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Process and device for cleaning vinyl chloride

## Description

5 US Patent 3 843 736 discloses a process for isolating vinyl chloride from the reaction mixture obtained in the incomplete thermal cracking of 1,2-dichloroethane at a superatmospheric pressure of preferably from 8 to 40 atm. absolute and temperatures between about 450 and 650°C in  
10 the absence of catalysts, with the gas mixture leaving the cracking zone, comprising vinyl chloride, hydrogen chloride, unreacted 1,2-dichloroethane and byproducts, being conveyed in partially condensed form into a first distillation stage to distill off the hydrogen chloride  
15 and subsequently being conveyed into a second distillation stage to distill off the vinyl chloride, the bottom product of the second distillation stage then being worked up in a known manner for the purpose of recycling the unreacted 1,2-dichloroethane, and with the vinyl  
20 chloride drawn off at the top of the second distillation stage and liquefied being partially pumped back into about the middle of the first distillation stage, in which process the vinyl chloride drawn off and liquefied as product, which still contains small amounts of hydro-  
25 gen chloride, is fed to the top of a degassing zone from which a part of the vinyl chloride is evaporated by means of a circulation evaporator together with the entire entrained hydrogen chloride, the evaporated vinyl chloride is condensed and pumped back into about the  
30 middle of the first distillation stage provided for distilling off the hydrogen chloride, while very pure vinyl chloride is taken off from the bottom of the degassing zone.

This patent also mentions that the small amounts of  
35 hydrogen chloride which are removed in the degassing zone



were formerly separated off by means of towers filled with sodium hydroxide.

However, the known process is disadvantageous if the vinyl chloride fed to the degassing zone still contains small amounts of water. These are unavoidable in practice; especially when running up the plant and during interruptions in operation, traces of water are unavoidably introduced. In practice, therefore, the degassing zone was then operated in such a way that these amounts of water were separated off via the bottom of the degassing column, together with hydrogen chloride, for which purpose the towers filled with sodium hydroxide were again required. If this separation of the water were not carried out via the bottom of the degassing column, the water would be circulated together with the recycled vinyl chloride and lead to corrosion in the affected parts of the plant. However, such corrosion is unacceptable not only for economic reasons, but especially for safety reasons.

It has now been found that the towers filled with sodium hydroxide can be omitted if the degassing column is operated in such a way that the major part of the water is taken off at the top and removed, advantageously by drying. The dry, hydrogen chloride-containing vinyl chloride recirculated to the process can no longer cause corrosion.

The invention accordingly provides a process for isolating vinyl chloride, which comprises distilling off the hydrogen chloride from the reaction mixture formed in the incomplete thermal cracking of 1,2-dichloroethane at superatmospheric pressure and temperatures of from about 450 to about 650°C in the absence of catalysts in a first distillation stage and distilling off the vinyl chloride in a second distillation stage, with the vinyl chloride drawn off at the top of the second distillation stage and liquefied being partially recirculated as runback into



the second distillation stage and the remaining liquefied vinyl chloride drawn off being fed to the top of a degassing zone from which a part of the vinyl chloride together with the entire entrained hydrogen chloride and water is evaporated and, after substantial removal of the water, recirculated into the first distillation stage, while pure vinyl chloride is taken off from the bottom of the degassing zone.

The invention further provides an apparatus for preparing vinyl chloride having a cracking zone (1), a first distillation stage (2) for separating off hydrogen chloride, a second distillation stage (3) for distilling off vinyl chloride from higher-boiling constituents and a third distillation stage (4) for separating off hydrogen chloride and water from the vinyl chloride, which comprises an apparatus (5) (drying zone) via which the hydrogen chloride and water separated off in the third distillation stage (4) are recirculated together with vinyl chloride to the first distillation stage (2) and in which the water is substantially removed.

