

# **Method for purification of meta-phenylenediamine**

## **BACKGROUND OF THE INVENTION**

Meta-phenylenediamine is a chemical intermediate widely used in the synthesis of various engineering polymers, aramid fibers, and thermoplastics, and in the production of dyes for textiles, leather and other materials. Other uses for meta-phenylenediamine include as a medical intermediate and a curing agent in epoxy coatings and polyurethane areas. As a consequence of its manifold applications, the production of meta-phenylenediamine has been continuously increased.

Various methods based on distillation or extraction or a combination thereof have been disclosed for the separation of the mixture of phenylenediamine to obtain an individual isomer with high purity in the prior art. British Patent 966,812, for example, describe the separation of the ortho-phenylenediamine from meta-phenylenediamine by distillation in the presence of a boric acid, a boronic acid or an ester or anhydride of such acids. A distillation may be carried out at a pressure higher than atmospheric or under a reduced pressure depending on different applications. A distillation under reduced pressure is normally used when the components to be separated tend to carry out reactions or decompose at a high temperature.

U.S. Patent 3,203,994 discloses that meta-phenylenediamine, when heated above its melting point, decomposes to a certain extent, resulting in a loss of about 5% by weight of the product. In addition, the presence of volatile organic impurities influences the decomposition of meta-phenylenediamine. It is therefore a novel process proposed for the separation of meta-phenylenediamine from volatile organic impurities utilizing a combination of extraction and distillation, which process comprises extracting meta-phenylenediamine at 60-80°C with a non-polar solvent having a boiling point between the melting and the boiling point of meta-phenylenediamine, separating the solvent layer from the meta-phenylenediamine, and vacuum distilling the meta-phenylenediamine layer to obtain an improved thermally stable product with a recovery of 85-95% by weight of m-phenylenediamine. However, the patent does not describe further processes for the separation of meta-phenylenediamine from the ortho and para isomers.

U.S. Patent 3,428,531 may be mentioned as one example of the separation of meta-phenylenediamine from the ortho and para isomers using a distillation process. Contrary to the

teaching of the prior art, it discloses that phenylenediamine does not decompose at a high temperature employed when the distillation is operated at atmospheric pressure. The method in accordance with U.S. Patent 3,428,531 also describes that the atmospheric distillation prevents the in-leakage of air which is present when commercial vacuum equipment is used. The exclusion of air from the column lessens the decomposition of the phenylenediamine into tar and produces a product of greater stability.

U.S. Patent 3,428,531 describes a feed comprising large proportions of meta-phenylenediamine and small proportions of isomers and tars is introduced to a de-tarring distillation column. While phenylenediamine distilled out as the overhead product of the de-tarring column is introduced to the inlet of the isomer removal distillation column, the bottoms product containing a small amount of phenylenediamine and the rest tars are drawn off at the bottom of the de-tarring column. A stream enriched in ortho-phenylenediamine and para-phenylenediamine is removed as the overhead product of the isomer removal distillation column, whereas the bottoms product stream of the isomer removal column is fed to the finishing column, which stream is substantially free of said ortho-phenylenediamine and para-phenylenediamine and which stream contains a small amount of tars formed during this distillation stage. The meta-phenylenediamine with high purity is obtained as the overhead product of the finishing column, and the tars are removed from the bottom of the finishing column. The de-tarring column may run at a pressure slightly lower than atmospheric at the top of the column. However, the isomer removal column and finishing column are operated at a pressure of 5-15 mmHg greater than atmospheric at the top of each column. Such an arrangement of the three columns is in general referred to as a conventional column sequence.

As described in the U.S. Patent 3,428,531, the operating pressure at the bottom of each column may vary from 100 to 500 mmHg above atmospheric. The reboiler temperature may vary from 285 to 320° C depending on the column and its pressure drop, which temperatures are close to the normal boiling points of commercially used heat transfer fluids. Working at this high temperature, heat transfer fluids, for example heating oils are likely to make oxidation, form solids and result in fouling in the heating system including reboilers, which has a negative impact on the heat transfer efficiency and distillation separation. In order to achieve a more practical, reliable and stable heating system and therefore accomplish a good separation, the separation of a mixture of isomeric phenylenediamine in plants is normally carried out under vacuum by using the above-mentioned conventional column sequence with three distillation columns.

While such a three-column distillation method allows to obtain purified meta-phenylenediamine, one disadvantage of the method is its elevated energy requirement. In conventional distillation columns, the feed stream is conventionally fractionated into two product streams: an overhead

product and a bottoms product. Any further separations which are required may, for example be performed by subjecting either the bottoms product stream or the overhead product stream to another distillation stage similar to the first. The operating costs of such a multi-stage distillation process are correspondingly high. In the case of three-column distillation for separation of meta-phenylenediamine from ortho and para isomers, each of the three columns has to be supplied with the thermal energy required to perform the evaporation of the liquid phase and the separation of phenylenediamine.

