

AS ORIGINALLY FILED**Purification of dimethylacetamide (DMAc)**

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5 Description

The invention relates to a process for distillatively purifying crude dimethylacetamide. For dimethylacetamide, the abbreviated term DMAc will be used hereinbelow.

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DMAc is used predominantly as a solvent, for example as a solvent for the solution spinning of elastic polyurethane block copolymers which are known by the brand names Spandex® or Lycra®, and also for the production of hollow fibers.

15 In order to be able to obtain high-quality fibers in solution spinning, the following specification requirements are made on the DMAc used here: water content < 100 ppm, pH between 6.5 and 7 and specific electrical conductivity < 0.6 $\mu\text{S}/\text{cm}$, or else < than 0.2 $\mu\text{S}/\text{cm}$. The electrical conductivity of the pure DMAc is brought about substantially by its content of impurities such as acids, especially acetic acid, and salts, especially the amine salts of acetic acid. The specifications of pure DMAc specified in relation to pH and electrical conductivity correspond to a content of acetic acid of less than 50 ppm by weight.

25 DMAc which fulfills these specification requirements is referred to hereinbelow as pure DMAc.

30 In contrast, crude DMAc refers to a mixture comprising DMAc which does not fulfill the above-defined specification requirements. Crude DMAc comprises, as main components in addition to DMAc, amines, acetic acid and water. The total content of acids, predominantly acetic acid, and additionally also traces of formic acid and of higher carboxylic acids, in crude DMAc to be purified in accordance with the invention is not greater than 20% by weight based on DMAc.

35 In the present context, aqueous crude DMAc refers to crude DMAc having a water content between 1 and 99% by weight, or else between 2 and 99% by weight, also between 80 and 98% by weight, especially between 95 and 98% by weight,

or else between 1 and 6% by weight.

Existing plants for distillatively purifying DMAc are operated under reduced pressure, in order to effectively suppress decomposition reactions of the DMAc
5 and thus to ensure compliance with the specification requirements.

However, it has been found that the specification requirements frequently cannot be fulfilled in distillation plants which have been operated under reduced pressure as hitherto customary.

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FR-C 1,406,279 describes a process for preparing DMAc by reacting acetic acid with dimethylamine and distillatively separating the reaction mixture in a two-column arrangement, the first column being operated at atmospheric pressure or slightly elevated pressure, a bottom temperature between 165 and 170°C, a top
15 temperature between 95 and 105°C and a temperature between 100 and 200°C in the region of the column feed which is disposed in about the middle of the column. From the first column, a top stream comprising dimethylamine and water is drawn off and a gaseous or liquid bottom stream comprising DMAc, acetic acid and monomethylacetamide. This bottom stream is fed to a second column, in about
20 the middle region thereof, and separated into a top stream comprising purified DMAc and a bottom stream comprising the ternary azeotrope of acetic acid, DMAc and monomethylacetamide.

On the design and on the operating conditions for the second column, it is stated
25 merely that the column is of a classical type and the operating conditions are classical. It can be taken from the examples that the second column is operated at a pressure of 400 mm Hg and a top temperature of 143°C, and that the purified DMAc still contains about 225 ppm of acetic acid and just as much water, and thus does not fulfill the high specification requirements as defined for pure DMAc
30 for the purposes of the present invention.

A specific problem which frequently occurs in practice is the excessively high content of amines in pure DMAc obtained by distillation.

35 The amines present in the present process are predominantly the volatile dimethylamine which has a boiling point of approx. 7°C at 1 bar absolute, and in

addition in particular monomethylamine.

In order to be able to comply with the specification requirement stated above for the pH in the range between 6.5 and 7, the amine concentration in the pure DMAc must not exceed a value of about 5 ppm by weight. Amines in higher concentration would have to be neutralized by adding acids. However, the electrical conductivity would increase impermissibly with the rise in the acid content.

10 In order to solve the problem of impermissibly high amine concentrations in pure DMAc obtained by distillation, the German patent application DE 103 15 214.8 which had not been published at the priority date of the present application therefore proposed a mode of operation at an increased pressure relative to customary processes, specifically a pressure in the region of standard pressure.