The apparatus of the invention is schematically shown in the figure. Besides the apparatus (1) to (5) already mentioned, this includes:

- (6) the feed line for 1,2-dichloroethane to the cracking zone (1),
- (7) a line for the cracking products to the first distillation stage (2),
- (8) a line for the hydrogen chloride separated off,
- (9) a line for the higher-boiling products to the second distillation stage (3),
- (10) a line to a condenser (11) for the liquefaction of the vinyl chloride,
- (12) a line for a substream of the liquefied vinyl chloride back to the second distillation stage (3),
- (13) a line for separating off high-boiling byproducts,
- (14) a line for a second substream of the liquefied vinyl chloride to the third distillation stage (4),



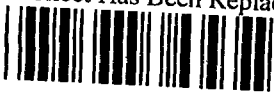
- (15) a line from the third distillation stage (4) to the drying zone (5),  
(16) a line for the dried mixture comprising hydrogen chloride and residual vinyl chloride back to the first distillation stage (2),  
5 (17) a line for the water separated off and  
(18) a line for the pure vinyl chloride.

In the separation of the water according to the invention, a highly corrosive mixture of vinyl chloride, hydrogen chloride and water enters the drying zone. It is known that under such circumstances polymerization of the vinyl chloride can occur (catalysis by traces of metals). Surprisingly, however, even on prolonged operation in metal apparatus, no deposit of polyvinyl chloride could  
10 be found.  
15

The substantial removal of the water according to the invention can be carried out in the manner known for acid fluids. This can be carried out by condensation of the water, but preferably by drying, for example using agents which undergo chemical transformation, for example liquid desiccants such as concentrated sulfuric acid or solid desiccants such as phosphorus pentoxide or calcium chloride. Preference is given to desiccants which retain the water adsorptively, such as molecular sieves and, in particular, silica gels.  
20  
25

The drying zone preferably comprises at least two dryers connected in parallel, with the water-containing mixture to be recirculated being conveyed through the one, while the other (or the others) is (are) regenerated or freshly charged. It is naturally also possible to operate a plurality of drying apparatus in series. The materials of value, vinyl chloride and hydrogen chloride, liberated on regeneration can be recirculated to the process.  
30

In a preferred embodiment of the invention, the drying apparatus are configured in such a way that for  
35



regeneration they can be heated and flushed with an inert gas such as carbon dioxide, a noble gas or, preferably, nitrogen. Suitable apparatus are, for example, tube heat exchangers or containers having internal coils of tubing.

- 5 According to the invention, the gas stream taken off via the top of the degassing column can be dried or the top product can be condensed and the condensate can be conducted through the dryer(s).

- 10 It is advantageous to install the dryers as close as possible to the degassing zone, since the greatest water concentration prevails at the top of this column, particularly when the gas phase is to be dried. In this case, the dryer can be installed at the beginning of the vapor line.

- 15 Even if, according to the invention, sodium hydroxide towers and the like can be omitted, the invention of course also includes embodiments in which such apparatus are retained, for example for safety reasons. In this case, these apparatus then have considerably higher  
20 operating lives and a correspondingly reduced formation of salt and wastewater.

- If subsequent treatment with sodium hydroxide or similar-acting agents is omitted, not only are these materials and the apparatus saved, but the expense of servicing and  
25 maintenance thereof is also saved. Furthermore, the entire apparatus can then be operated in a closed system. This also eliminates emissions or the facilities used for their prevention during opening, cleaning and charging of these apparatus.

- 30 The invention is illustrated by the following examples.

#### Example 1

A vinyl chloride stream of 39 kg/h having an average



5 water content of 29.5 ppm is pumped through a tube (length 200 mm, diameter 80 mm) filled with a wire mesh having a mesh spacing of 125  $\mu$ m and charged with 740 g of silica gel (commercial "Blaugel", fine-pored, particle size from 1 to 3 mm); the pressure at the inlet of the tube is 16 bar. After a running time of 21 hours, the silica gel has adsorbed 15.45 g of water, corresponding to a loading of 2.1% by weight. The water content in the vinyl chloride flowing out is 7.1 ppm.

