated water content compared to the liquid absorption medium **A**₁,

wherein Q^+ is a dialkylimidazolium cation and in which in particular the alkyl groups each independently have 1 to 10 carbon atoms,

wherein A^- is an anion selected from the group consisting of R^*COO^- , $\text{R}'\text{SO}_3^-$, HSO_4^- , $\text{R}''\text{SO}_4^-$, where R^* , R' , R'' , R^{A} , R^{B} , R^{C} are each independently an alkyl group, in particular having 1 to 10 carbon atoms,

where R^1 , R^2 , R^3 are each independently an alkyl group, in particular having 1 to 10 carbon atoms, and where M^+ is an alkali metal ion, preferably Li^+ , K^+ or Na^+ , more preferably K^+ or Na^+ .

"Moist" is to be understood as meaning in the context of the invention "comprising water, in particular water vapour". "Dehumidifying" is to be understood as meaning "at least partially removing water".

"At least partially" is to be understood as meaning in the context of the invention "partially or completely".

"Moist gas mixture **G**₁" is accordingly to be understood as meaning in the context of the invention that the gas mixture **G**₁ comprises water, preferably water vapour ("water vapour" is to be understood as meaning water in the gaseous physical state), and that its composition is otherwise not subject to any particular restrictions. The water content of the moist gas mixture is not subject to any particular restrictions and is in particular from 0.01 vol% to 99.99 vol% ("vol%" indicates the volume of water vapour based on the overall volume of the moist gas mixture **G**₁). The composition of the moist gas mixture **G**₁ may otherwise vary depending on the application of the process according to the invention. The moist gas mixture **G**₁ is in particular selected from moist natural gas, moist air (this may be moist indoor air or the moist air resulting from evaporation of water in absorption chillers), preferably moist air. For moist natural gas the water content is in particular from 0.01 vol% to 15.00 vol%, for moist air said content is in particular from 0.01 vol% to 15.00 vol% in the case of moist indoor air or in particular from 95.00 vol% to 99.99 vol% which is the preferred range when moist air resulting from evaporation of water in absorption chillers is concerned.

The moist gas mixture **G**₁ used in the process has in particular a temperature of 2°C to 100°C, preferably 3°C to 60°C, more preferably 4°C to 50°C, even more preferably 5°C to 40°C and is

otherwise not subject to any particular restrictions. However, since the absorption capacity in this temperature range is so good, the process according to the invention is particularly well-suited for dehumidifying natural gas wherein processing of said gas often occurs in this temperature range.

In the process according to the invention, the absorption medium A_1 preferably also has a
 5 temperature of 10°C to 100°C, preferably 15°C to 80°C, more preferably 20°C to 50°C, even more preferably 20°C to 30°C.

The contacting may be effected in any way known to those skilled in the art, in particular in a water absorption unit W_{abs1} (elucidated below). The contacting causes the absorption medium A_1 to at least partially absorb moisture, i.e. water, from the moist gas stream gas mixture G_1 .

10 The process according to the invention is in particular carried out in an apparatus V_1 . The apparatus V_1 is restricted only to the extent that it shall be suitable for carrying out the process according to the invention. In particular, an apparatus V_1 comprising the following components may be employed:

(i) at least one water absorption unit W_{abs1} set up for contacting the moist gas mixture with the
 15 liquid absorption medium, in particular A_1 .

Apparatus V_1 also optionally comprises the following components:

(ii) at least one water desorption unit W_{des1} which comprises a heat exchanger W_{x1} and which is set up for at least partially removing water from a liquid absorption medium, in particular A_2 ,

20 (iii) and a circuit U_1 , which connects the water absorption unit W_{abs1} with the water desorption unit W_{des1} and by means of which the liquid absorption medium, in particular A_1 and A_2 , may be circulated.

The process according to the invention may accordingly be carried out in a water absorption unit W_{abs1} familiar to the person skilled in the art. Employable water absorption units W_{abs1} include in
 25 particular the water absorbers known to those skilled in the art. Said absorbers are based on the principle of increasing the surface area of the liquid absorption medium A_1 and simultaneously achieving the longest possible residence time of the liquid absorption medium A_1 in the water absorber during absorption of water. It is in particular possible here to employ water absorbers selected from the group of: packed beds, spray columns, falling-films, bubble columns, tray
 30 columns, wet scrubbers (for example Venturi scrubbers), stirred tanks and combinations of these absorbers. It is particularly preferable to employ falling-films, in particular shell and tube falling-films, as water absorbers. The water absorption unit W_{abs1} may in particular also comprise an additional heat exchanger W_{z1} set up such that the liquid absorption medium A_1 is adjustable to the desired temperature.

35 In a water desorption unit W_{des1} , which comprises a heat exchanger W_{x1} , the same can again be withdrawn to the water-laden liquid absorption medium, in particular A_2 . The water desorption unit

W_{des1} is based on the principle of supplying heat to the water-laden liquid absorption medium, in particular A_2 , increasing the surface area of the water-laden liquid absorption medium A_1 and simultaneously achieving the longest possible residence time of the water-laden liquid absorption medium, in particular A_2 , in the water desorption unit W_{des1} .