15 However, this mode of operation is thermodynamically unfavorable for the distillative separation of substance mixtures having predominantly van der Waals forces and without formation of hydrogen bonds, since the partition coefficient of the lower-boiling components becomes smaller and the complexity of separation thus larger with the increase in the pressure. This effect is particularly marked in the case of the substance mixture to be separated in the present context.

25 It is therefore an object of the present invention to provide a process for distillatively obtaining pure DMAc which ensures compliance with the required specifications, especially for the solution spinning to produce elastic polyurethane block copolymer fibers and for producing hollow fibers, and which does not have the disadvantages of existing processes.

30 In addition, the process should ensure the removal of the water from the crude DMAc in a degree of purity, especially with a residual content of DMAc of below 50 ppm, which allows the reuse or the problem-free disposal thereof as wastewater.

35 The achievement of the object starts from a process for distillatively purifying aqueous crude dimethylacetamide (crude DMAc) comprising DMAc, low boilers and high boilers, the low boilers and the high boilers being removed to obtain pure

DMAc in a column or in a plurality of columns connected in series.

The invention comprises drawing off the pure DMAc as a liquid sidestream from the one column or from the last of the plurality of columns connected in series.

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It has been found that, surprisingly, it is possible to deplete the amine concentration in the pure DMAc to below about 5 ppm by weight by a distillative route and thus comply with the required specifications for pure DMAc. This result is surprising, since, in the practical performance of distillative separation processes, it is generally difficult to deplete components to residual contents below 10 ppm, especially since zones having poor mixing, particularly in edge regions of packings, cannot be completely prevented in the practical performance of distillations. In addition, very complex reactions take place under the process conditions of the distillation in the substance mixtures which are used in the present separating process, some of which lead to the new formation of amines.

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In view of this, it has been found that, unexpectedly, the desired low amine concentration in the pure DMAc product of value can be achieved when it is withdrawn from the distillation as a liquid side draw.

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As usual, side draw means that at least one further theoretical plate is present in the column above the draw point.

In the present context, low boilers refer to substances whose boiling point is below the boiling point of DMAc (166°C at atmospheric pressure), and high boilers to substances whose boiling point is above the boiling point of DMAc.

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In the present process, low boilers are in particular water, and in addition dimethylamine and diethylamine.

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High boilers are in particular the azeotrope of DMAc with acetic acid, and in addition ethanolamines, and also what are known as heavy ends, i.e. high molecular weight decomposition products in the form of highly viscous liquids or solids.

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A column in stripping mode refers to a column which has separating internals only

below the feed of the mixture to be separated in the column. In contrast, a column in rectifying mode has separating internals only above the feed of the mixture to be separated in the column.

- 5 As is well known, a dividing wall column refers to a column having a dividing wall arranged in the longitudinal direction of the column and prevents mixing of liquid and vapor streams in subregions of the column. The dividing wall divides the column interior into a feed region, a withdrawal region, an upper combined column region and a lower combined column region.

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In the present separating task, low boilers and high boilers have to be removed from the crude DMAc starting mixture and the pure DMAc product of value has to be drawn off as a medium boiler.

- 15 For this separation task, those skilled in the art will select the most favorable column configuration in the individual case taking into account economic considerations, especially the composition of the crude DMAc feedstream and the required specification for the pure DMAc, current energy costs, etc.

- 20 For economic reasons, especially capital and energy costs, it is frequently particularly advantageous to select a dividing wall column for the performance of the process according to the invention.

- 25 The fundamental construction of a dividing wall column with a dividing wall which is arranged vertically in the longitudinal direction of the column and prevents mixing of liquid and vapor streams in subregions of the column has been specified above.

- 30 The dividing wall may be configured in a manner known to those skilled in the art; it is particularly advantageous for it to have a loose, especially inserted, design.

- 35 The separating internals which are the most favorable in the individual case are determined by those skilled in the art in accordance with customary process technology considerations. For reasons of construction technology, especially structured or unstructured packings are to be preferred for the dividing wall column; trays are less suitable.

The determination of the number, optimal in the individual case, of separating stages in the region of the dividing wall will be undertaken by those skilled in the art according to general process technology considerations and they will take into account here especially that, depending upon the predefined specification for the product of value, the low boiler concentration at the lower end of the dividing wall does not exceed a predefined value and, correspondingly, the high boiler concentration at the upper end of the dividing wall does not exceed a predefined value.