10 For desorption, low-pressure steam is passed through the apparatus. After 180 minutes, the residual loading of the silica gel is < 0.3%.

#### Example 2

15 In a pilot plant, a vinyl chloride stream of 39 kg/h is conveyed through a cylindrical container for 19 hours. Dimensions and charging otherwise correspond to the container described in Example 1. After a running time of 19 hours, the loading of the silica gel is 3.07% by weight. The water content of the dried vinyl chloride is  
20 6.5 ppm.

For regeneration, the container is heated to about 120°C (internal temperature), with a stream of nitrogen of 100 l/h being passed through the apparatus. After 3 hours, the loading of the silica gel is 0.25%.

#### 25 Example 3

In a pilot plant, a vinyl chloride stream of 34 kg/h having an average water content of 30 ppm is pumped at a pressure of about 16 bar through a tube (length 200 mm, diameter 80 mm) filled with molecular sieve (WESSALITH  
30 US 330, Degussa, Hanau). After a running time of 88 hours, the molecular sieve has adsorbed 738 g of water which corresponds to a loading of 31.9% by weight, based on the adsorbent. After desorption for 23 hours at 250°C,



the residual loading is about 13% by weight.

#### Example 4

A substream of the top stream from the third distillation stage comprising 0.37 kg of vinyl chloride having a  
5 hydrogen chloride content of about 4 g (1,000 ppm) and a water content of about 6 mg (16 ppm) is drawn off in gaseous form and conveyed through a drying apparatus. The drying apparatus comprises a tube having a length of 200 mm and a diameter of 15 mm. It is filled with 35 g of  
10 silica gel (commercial "Blaugel", fine-pored, particle size from 1 to 3 mm). After 100 l of the specified gas stream had been conveyed through this dryer, the loading of the desiccant was 12.8% by weight. The gas flowing out had an average water content of 0.5 ppm.



## Claims

1. A process for isolating vinyl chloride, which comprises distilling off the hydrogen chloride from the reaction mixture formed in the incomplete thermal cracking of 1,2-dichloroethane at superatmospheric pressure and temperatures of from about 450 to about 650°C in the absence of catalysts in a first distillation stage and distilling off the vinyl chloride in a second distillation stage, with the vinyl chloride drawn off at the top of the second distillation stage and liquefied being partially recirculated as runback into the second distillation stage and the remaining liquefied vinyl chloride drawn off being fed to the top of a degassing zone from which a part of the vinyl chloride together with the entire entrained hydrogen chloride and water is evaporated and, after substantial removal of the water, recirculated into the first distillation stage, while pure vinyl chloride is taken off from the bottom of the degassing zone.
2. The process as claimed in claim 1, wherein the removal of the water is carried out with the aid of a desiccant.
3. The process as claimed in claim 2, wherein the desiccant used adsorbs the water.
4. The process as claimed in claim 3, wherein the desiccant used is a molecular sieve or silica gel.
5. An apparatus for preparing vinyl chloride having a cracking zone (1), a first distillation stage (2) for separating off hydrogen chloride, a second distillation stage (3) for distilling off vinyl chloride from higher-boiling constituents and a third distillation stage (4) for separating off hydrogen chloride and water from the vinyl chloride,



5 which comprises an apparatus (5) (drying zone) via which the hydrogen chloride and water separated off in the third distillation stage (4) are recirculated together with vinyl chloride to the first distillation stage (2) and in which the water is substantially removed.

6. The apparatus as claimed in claim 5, which comprises a dryer charged with an agent which physically adsorbs water.

10 7. The apparatus as claimed in claim 5 or 6, which comprises dryers connected in parallel.