- 5 Employable water desorption units W_{des1} comprising a heat exchanger W_{x1} include in particular the combinations of heat exchanger and water desorber known to those skilled in the art, in particular horizontal tube evaporators having an upstream heat exchanger, in particular shell and tube heat exchangers, plate and frame heat exchangers. In addition, the water desorption unit W_{des1} comprising a heat exchanger W_{x1} may also be a water desorber having an integrated heat
- 10 exchanger. Such water desorbers having an integrated heat exchanger are in particular climbing film evaporators, long tube vertical evaporators, short tube vertical evaporators, forced circulation evaporators, agitated thin film evaporators. It is particularly preferable to employ falling-films, in particular shell and tube falling-films, as water desorption unit W_{des1} .

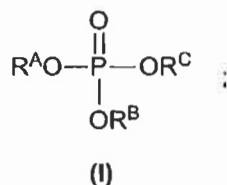
- In the circuit U_1 , in particular the water-laden liquid absorption medium A_2 from the water absorption unit W_{abs1} is conducted to the water desorption unit W_{des1} and even more preferably - particularly when the process according to the invention is carried out continuously - liquid absorbent from the water desorption unit W_{des1} is conducted to the water absorption unit W_{abs1} .

The circuit U_1 is in particular a conduit, in particular selected from the group consisting of tube, hose.

- 20 In a further preferred embodiment the circuit U_1 also comprises a pump.

It is preferable to cool the absorption medium A_1 during contacting of the moist gas mixture G_1 in order that as much moisture as possible is absorbed from the moist gas mixture G_1 . This may be achieved, for example, via an additional heat exchanger W_{z1} in the water absorption unit W_{abs1} .

- In the process according to the invention, the moist gas mixture G_1 is contacted with a liquid absorption medium A_1 , which comprises a mixture of at least one trialkyl phosphate of structure (I)



- and at least one salt S selected from the group consisting of Q^+A^- , $Q^+(R^1O)_2PO_2^-$, $(Q^+)_2R^2OPO_3^{2-}$, $Q^+M^+R^3OPO_3^{2-}$, to obtain a gas mixture G_2 which has a lower water content compared to the moist gas mixture G_1 and a liquid absorption medium A_2 which has an elevated water content compared to the liquid absorption medium A_1 ,
- 30

where Q^+ is a dialkylimidazolium cation, in which in particular the alkyl groups each independently have 1 to 10, preferably 1 to 8, more preferably 1 to 6, still more preferably 1 to 4, even more preferably 1 or 2 carbon atoms,

where A^- is an anion selected from the group consisting of R^*COO^- , $R'SO_3^-$, HSO_4^- , $R''SO_4^-$,

where R^* , R' , R'' , R^A , R^B , R^C , R^1 , R^2 , R^3 are each independently an alkyl group, in particular having 1 to 10, preferably 1 to 8, more preferably 1 to 6, still more preferably 1 to 4, even more preferably 1 or 2 carbon atoms,

5 and where M^+ is an alkali metal ion, preferably Li^+ , K^+ or Na^+ , more preferably K^+ or Na^+ .

In a preferred embodiment of the process according to the invention the salt **S** is selected from the group consisting of Q^+A^- , $Q^+(R^1O)_2PO_2^-$, and Q^+ is a dialkylimidazolium cation, in which the alkyl groups each independently have 1 to 6, preferably 1 to 4, more preferably 1 or 2 carbon atoms, and A^- is an anion selected from the group consisting of R^*COO^- , $R'SO_3^-$, $R''SO_4^-$, where R^* , R^1 , R' ,

10 R'' , R^A , R^B , R^C are each independently an alkyl group having 1 to 6, preferably 1 to 4, more preferably 1 or 2 carbon atoms.

In a more preferred embodiment of the process according to the invention, the salt **S** has the general formula $Q^+(R^1O)_2PO_2^-$, and Q^+ is a dialkylimidazolium cation, in which the alkyl groups are each independently methyl or ethyl, and R^1 , R^A , R^B , R^C are each independently methyl or ethyl.

15 In a still more preferred embodiment of the process according to the invention, the salt **S** has the general formula $Q^+(R^1O)_2PO_2^-$, and Q^+ is selected from the group consisting of 1,3-dimethylimidazolium, 1,3-diethylimidazolium, 1-ethyl-3-methylimidazolium, and R^A , R^B , R^C , R^1 are each independently methyl or ethyl. Even more preferably, Q^+ is then 1-ethyl-3-methylimidazolium and R^A , R^B , R^C , R^1 are each independently methyl or ethyl.

20 Furthermore, in all the aforementioned embodiments of the process according to the invention, it is particularly preferred if R^A , R^B , R^C are each independently selected from methyl, ethyl, more preferably $R^A = R^B = R^C = \text{methyl}$ or $R^A = R^B = R^C = \text{ethyl}$, particularly preferably $R^A = R^B = R^C = \text{ethyl}$.

The liquid absorption medium **A₁** may be employed in the process according to the invention in the form of the pure mixture of the trialkyl phosphates of structure (I) and the salts **S**. Alternatively and more preferably in the process according to the invention, the liquid absorption medium **A₁** is an aqueous solution, in which in particular the total weight of all trialkyl phosphates of structure (I) and all salts **S** is in the range of 65% by weight to 95% by weight, based on the total weight of the aqueous solution. Still more preferably, the total weight of all trialkyl phosphates of structure (I) and all salts **S** in **A₁** is in the range of 70% by weight to 90% by weight, based on the total weight of the aqueous solution, even more preferably in the range of 75% by weight to 87% by weight.