In addition, it is possible to use column configurations composed of a plurality of columns connected in series for the present separation task, especially a column configuration composed of a main column and a side draw column, in which the pure DMAc is removed from the side draw column. This column configuration is particularly advantageous for the distillative purification of crude DMAc having a relatively high water content.

Depending on the composition of the crude DMAc stream, the purity requirements on the pure DMAc and on economic considerations, it may be advantageous in the column configuration having main column and side draw column to draw off the sidestream from the main column in liquid form and to operate the side draw column in stripping mode.

In the column configuration having main column and side draw column, those skilled in the art will determine the separating internals which are best suited in the individual case according to customary process technology considerations, and use in particular trays, random packings or structured packings.

Suitable internals are customary internals such as commercially available trays, random packings or structured packings, for example bubble-cap trays, tunnel-cap trays, valve trays, sieve trays, dual-flow trays and grid trays, Pall Rings®, Berl® saddles, wire mesh rings, Raschig Rings®, Intalox® random packings and Intos®, but also structured packings, for example Sulzer Mellapak®, Sulzer Optiflow®, Kühni Rombopak® and Montz-Pak®, and also fabric packings. Preference is given to high-performance structured packings.

The above-described structured packings may equally be used in the column configuration having dividing wall columns.

5 The diameter of the columns with regard to height and positioning of feeds and outlets may be determined by the known concept of theoretical plates in conjunction with the internals selected.

10 In a well known manner, one theoretical plate refers to that column unit which brings about an enrichment of the less volatile component in accordance with the thermodynamic equilibrium, assuming an ideal mixture, that liquid and gaseous phase are in equilibrium and that there is no entrainment of liquid drops (cf. Vauck, Müller: Grundoperationen chemischer Verfahrenstechnik, VCH-Verlagsgesellschaft mbH, Weinheim, 1988).

15 The number of theoretical plates for the region above the feed of the crude DMAc stream to be purified, i.e. for the upper region of the main column or for the region above the dividing sheet in the dividing wall column is laid down according to customary process technology considerations as a function of low boiler content in the crude DMAc and the permissible loss of DMAc via the top of the first column.

20 The number of theoretical plates in the stripping section of the main column or of the dividing wall column below the dividing sheet is preferably laid down within the range from 5 to 30, in particular within the range from 10 to 25, more preferably within the range from 12 to 18.

25 The main column or the dividing wall column are preferably each equipped with a bottom evaporator and a condenser at the top of the column.

30 Advantageously, the temperature at the top of the main column or of the dividing wall column is controlled within a range from 40 to 130°C, preferably within a range from 50 to 80°C, more preferably within a range from 50 to 70°C, and the temperature in the bottom of the main column or of the dividing wall column in each case within a range from 90 to 200°C, preferably within a range from 110 to 170°C, more preferably within a range from 120 to 140°C.

35 Irrespective of the column configuration selected in the individual case it may be

advantageous to operate the column from which the pure DMAc is drawn off, i.e. especially the dividing wall column and the side draw column connected downstream of the main column, at a top pressure < than 1 bar absolute, preferably at a top pressure in the range from 0.1 to 0.7 bar absolute, more
5 preferably at a top pressure in the range from 0.2 to 0.4 bar absolute. The mode of operation at atmospheric pressure or below atmospheric pressure leads in particular to advantageously smaller column dimensions.

10 In addition to acetic acid, the high boiler effluent also comprises the DMAc product of value, since acetic acid and DMAc form a high boiler azeotrope. It is therefore impossible to fully thermally separate acetic acid and DMAc by distillation. Typically, acetic acid is therefore initially neutralized with alkali and the remaining mixture is concentrated by evaporation. The vapors, substantially the DMAc, are recycled into the distillation and the remaining residue is disposed of. The
15 neutralization and the subsequent concentration by evaporation may be either continuous or batchwise.

Advantageously, the distillative purification is operated continuously.

20 The process according to the invention thus provides, in a surprisingly simple manner, pure DMAc which fulfills the required specifications with regard to water content, electrical conductivity and in particular pH.

25 The invention is illustrated in detail hereinbelow with reference to a drawing and to a working example.

The individual figures show:

30 Figure 1 a process scheme with dividing wall column and

Figure 2 a process scheme with main column and side draw column.