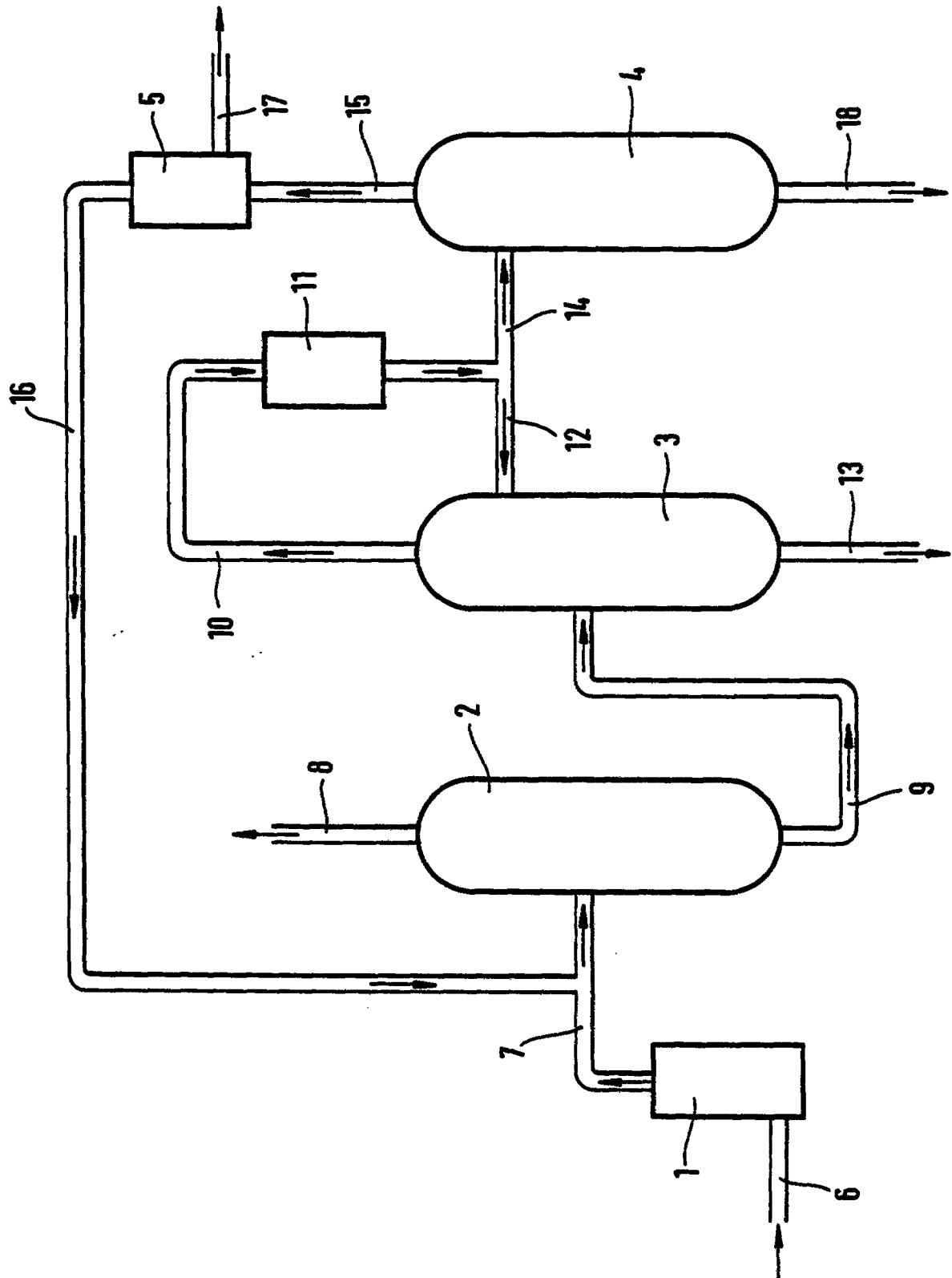


# Abstract

In the preparation of vinyl chloride by thermal cracking of 1,2-dichloroethane, three distillation stages are used to distill off first hydrogen chloride, then vinyl chloride and finally entrained hydrogen chloride with vinyl chloride. If, in the last stage, entrained water is not drawn off via the bottom, it is recirculated with the top product to the first stage and causes corrosion. Removal of the water at the top of the third distillation stage, advantageously by drying, prevents the corrosion.