In the process according to the invention, the ratio of all trialkyl phosphates of structure (I) to the salts **S** in the absorption medium **A₁** is not subject to any further restrictions. However, it is preferable to employ in the process according to the invention an absorption medium **A₁** in which the ratio of the total weight of all trialkyl phosphates of structure (I) to the total weight of all salts **S** is in the range

1: 9999 to 1: 9, more preferably 1: 9999 to 1: 99, yet more preferably 1: 9999 to 1: 999.

The gas mixture G_2 obtained in the process according to the invention, which has a lower water content compared to the moist gas mixture G_1 , then represents the dehumidified gas stream which, in the case of dehumidified natural gas, can be supplied to power generation.

The liquid absorption medium A_2 obtained in the process according to the invention has an elevated water content compared to the liquid absorption medium A_1 . It will be appreciated that in terms of the salts S comprised by it and in terms of the trialkyl phosphates of structure (I) comprised by it, A_2 is identical to A_1 and is preferably distinguished therefrom only by its water content.

In a preferred embodiment of the process according to the invention, in a further step ["optional step b)"], wherein the process according to the invention is to be understood in this context as "step a)"], the at least partial removal of water from the liquid absorption medium A_2 to obtain a liquid absorption medium A_3 having a lower water content compared to the liquid absorption medium A_2 is then effected. Heat is additionally supplied to the liquid absorption medium A_2 here. The supply of heat and the at least partial removal may be effected in any way known to those skilled in the art, in particular in a water desorption unit W_{des1} comprising a heat exchanger W_{x1} . The at least partial removal of water from the liquid absorption medium A_2 affords a liquid absorption medium A_3 having a lower water content compared to the liquid absorption medium A_2 .

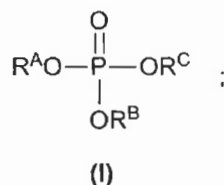
It will be appreciated that in terms of the salts S comprised by it and in terms of the trialkyl phosphates of structure (I) comprised by it, the liquid absorption medium A_3 is identical to A_2 and is preferably distinguished therefrom only by its water content.

In a further preferred embodiment the process according to the invention is carried out in continuous fashion. This is to be understood as meaning in particular that following step b) the steps a) and b) are performed at least one more time and that the liquid absorption medium A_1 employed in the steps a) additionally performed in each case is at least partially the liquid absorption medium A_3 obtained from the step b) performed immediately beforehand, i.e. in particular the water content of the liquid absorption medium A_1 employed in the step a) additionally performed in each case and of the liquid absorption medium A_3 from the immediately preceding step b) are identical.

It is yet more preferable when in this embodiment liquid absorption medium A_2 is supplied with heat from liquid absorption medium A_3 . This may be carried out in an additional heat exchanger W_{y1} , in particular selected from the group consisting of shell and tube heat exchangers and plate and frame heat exchangers. This makes it possible to carry out the process according to the invention in a particularly energy efficient fashion.

The invention also relates in a further aspect to an apparatus V_2 for dehumidifying a moist gas mixture, in particular moist air, comprising the components

- (i) a liquid absorption medium A_1 , which comprises a mixture of at least one trialkyl phosphate of structure (I)



and at least one salt **S** selected from the group consisting of Q^+A^- , $\text{Q}^+(\text{R}^1\text{O})_2\text{PO}_2^-$, $(\text{Q}^+)_2\text{R}^2\text{OPO}_3^{2-}$, $\text{Q}^+\text{M}^+\text{R}^3\text{OPO}_3^{2-}$,

- (ii) at least one water absorption unit $\text{W}_{\text{abs}2}$ set up for contacting the moist gas mixture with the liquid absorption medium A_{1^*} ,
- (iii) at least one water desorption unit $\text{W}_{\text{des}2}$ which comprises a heat exchanger $\text{W}_{\text{x}2}$ and is set up for at least partially removing water from a liquid absorption medium A_{1^*} ,
- (iv) and a circuit U_2 which connects the water absorption unit $\text{W}_{\text{abs}2}$ with the water desorption unit $\text{W}_{\text{des}2}$ and by means of which the liquid absorption medium A_{1^*} may be circulated,
- characterized in that

Q^+ is a dialkylimidazolium cation, in which in particular the alkyl groups each independently have 1 to 10, preferably 1 to 8, more preferably 1 to 6, still more preferably 1 to 4, even more preferably 1 or 2 carbon atoms,

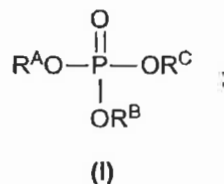
where A^- is an anion selected from the group consisting of R^*COO^- , $\text{R}'\text{SO}_3^-$, HSO_4^- , $\text{R}''\text{SO}_4^-$,

- where R^* , R' , R'' , R^{A} , R^{B} , R^{C} , R^1 , R^2 , R^3 are each independently an alkyl group, in particular having 1 to 10, preferably 1 to 8, more preferably 1 to 6, still more preferably 1 to 4, even more preferably 1 or 2 carbon atoms,

and where M^+ is an alkali metal ion, preferably Li^+ , K^+ or Na^+ , more preferably K^+ or Na^+ .