35 Figure 1 shows a dividing wall column DWC with dividing wall DW which is arranged in the longitudinal direction of the column and divides the column interior into a feed region A, a withdrawal region B, an upper combined column region C and a lower combined column region D.

The feedstream 1, crude DMAc, is fed to the feed region A of the dividing wall column DWC. From the lower combined column region D, a bottom stream 2 is drawn off, from the upper combined column region C a top stream 3 and from the withdrawal region B a sidestream 4 comprising pure DMAc.

Figure 2 shows a process scheme for a column configuration having main column MC and a side draw column SC. The streams are designated in the same manner as in figure 1, i.e. the feed stream comprising crude DMAc as stream 1, the bottom stream, in the present embodiment from the main column MC, as stream 2, the top stream, in the present embodiment from the main column MC, as stream 3, and the stream comprising pure DMAc which is withdrawn in the present embodiment as the top stream from the side draw column SC as stream 4.

Working example

A dividing wall column DWC as shown schematically in figure 1, having theoretical plates, having a dividing wall DW which extended between the 18th and the 38th theoretical plate, counting the plates from bottom to top in the column, was fed with a crude DMAc stream 1 having the following composition:

DMAc 99.1% by weight, dimethylamine 30 ppm, dimethylformamide 0.2% by weight, water 0.3% by weight, acetic acid 1000 ppm, formic acid 350 ppm, phosphoric acid 50 ppm and heavy ends 0.2% by weight.

The top pressure in the dividing wall column DWC was approx. 250 mbar.

At the same height as the crude DMAc stream 1, i.e. likewise from the 30th theoretical plate, a liquid sidestream was drawn off from the withdrawal region B of the dividing wall column DWC at a temperature of 125.5°C and had the following composition:

DMAc 99.9% by weight, dimethylformamide 720 ppm, acetic acid 30 ppm, water 80 ppm and dimethylamine < 5 ppm. The composition corresponded to the specification requirements for use in fiber production.

What is claimed is:

1. A process for distillatively purifying aqueous crude dimethylacetamide (crude DMAc) comprising DMAc, low boilers and high boilers, the low
5 boilers and the high boilers being removed to obtain pure DMAc in a column or in a plurality of columns connected in series, which comprises drawing off the pure DMAc as a liquid sidestream (4) from the one column or from the last of the plurality of columns.
- 10 2. The process according to claim 1, wherein the one column is a dividing wall column (DWC), with a dividing wall (DW) arranged in the longitudinal direction of the column which divides the column interior into a feed region (A), a withdrawal region (B), an upper combined column region (C) and a lower combined column region (D), and the pure DMAc is drawn off from
15 the withdrawal region (B) of the dividing wall column (DWC).
3. The process according to claim 1, wherein the plurality of columns are a main column (MC) and a side draw column (SC) and the pure DMAc is removed from the side draw column (SC).
- 20 4. The process according to any of claims 1 to 3, wherein the column from which the pure DMAc is drawn off is operated at a top pressure of less than 1 bar absolute, preferably at a top pressure in the range from 0.1 to 0.7 bar absolute, particularly at a top pressure in the range from 0.2 to
25 0.4 bar absolute.
5. The process according to claim 2 or 4, wherein the feedpoint for the crude DMAc and the withdrawal point for the pure DMAc are positioned at the same height in the dividing wall column.
- 30 6. The process according to any of claims 1 to 5, which is operated continuously.
7. The process according to any of claims 2 to 6, wherein the stripping
35 section of the main column (MC) or of the dividing wall column (DWC) has from 5 to 30, preferably from 10 to 25, more preferably from 12 to 18,

theoretical plates.

- 5 8. The process according to any of claims 2 to 7, wherein the dividing wall column (DWC) or the main column (MC) each have a bottom evaporator and a condenser at the top of the column.
- 10 9. The process according to any of claims 2 to 8, wherein the temperature at the top of the dividing wall column (DWC) or of the main column (MC) is set within a range from 40 to 130°C, preferably within a range from 50 to 80°C, more preferably within a range from 50 to 70°C, and the temperature in the bottom of the dividing wall column (DWC) or of the main column (MC) in each case within a range from 90 to 200°C, preferably within a range from 110 to 170°C, more preferably within a range from 120 to 140°C.
- 15 10. The process according to any of claims 3 to 9, wherein the main column (MC) has a gaseous side draw and the side draw column (SC) is operated in rectifying mode.