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Description

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## Process and device for cleaning vinyl chloride

US Patent 3 843 736 discloses a process for isolating vinyl chloride from the reaction mixture obtained in the incomplete thermal cracking of 1,2-dichloroethane at a  
5 superatmospheric pressure of preferably from 8 to 40 atm. absolute and temperatures between about 450 and 650°C in the absence of catalysts, with the gas mixture leaving the cracking zone, comprising vinyl chloride, hydrogen  
10 chloride, unreacted 1,2-dichloroethane and byproducts, being conveyed in partially condensed form into a first distillation stage to distill off the hydrogen chloride and subsequently being conveyed into a second distillation stage to distill off the vinyl chloride, the bottom  
15 product of the second distillation stage then being worked up in a known manner for the purpose of recycling the unreacted 1,2-dichloroethane, and with the vinyl chloride drawn off at the top of the second distillation stage and liquefied being partially pumped back into  
20 about the middle of the first distillation stage, in which process the vinyl chloride drawn off and liquefied as product, which still contains small amounts of hydrogen chloride, is fed to the top of a degassing zone from which a part of the vinyl chloride is evaporated by means  
25 of a circulation evaporator together with the entire entrained hydrogen chloride, the evaporated vinyl chloride is condensed and pumped back into about the middle of the first distillation stage provided for distilling off the hydrogen chloride, while very pure  
30 vinyl chloride is taken off from the bottom of the degassing zone.

This patent also mentions that the small amounts of hydrogen chloride which are removed in the degassing zone were formerly separated off by means of towers filled  
35 with sodium hydroxide.

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However, the known process is disadvantageous if the vinyl chloride fed to the degassing zone still contains small amounts of water. These are unavoidable in practice; especially when running up the plant and during  
5 interruptions in operation, traces of water are unavoidably introduced. In practice, therefore, the degassing zone was then operated in such a way that these amounts of water were separated off via the bottom of the degassing column, together with hydrogen chloride, for  
10 which purpose the towers filled with sodium hydroxide were again required. If this separation of the water were not carried out via the bottom of the degassing column, the water would be circulated together with the recycled vinyl chloride and lead to corrosion in the affected  
15 parts of the plant. However, such corrosion is unacceptable not only for economic reasons, but especially for safety reasons.

It has now been found that the towers filled with sodium hydroxide can be omitted if the degassing column is  
20 operated in such a way that the major part of the water is taken off at the top and removed, advantageously by drying. The dry, hydrogen chloride-containing vinyl chloride recirculated to the process can no longer cause corrosion.

25 The invention accordingly provides a process for isolating vinyl chloride, which comprises distilling off the hydrogen chloride from the reaction mixture formed in the incomplete thermal cracking of 1,2-dichloroethane at superatmospheric pressure and temperatures of from about  
30 450 to about 650°C in the absence of catalysts in a first distillation stage and distilling off the vinyl chloride in a second distillation stage, with the vinyl chloride drawn off at the top of the second distillation stage and liquefied being partially recirculated as runback into  
35 the second distillation stage and the remaining liquefied vinyl chloride drawn off being fed to the top of a degassing zone from which a part of the vinyl chloride

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together with the entire entrained hydrogen chloride and water is evaporated and, after substantial removal of the water, recirculated into the first distillation stage, while pure vinyl chloride is taken off from the bottom of the degassing zone.

The invention further provides a device for preparing vinyl chloride having a cracking zone (1), a first distillation stage (2) for separating off hydrogen chloride, a second distillation stage (3) for distilling off vinyl chloride from higher-boiling constituents and a third distillation stage (4) for separating off hydrogen chloride and water from the vinyl chloride, which comprises a device (5) (drying zone) via which the hydrogen chloride and water separated off in the third distillation stage (4) are recirculated together with vinyl chloride to the first distillation stage (2) and in which the water is substantially removed.