- The apparatus V_2 according to the invention is suitable for dehumidifying a moist gas mixture, in particular moist air. Said apparatus comprises the following components:

As first component, the apparatus V_2 according to the invention comprises a liquid absorption medium A_{1^*} , which comprises a mixture of at least one trialkyl phosphate of structure (I)



- and at least one salt **S** selected from the group consisting of Q^+A^- , $\text{Q}^+(\text{R}^1\text{O})_2\text{PO}_2^-$, $(\text{Q}^+)_2\text{R}^2\text{OPO}_3^{2-}$, $\text{Q}^+\text{M}^+\text{R}^3\text{OPO}_3^{2-}$,

Q^+ is a dialkylimidazolium cation, in which in particular the alkyl groups each independently have 1 to 10, preferably 1 to 8, more preferably 1 to 6, still more preferably 1 to 4, even more preferably 1 or 2 carbon atoms,

where A^- is an anion selected from the group consisting of R^*COO^- , $R'SO_3^-$, HSO_4^- , $R''SO_4^-$,

- 5 where R^* , R' , R'' , R^A , R^B , R^C , R^1 , R^2 , R^3 are each independently an alkyl group, in particular having 1 to 10, preferably 1 to 8, more preferably 1 to 6, still more preferably 1 to 4, even more preferably 1 or 2 carbon atoms,

and where M^+ is an alkali metal ion, preferably Li^+ , K^+ or Na^+ , more preferably K^+ or Na^+ .

- 10 In a preferred embodiment of the apparatus V_2 according to the invention, in A_1 the salt S is selected from the group consisting of Q^+A^- , $Q^+(R^1O)_2PO_2^-$, and Q^+ is a dialkylimidazolium cation, in which the alkyl groups each independently have 1 to 6, preferably 1 to 4, more preferably 1 or 2 carbon atoms, and A^- is an anion selected from the group consisting of R^*COO^- , $R'SO_3^-$, $R''SO_4^-$, where R^* , R^1 , R' , R'' , R^A , R^B , R^C are each independently an alkyl group having 1 to 6, preferably 1 to 4, more preferably 1 or 2 carbon atoms.

- 15 In a more preferred embodiment of the apparatus V_2 according to the invention, in A_1 the salt S has the general formula $Q^+(R^1O)_2PO_2^-$, and Q^+ is a dialkylimidazolium cation, in which the alkyl groups are each independently methyl or ethyl, and R^1 , R^A , R^B , R^C are each independently methyl or ethyl.

- 20 In a still more preferred embodiment of the apparatus V_2 according to the invention, in A_1 the salt S has the general formula $Q^+(R^1O)_2PO_2^-$, and Q^+ is selected from the group consisting of 1,3-dimethylimidazolium, 1,3-diethylimidazolium, 1-ethyl-3-methylimidazolium, and R^A , R^B , R^C , R^1 are each independently methyl or ethyl. Even more preferably, Q^+ is then 1-ethyl-3-methylimidazolium and R^A , R^B , R^C , R^1 are each independently methyl or ethyl.

- 25 Furthermore, in all the aforementioned embodiments of the apparatus V_2 according to the invention, it is particularly preferred if in A_1 R^A , R^B , R^C are each independently selected from methyl, ethyl, more preferably $R^A = R^B = R^C = \text{methyl}$ or $R^A = R^B = R^C = \text{ethyl}$, particularly preferably $R^A = R^B = R^C = \text{ethyl}$.

- 30 The liquid absorption medium A_1 may be employed in the process according to the invention in the form of the pure mixture of the trialkyl phosphates of structure (I) and the salts S . Alternatively and more preferably, in the process according to the invention the liquid absorption medium A_1 is an aqueous solution, in which in particular the total weight of all trialkyl phosphates of structure (I) and all salts S is in the range of 65% by weight to 95% by weight, based on the total weight of the aqueous solution. Still more preferably, the total weight of all trialkyl phosphates of structure (I) and all salts S in A_1 is in the range of 70% by weight to 90% by weight, based on the total weight of the aqueous solution, even more preferably in the range of 75% by weight to 87% by weight.
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The ratio of all trialkyl phosphates of structure (I) to the salts **S** in the liquid absorption medium **A₁*** is not subject to any further restrictions. However, it is preferable to employ an absorption medium **A₁*** in the apparatus **V₂** according to the invention in which the ratio of the total weight of all trialkyl phosphates of structure (I) to the total weight of all salts **S** is in the range 1: 9999 to 1:9, more preferably 1:9999 to 1: 99, even more preferably 1:9999 to 1: 999.

As a second component the apparatus **V₂** according to the invention comprises a water absorption unit **W_{abs2}** set up for contacting the moist gas mixture with the liquid absorption medium **A₁***. The water absorption unit **W_{abs2}** may in particular comprise an additional heat exchanger **W_{x2}** set up such that the liquid absorption medium **A₁*** is coolable. Employable water absorption units **W_{abs2}** of this kind include in particular the water absorbers known to those skilled in the art. Said absorbers are based on the principle of increasing the surface area of the liquid absorption medium **A₁*** and simultaneously achieving the longest possible residence time of the liquid absorption medium **A₁*** in the water absorber during absorption of water. It is in particular possible here to employ water absorbers selected from the group of: packed beds, spray columns, falling-films, bubble columns, tray columns, wet scrubbers (for example Venturi scrubbers), stirred tanks and combinations of these absorbers. It is particularly preferable to employ falling-films, in particular shell and tube falling-films, as water absorbers.

As a third component the apparatus **V₂** according to the invention comprises a water desorption unit **W_{des2}** which comprises a heat exchanger **W_{x2}** and is set up for at least partially removing water from the liquid absorption medium **A₁***. Particularly the combinations of heat exchanger and water desorber known to those skilled in the art may be employed therefor. The water desorption unit **W_{des2}** is based on the principle of supplying heat to the liquid absorption medium **A₁***, increasing the surface area of the liquid absorption medium **A₁*** and simultaneously achieving the longest possible residence time of the liquid absorption medium **A₁*** in the water desorption unit.

Employable water desorption units **W_{des2}** comprising a heat exchanger **W_{x2}** include in particular the combinations of heat exchanger and water desorber known to those skilled in the art, in particular horizontal tube evaporators having an upstream heat exchanger, in particular shell and tube heat exchangers, plate and frame heat exchangers. In addition, the water desorption unit **W_{des2}** comprising a heat exchanger **W_{x2}** may also be a water desorber having an integrated heat exchanger. Such water desorbers having an integrated heat exchanger are in particular climbing film evaporators, long tube vertical evaporators, short tube vertical evaporators, forced circulation evaporators, agitated thin film evaporators. It is particularly preferable to employ as water desorption unit **W_{des2}** falling-films, in particular shell and tube falling-films.

As a fourth component the apparatus **V₂** according to the invention comprises a circuit **U₂** which connects the water absorption unit **W_{abs2}** with the water desorption unit **W_{des2}** and by means of which the liquid absorption medium **A₁*** may be circulated. The circuit **U₂** is preferably a conduit, more preferably selected from the group consisting of tube, hose. In a further preferred embodiment the circuit **U₂** also comprises a pump.

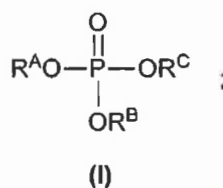
In a preferred embodiment the apparatus V_2 comprises a further heat exchanger W_{y2} (additional to the heat exchanger W_{x2} comprised in the water desorption unit W_{des2}). The heat exchanger W_{y2} is set up such that liquid absorption medium A_1 , sent from the water absorption unit W_{abs2} to the water desorption unit W_{des2} may be supplied with heat from liquid absorption medium A_1 , said
 5 medium being conducted away from the water desorption unit W_{des2} . This can be ensured by employing as heat exchanger W_{y2} in particular a heat exchanger selected from shell and tube heat exchangers, plate and frame heat exchangers.

In a further preferred embodiment, the apparatus V_2 is part of an absorption heat pump. This absorption heat pump then comprises as further components a condenser, an evaporator and a
 10 coolant, wherein the coolant is water.

The condenser is in particular connected to the water desorption unit W_{des2} via a conduit and is set up for condensing water at least partially removed from the liquid absorption medium A_1 in the water desorption unit W_{des2} . The condenser preferably also comprises a cooling water circuit.

The evaporator is in particular connected to the condenser via a conduit (which may comprise a throttling means) and connected to the water absorption unit W_{abs2} via a further conduit and is set up for evaporating condensed water from the condenser. The evaporator preferably also comprises
 15 a pressure of < 1 bar, more preferably < 0.1 bar, to permit evaporation of the condensed water at the lowest possible temperatures. The evaporator may further preferably additionally comprise an apparatus from which heat may be drawn and so that the condensed water may be evaporated (for
 20 example a coolant conduit in which coolant is passed into the space in which water is evaporated).

Finally, the present invention also relates to the absorption medium A_1 itself, in which the absorption medium A_1 comprises a mixture of at least one trialkyl phosphate of structure (I)



and at least one salt S selected from the group consisting of Q^+A^- , $Q^+(R^1O)_2PO_2^-$, $(Q^+)_2R^2OPO_3^{2-}$,
 25 $Q^+M^+R^3OPO_3^{2-}$,

where Q^+ is a dialkylimidazolium cation, in which in particular the alkyl groups each independently have 1 to 10, preferably 1 to 8, more preferably 1 to 6, still more preferably 1 to 4, even more preferably 1 or 2 carbon atoms,

where A^- is an anion selected from the group consisting of $R^*\text{COO}^-$, $R'\text{SO}_3^-$, HSO_4^- , $R''\text{SO}_4^-$,

30 where R^* , R' , R'' , R^{A} , R^{B} , R^{C} , R^1 , R^2 , R^3 are each independently an alkyl group, in particular having 1 to 10, preferably 1 to 8, more preferably 1 to 6, still more preferably 1 to 4, even more preferably 1 or 2 carbon atoms,

and where M^+ is an alkali metal ion, preferably Li^+ , K^+ or Na^+ , more preferably K^+ or Na^+ .