The device of the invention is schematically shown in the figure. Besides the apparatus (1) to (5) already mentioned, this includes:

- (6) the feed line for 1,2-dichloroethane to the cracking zone (1),
- (7) a line for the cracking products to the first distillation stage (2),
- (8) a line for the hydrogen chloride separated off,
- (9) a line for the higher-boiling products to the second distillation stage (3),
- (10) a line to a condenser (11) for the liquefaction of the vinyl chloride,
- (12) a line for a substream of the liquefied vinyl chloride back to the second distillation stage (3),
- (13) a line for separating off high-boiling byproducts,
- (14) a line for a second substream of the liquefied vinyl chloride to the third distillation stage (4),
- (15) a line from the third distillation stage (4) to the drying zone (5),
- (16) a line for the dried mixture comprising hydrogen

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chloride and residual vinyl chloride back to the first distillation stage (2),

(17) a line for the water separated off and

(18) a line for the clean vinyl chloride.

- 5 In the separation of the water according to the invention, a highly corrosive mixture of vinyl chloride, hydrogen chloride and water enters the drying zone. It is known that under such circumstances polymerization of the vinyl chloride can occur (catalysis by traces of metals).  
10 Surprisingly, however, even on prolonged operation in metal apparatus, no deposit of polyvinyl chloride could be found.

The substantial removal of the water according to the invention can be carried out in the manner known for acid  
15 fluids. This can be carried out by condensation of the water, but preferably by drying, for example using agents which undergo chemical transformation, for example liquid desiccants such as concentrated sulfuric acid or solid desiccants such as phosphorus pentoxide or calcium  
20 chloride. Preference is given to desiccants which retain the water adsorptively, such as molecular sieves and, in particular, silica gels.

The drying zone preferably comprises at least two dryers connected in parallel, with the water-containing mixture  
25 to be recirculated being conveyed through the one, while the other (or the others) is (are) regenerated or freshly charged. It is naturally also possible to operate a plurality of drying apparatus in series. The materials of value, vinyl chloride and hydrogen chloride, liberated on  
30 regeneration can be recirculated to the process.

In a preferred embodiment of the invention, the drying apparatus are configured in such a way that for regeneration they can be heated and flushed with an inert gas such as carbon dioxide, a noble gas or, preferably,  
35 nitrogen. Suitable apparatus are, for example, tube heat

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exchangers or containers having internal coils of tubing.

According to the invention, the gas stream taken off via the top of the degassing column can be dried or the top product can be condensed and the condensate can be  
5 conducted through the dryer(s).

It is advantageous to install the dryers as close as possible to the degassing zone, since the greatest water concentration prevails at the top of this column, particularly when the gas phase is to be dried. In this  
10 case, the dryer can be installed at the beginning of the vapor line.

Even if, according to the invention, sodium hydroxide towers and the like can be omitted, the invention of course also includes embodiments in which such devices  
15 are retained, for example for safety reasons. In this case, these devices then have considerably higher operating lives and a correspondingly reduced formation of salt and wastewater.

If subsequent treatment with sodium hydroxide or similar-  
20 acting agents is omitted, not only are these materials and the apparatus saved, but the expense of servicing and maintenance thereof is also saved. Furthermore, the entire apparatus can then be operated in a closed system. This also eliminates emissions or the facilities used for  
25 their prevention during opening, cleaning and charging of these apparatus.

The invention is illustrated by the following examples.

#### Example 1

A vinyl chloride stream of 39 kg/h having an average  
30 water content of 29.5 ppm is pumped through a tube (length 200 mm, diameter 80 mm) filled with a wire mesh having a mesh spacing of 125  $\mu$ m and charged with 740 g of

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silica gel (commercial "Blaugel", fine-pored, particle size from 1 to 3 mm); the pressure at the inlet of the tube is 16 bar. After a running time of 21 hours, the silica gel has adsorbed 15.45 g of water, corresponding to a loading of 2.1% by weight. The water content in the vinyl chloride flowing out is 7.1 ppm.

For desorption, low-pressure steam is passed through the apparatus. After 180 minutes, the residual loading of the silica gel is < 0.3%.

#### 10 Example 2

In a pilot plant, a vinyl chloride stream of 39 kg/h is conveyed through a cylindrical container for 19 hours. Dimensions and charging otherwise correspond to the container described in Example 1. After a running time of 19 hours, the loading of the silica gel is 3.07% by weight. The water content of the dried vinyl chloride is 6.5 ppm.

For regeneration, the container is heated to about 120°C (internal temperature), with a stream of nitrogen of 100 l/h being passed through the apparatus. After 3 hours, the loading of the silica gel is 0.25%.

#### Example 3

In a pilot plant, a vinyl chloride stream of 34 kg/h having an average water content of 30 ppm is pumped at a pressure of about 16 bar through a tube (length 200 mm, diameter 80 mm) filled with molecular sieve (WESSALITH US 330, Degussa, Hanau). After a running time of 88 hours, the molecular sieve has adsorbed 738 g of water which corresponds to a loading of 31.9% by weight, based on the adsorbent. After desorption for 23 hours at 250°C, the residual loading is about 13% by weight.

Example 4

A substream of the top stream from the third distillation stage comprising 0.37 kg of vinyl chloride having a hydrogen chloride content of about 4 g (1,000 ppm) and a water content of about 6 mg (16 ppm) is drawn off in gaseous form and conveyed through a drying apparatus. The drying apparatus comprises a tube having a length of 200 mm and a diameter of 15 mm. It is filled with 35 g of silica gel (commercial "Blaugel", fine-pored, particle size from 1 to 3 mm). After 100 l of the specified gas stream had been conveyed through this dryer, the loading of the desiccant was 12.8% by weight. The gas flowing out had an average water content of 0.5 ppm.

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Claims

1. A process for isolating vinyl chloride, which comprises distilling off the hydrogen chloride from the reaction mixture formed in the incomplete thermal cracking of 1,2-dichloroethane at superatmospheric pressure and temperatures of from about 450 to about 650°C in the absence of catalysts in a first distillation stage and distilling off the vinyl chloride in a second distillation stage, with the vinyl chloride drawn off at the top of the second distillation stage and liquefied being partially recirculated as runback into the second distillation stage and the remaining liquefied vinyl chloride drawn off being fed to the top of a degassing zone from which a part of the vinyl chloride together with the entire entrained hydrogen chloride and water is evaporated and, after substantial removal of the water, recirculated into the first distillation stage, while clean vinyl chloride is taken off from the bottom of the degassing zone.
2. The process as claimed in claim 1, wherein the removal of the water is carried out with the aid of a desiccant.
3. The process as claimed in claim 2, wherein the desiccant used adsorbs the water.
4. The process as claimed in claim 3, wherein the desiccant used is a molecular sieve or silica gel.
5. A device for preparing vinyl chloride having a cracking zone (1), a first distillation stage (2) for separating off hydrogen chloride, a second distillation stage (3) for distilling off vinyl chloride from higher-boiling constituents and a third distillation stage (4) for separating off hydrogen chloride and water from the vinyl chloride, which comprises a device (5) (drying zone) via which

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5 the hydrogen chloride and water separated off in the third distillation stage (4) are recirculated together with vinyl chloride to the first distillation stage (2) and in which the water is substantially removed.

6. The device as claimed in claim 5, which comprises a dryer charged with an agent which physically adsorbs water.

10 7. The device as claimed in claim 5 or 6, which comprises dryers connected in parallel.

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## PROCESS AND DEVICE FOR CLEANING VINYL CHLORIDE

### Abstract

In the preparation of vinyl chloride by thermal cracking of 1,2-dichloroethane, three distillation stages are used to distill off first hydrogen chloride, then vinyl chloride and finally entrained hydrogen chloride with vinyl chloride. If, in the last stage, entrained water is not drawn off via the bottom, it is recirculated with the top product to the first stage and causes corrosion. Removal of the water at the top of the third distillation stage, advantageously by drying, prevents the corrosion.