In a preferred embodiment of the absorption medium $A_{1\bullet}$ according to the invention, in said medium the salt S is selected from the group consisting of Q^+A^- , $Q^+(R^1O)_2PO_2^-$, and Q^+ is a

5 dialkylimidazolium cation, in which the alkyl groups each independently have 1 to 6, preferably 1 to 4, more preferably 1 or 2 carbon atoms, and A^- is an anion selected from the group consisting of R^*COO^- , $R'SO_3^-$, $R''SO_4^-$, where R^* , R^1 , R' , R'' , R^A , R^B , R^C are each independently an alkyl group having 1 to 6, preferably 1 to 4, more preferably 1 or 2 carbon atoms.

10 In a more preferred embodiment of the absorption medium $A_{1\bullet}$ according to the invention, in said medium the salt S has the general formula $Q^+(R^1O)_2PO_2^-$, and Q^+ is a dialkylimidazolium cation, in which the alkyl groups are each independently methyl or ethyl, and R^1 , R^A , R^B , R^C are each independently methyl or ethyl.

15 In a still more preferred embodiment of the absorption medium $A_{1\bullet}$ according to the invention, in said medium the salt S has the general formula $Q^+(R^1O)_2PO_2^-$, and Q^+ is selected from the group consisting of 1,3-dimethylimidazolium, 1,3-diethylimidazolium, 1-ethyl-3-methylimidazolium, and R^A , R^B , R^C , R^1 are each independently methyl or ethyl. Even more preferably, Q^+ is then 1-ethyl-3-methylimidazolium and R^A , R^B , R^C , R^1 are each independently methyl or ethyl.

20 Furthermore, in all the aforementioned embodiments of the absorption medium $A_{1\bullet}$ according to the invention, it is particularly preferred if in $A_{1\bullet}$ R^A , R^B , R^C are each independently selected from methyl, ethyl, more preferably $R^A = R^B = R^C = \text{methyl}$ or $R^A = R^B = R^C = \text{ethyl}$, particularly preferably $R^A = R^B = R^C = \text{ethyl}$.

25 The liquid absorption medium $A_{1\bullet}$ may be present in the form of the pure mixture of the trialkyl phosphates of structure (I) and the salts S . Alternatively and more preferably, the liquid absorption medium $A_{1\bullet}$ is an aqueous solution, in which in particular the total weight of all trialkyl phosphates of structure (I) and all salts S is in the range of 65% by weight to 95% by weight, based on the total weight of the aqueous solution. Still more preferably, the total weight of all trialkyl phosphates of structure (I) and all salts S in $A_{1\bullet}$ is in the range of 70% by weight to 90% by weight, based on the total weight of the aqueous solution, even more preferably in the range of 75% by weight to 87% by weight.

30 The ratio of all trialkyl phosphates of structure (I) to the salts S in the liquid absorption medium $A_{1\bullet}$ is not subject to any further restrictions. In the liquid absorption medium $A_{1\bullet}$, the ratio of the total weight of all trialkyl phosphates of structure (I) to the total weight of all salts S is preferably in the range of 1: 9999 to 1: 9, more preferably 1: 9999 to 1: 99, yet more preferably 1: 9999 to 1: 999.

35 Figures 1 and 2 elucidated hereinbelow show preferred embodiments of the process according to the invention and of the apparatus according to the invention.

Figure 1 (abbreviated to "Fig. 1") shows an embodiment of the apparatus V_2/V_1 according to the invention.

The apparatus V_1 shown in Figure 1 comprises a water absorption unit W_{abs1} <103> (with optional additional heat exchanger W_{z1} <104>) to which a conduit <101> leads and from which a conduit <102> leads away, a water desorption unit W_{des1} which comprises a heat exchanger W_{x1} <108> and a water desorber <109> and to which conduit <111> leads and from which conduits <110>, <112> and <113> lead away, and a circuit U_2 formed from conduits <106>, <111> and <113> or <106>, <111>, <112> and <105> (in each case optionally with conduit <114>). The apparatus in Figure 1 may also optionally comprise a further heat exchanger W_{y1} <107> to which conduits <106> and <112> lead and from which conduits <105> and <111> lead away. In addition the apparatus V_1 also comprises a liquid absorption medium A_1 . Said medium is located in one or more of the abovementioned components water absorption unit W_{abs1} , water desorption unit W_{des1} , circuit U_1 . The water absorption unit W_{abs1} <103> may optionally also comprise an additional heat exchanger W_{z1} <104> with which the liquid absorption medium A_1 may be brought, for example, to a temperature of 10°C to 100°C, preferably 15°C to 80°C, more preferably 20°C to 50°C, yet more preferably 20°C to 30°C. Optionally, circuit U_2 may also additionally comprise a pump for conveying the liquid absorption medium A_1 .