Figure 1

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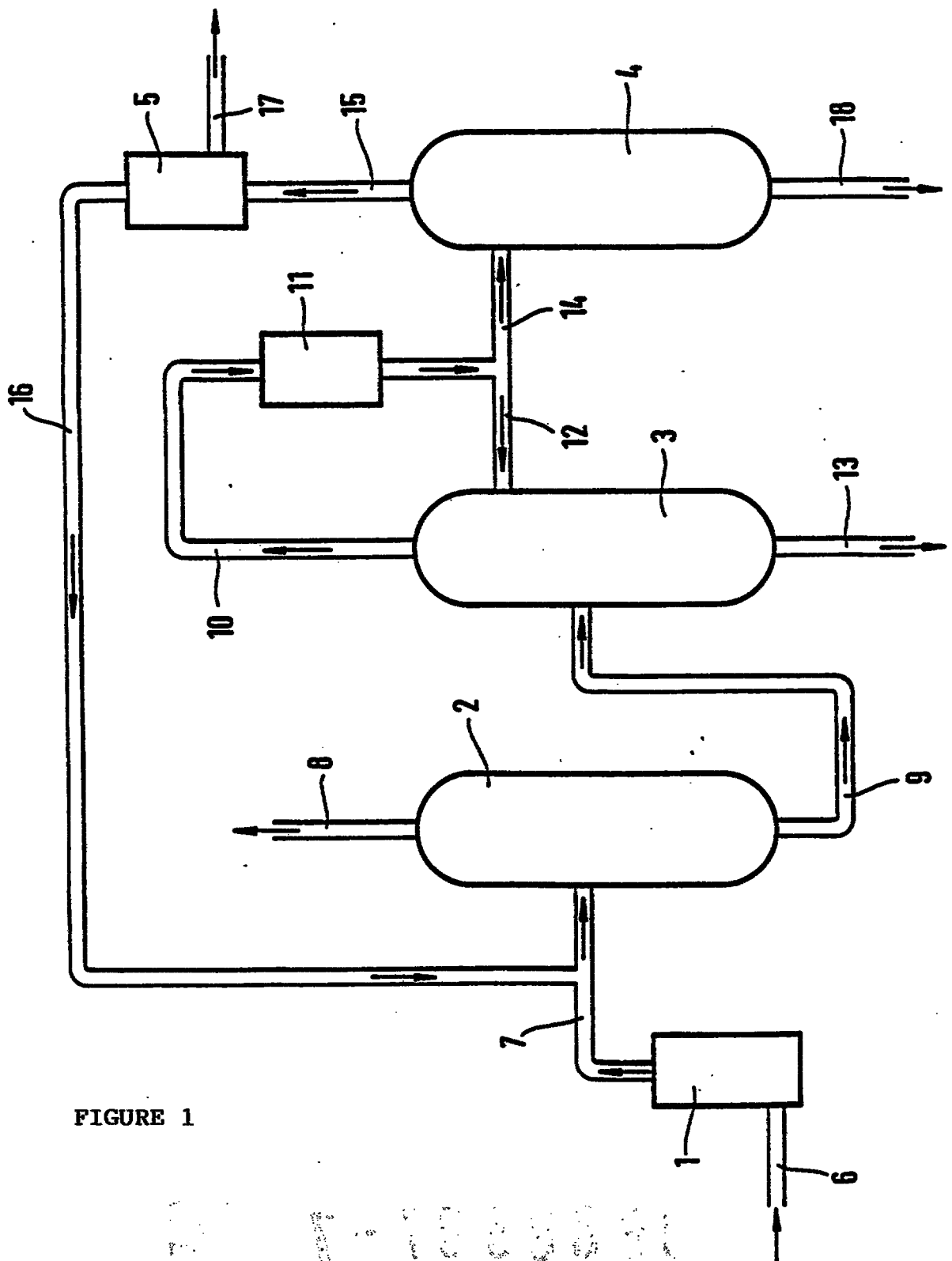


FIGURE 1

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