The process according to the invention will now be illustratively described with reference to apparatus V_1 using Figure 1:

A stream of moist gas mixture G_1 having, for example, a temperature of 2°C to 100°C (said stream may be moist air, moist natural gas or moist gas mixture - see also Figure 2 with regard to this option) is supplied via conduit <101> to a water absorption unit W_{abs1} <103> and contacted there with the liquid absorption medium A_1 supplied to the water absorption unit W_{abs1} <103> via the conduit <105> or via the conduit <113>. The water absorption unit W_{abs1} <103> may be any of the water absorbers recited hereinabove for W_{abs1} , in particular a falling-film. Contacting, in the water absorption unit W_{abs1} <103>, the gas mixture G_1 supplied via conduit <101> with the liquid absorption medium A_1 supplied via the conduit <105> or via the conduit <113> affords a liquid absorption medium A_2 having an elevated water content compared to the liquid absorption medium A_1 and a stream of a gas mixture G_2 discharged via the conduit <102>, wherein G_2 has a lower water content compared to the moist gas mixture G_1 . Depending on the application, G_2 is in particular dehumidified natural gas. The water absorption unit W_{abs1} <103> may optionally also comprise an additional heat exchanger W_{z1} <104> with which the liquid absorption medium A_1 may be adjusted, for example, to a temperature in the range of 10°C to 100°C, preferably 15°C to 80°C, more preferably 20°C to 50°C, yet more preferably 20°C to 30°C. Preferably via the conduits <106>, <111> and the heat exchanger W_{y1} <107> (or, when the heat exchanger W_{y1} <107> is not employed, via conduits <106>, <111> and <114>) the liquid absorption medium A_2 is then passed to the water desorption unit W_{des1} composed of the heat exchanger W_{x1} <108> and the water desorber <109>. The water-laden liquid absorption medium A_2 may additionally be supplied with

heat in the optional heat exchanger W_{y1} <107>. The at least partial removal of water from the liquid absorption medium A_2 is then carried out in the water desorber <109> to afford a liquid absorption medium A_3 having a lower water content compared to the liquid absorption medium A_2 . The water removed is then discharged from the water desorber <109> as liquid or vapour, preferably as vapour, via a conduit <110>. The liquid absorption medium A_3 is then discharged from the water desorber <109> and returned to the water absorption unit W_{abs1} <103>. This may either be carried out directly, i.e. via the conduit <113> which is shown in dashed form in Figure 1. Alternatively and preferably, the liquid absorption medium A_3 may also be supplied via the conduit <112> to the optional heat exchanger W_{y1} <107> in which the liquid absorption medium A_2 supplied via conduit <106> to the optional heat exchanger W_{y1} <107> is then supplied with heat from the liquid absorption medium A_3 supplied via conduit <112> to the optional heat exchanger W_{y1} <107>. Once the concentrated liquid absorption medium A_3 has been supplied to the water absorption unit W_{abs1} via conduit <105> or <113>, said medium is reused as A_1 for at least partially dehumidifying the gas stream in a new cycle.

Figure 2 (abbreviated as "Fig. 2") shows in schematic fashion an absorption chiller into which an apparatus V_2 is integrated. The constituents <101> to <114> are shown as for the apparatus V_2 described in Figure 1. Additionally, the absorption chiller in Figure 2 also comprises a condenser <211> which is connected to the water desorption unit W_{des2} <109> via the conduit <110> and is set up for condensing water at least partially removed from the liquid absorption medium A_1 in the water desorption unit W_{des2} . The condenser <211> preferably also comprises a heat exchanger <212> with which cooling water may be supplied.

The absorption chiller shown in Figure 2 also comprises an evaporator <214> connected to the condenser <211> via a conduit <216> (which may optionally comprise a throttling means <213>) and connected via the conduit <101> with the water absorption unit W_{abs2} . The evaporator <214> is set up to evaporate condensed water from the condenser. Additionally, the evaporator <214> can further preferably also comprise a heat exchanger <215> which supplies a medium, heat being drawn off from the medium to thus evaporate the condensed water (for example a coolant conduit with, in particular, water as coolant, this coolant being passed into the evaporator <214>).

In an embodiment of the process according to the invention (described hereinbelow with reference to apparatus V_1 using Figure 2) moist gas mixture G originating from the evaporator <214> is passed via the conduit <101> to the water absorption unit W_{abs1} <103>. The water removed in water desorption unit W_{des1} is supplied via the conduit <110> to the condenser <211> in which said water is recondensed. A cooling water circuit as heat exchanger <212> installed in the condenser is optionally likewise used therefor. The condensed water is then supplied via a conduit <216> to the evaporator <214> in which the evaporation of water is effected in particular at low pressures, thus bringing about a cooling effect. This may optionally also be effected using a throttling means <213>. This achieves a cooling action in the evaporator <214> and, for example, coolant may be

cooled via the heat exchanger <215>. The water vapour generated is then returned to the water absorption unit W_{abs1} <103> via conduit <101>.

The examples which follow are intended to elucidate the present invention without limiting said
5 invention in any way.

Examples

In order to simulate the decomposition, 0.1 g of the following mixtures of 1-ethyl-3-
10 methylimidazolium diethyl phosphate ("EMIM DEP", prepared according to WO 2004/016631 A1) and triethyl phosphate ("TEP"; purchased from Sigma Aldrich; CAS number: 78-40-0) were incubated at 150°C for 20 minutes.

C1: Mixture of 85% by weight EMIM DEP and 15% by weight H₂O;

I1: Mixture of 75% by weight EMIM DEP, 15% by weight H₂O, 10% by weight TEP;

15 **I2:** Mixture of 80% by weight EMIM DEP, 15% by weight H₂O, 5% by weight TEP;

I3: Mixture of 84% by weight EMIM DEP, 15% by weight H₂O, 1% by weight TEP.

After the incubation, the gas phase was investigated by gas chromatography and mass spectrometry for the decomposition product *N*-methylimidazole.

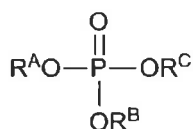
The areas of the intensity peaks of the *N*-methylimidazole peak, measured using a flame ionization
20 detector, are directly proportional to the proportion in the gas phase.

Whereas in the sample **C1** a distinct *N*-methylimidazole peak was observed, this peak is absent in the samples **I1**, **I2**, **I3**. This shows the surprisingly stabilizing effect of triethyl phosphate.

Corresponding results are also observed for other trialkyl phosphates.

Claims

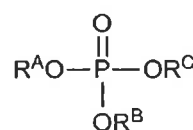
1. Process for dehumidifying a moist gas mixture **G**₁, wherein the moist gas mixture **G**₁ is contacted with a liquid absorption medium **A**₁, which comprises a mixture of at least one trialkyl phosphate of structure (I)



(I)

- and at least one salt **S** selected from the group consisting of $\text{Q}^+(\text{R}^1\text{O})_2\text{PO}_2^-$, to obtain a gas mixture **G**₂ which has a lower water content compared to the moist gas mixture **G**₁ and a liquid absorption medium **A**₂ which has an elevated water content compared to the liquid absorption medium **A**₁, where Q^+ is 1-ethyl-3-methylimidazolium, where R^{A} , R^{B} , R^{C} , R^1 are each ethyl.

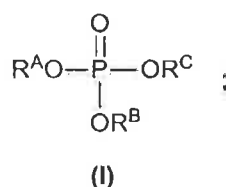
2. Process according to Claim 1, wherein the liquid absorption medium **A**₁ is an aqueous solution.
3. Process according to Claim 2, wherein in the liquid absorption medium **A**₁, the total weight of all trialkyl phosphates of structure (I) and all salts **S** is in the range of 65% by weight to 95% by weight, based on the total weight of the aqueous solution.
4. Process according to any of Claims 1 to 3, wherein in the liquid absorption medium **A**₁, the ratio of the total weight of all trialkyl phosphates of structure (I) to the total weight of all salts **S** is in the range from 1: 9999 to 1: 9.
5. Process according to any of Claims 1 to 4, wherein said process is carried out continuously.
6. Apparatus **V**₂ for dehumidifying a moist gas mixture, comprising the components
- (i) a liquid absorption medium **A**₁, which comprises a mixture of at least one trialkyl phosphate of structure (I)



(I)

- and at least one salt **S** selected from the group consisting of $\text{Q}^+(\text{R}^1\text{O})_2\text{PO}_2^-$,

- (ii) at least one water absorption unit W_{abs2} set up for contacting the moist gas mixture with the liquid absorption medium A_{1*} ,
- (iii) at least one water desorption unit W_{des2} which comprises a heat exchanger W_{x2} and is set up for at least partially removing water from a liquid absorption medium A_{1*} ,
- 5 (iv) and a circuit U_2 which connects the water absorption unit W_{abs2} with the water desorption unit W_{des2} and by means of which the liquid absorption medium A_{1*} may be circulated, wherein
- Q^+ is 1-ethyl-3-methylimidazolium, where R^A , R^B , R^C , R^1 are each ethyl.
7. Apparatus V_2 according Claim 6, wherein the liquid absorption medium A_{1*} is an aqueous solution.
- 10 8. Apparatus V_2 according to Claim 7, wherein in A_{1*} , the total weight of all trialkyl phosphates of structure (I) and all salts S is in the range of 65% by weight to 95% by weight, based on the total weight of the aqueous solution.
9. Apparatus V_2 according to any of Claims 6 to 8, wherein in A_{1*} , the ratio of the total weight of all trialkyl phosphates of structure (I) to the total weight of all salts S is in the range from
- 15 1: 9999 to 1: 9.
10. Absorption heat pump, comprising an apparatus V_2 according to any of Claims 6 to 9 and, as further components, a condenser, an evaporator and a coolant, wherein the coolant is water.
11. Use of the apparatus V_2 according to any of Claims 6 to 9 for carrying out a process according to any of Claims 1 to 5.
- 20 12. Absorption medium A_{1*} , which comprises a mixture of at least one trialkyl phosphate of structure (I)



and at least one salt S selected from the group consisting of $Q^+(R^1\text{O})_2\text{PO}_2^-$, where Q^+ is 1-ethyl-3-methylimidazolium,

25

where R^A , R^B , R^C , R^1 are each ethyl,

in which the ratio of the total weight of all trialkyl phosphates of structure (I) to the total weight of all salts S is in the range from 1: 9999 to 1: 9.

13. Absorption medium **A₁*** according to Claim 12, which is an aqueous solution.
14. Absorption medium **A₁*** according to Claim 13, in which the total weight of all trialkyl phosphates of structure **(I)** and all salts **S** is in the range of 65% by weight to 95% by weight, based on the total weight of the aqueous solution.