In addition, the investment costs for the three-column distillation system are high. This is not only due to the fact that investment has to be made for three distillation columns, but expenses are also necessary for the equipment associated therewith, for example condensers, drums, reboilers and pumps.

Furthermore, it has been recognized that although the starting mixture of isomeric phenylenediamine is subjected to a distillation in a de-tarring column prior to the isomer removal column, the bottoms product of the isomer removal column still contains a certain amount of higher-boiling compositions, for example tars, which are formed by the exposure to elevated temperatures at the presence of in-leakage air over three distillation stages. The formation of tars results in a loss of about 1-2% of the product for the three-column distillation system.

## **SUMMARY OF THE INVENTION**

The object underlying the present invention is to provide a method for the distillation of a mixture of isomeric phenylenediamines which includes meta-phenylenediamine, ortho-phenylenediamine and para-phenylenediamine, in which meta-phenylenediamine is obtained with high purity of at least 99.7% by weight. The intention of the proposed distillation method is to save equipment investment costs and energy input and lessen the formation of tars than the conventional column sequence of three-column distillation.

These and other objects are accomplished by providing a method for the separation of meta-phenylenediamine from the ortho-phenylenediamine and para-phenylenediamine by means of distillation, wherein the distillation may be performed in one stage, i.e. a main distillation stage or in two stages, i.e. a secondary distillation stage prior to a main distillation stage. In any case a divided wall column is used in the main distillation stage.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a diagram in accordance with a first embodiment of the process of the present invention utilizing a single stage of a main distillation stage with a divided wall column.

FIG. 2 is a diagram in accordance with a second embodiment of the process of the present invention utilizing two stages in which a conventional distillation column is used in the secondary distillation stage and a divided-wall column is used in the main distillation stage.

## **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION**

With regard to the conventional column sequence, the liquid fraction enriched in phenylenediamine is drawn off from the overhead of the de-tarring column and then fed into the isomer removal column and finally the bottoms product of the isomer removal column is distilled to obtain meta-phenylenediamine with high purity in the finishing column. In order to minimize the amount of tars formed in these distillation stages, it is therefore proposed to use a distillation system with fewer distillation stages to reduce the exposure to the elevated temperatures and in-leakage air. The fewer distillation stages mean that the residence time of phenylenediamine is greatly reduced, reducing the formation of tars and therefore increasing the quantity of target product, i.e. meta-phenylenediamine.

In accordance with the present invention, the three conventional distillation columns, i.e. de-tarring, isomer removal and finishing columns, are replaced by a single distillation column, i.e. a divided wall column. The expenditure on plant and equipment and the space required for the installation of the distillation are significantly decreased. Moreover it is observed that utilizing of the divided wall column in replace of the three conventional distillation stages has advantages that not only the energy consumption is significantly reduced in comparison to the methods known in the prior art, but that product of meta-phenylenediamine with at least the same purity is obtained, meaning the separation efficiency of the proposed process is comparable with the above-mentioned three-column distillation method.

In accordance with the usual definition of the term "divided wall column", the divided wall column preferably comprises:

a divided wall provided vertically inside the column shell, defining a divided wall section between an upper undivided section as a rectifying zone for concentrating lower-boiling components of having a lower boiling point than meta-phenylenediamine and a lower undivided section as a stripping zone for concentrating higher-boiling components of having a higher boiling point than meta-phenylenediamine;

a divided wall section located between the rectifying zone and the stripping zone having a vertical dividing wall dividing the inner space of the divided wall section into a pre-fractionation zone at one side of the divided wall and a main fractionation zone at the other side of the divided wall;

an inlet for the feed of the mixture of isomeric phenylenediamine in the pre-fractionation zone, a side draw outlet for the purified meta-phenylenediamine in the main fractionation zone, an overhead product stream drawn off from the rectification zone, and a bottoms product stream removed from the stripping zone.

The mixture of isomeric phenylenediamine applied as starting material can be separated using the method in accordance with the present invention. In the starting material, the proportions of meta-phenylenediamine are preferably from 65 to 95% by weight, and more preferably from 75 to 90% by weight, the total proportions of ortho-phenylenediamine and para-phenylenediamine are preferably from 5 to 25% by weight and more preferably 10 to 20% by weight, respectively.

The starting mixture may further contain: water and other lower-boiling components, for example aniline, with a total content of less than 2% by weight; 0 to 15% by weight of higher-boiling components, for example tars which have been carried over from previous processes. The starting mixture of isomeric phenylenediamine is fed into the inlet of the pre-fractionation zone of the divided-wall column.

The distillation in the divided wall column is preferably carried out in reduced pressure. The pressure and temperature at the top of the divided wall column are preferably in the ranges of 20 to 555 mbar and of 150 to 240°C, and more preferably of 35 to 200 mbar and of 160 to 205°C. The pressure and temperature at the bottom of the divided wall column are preferably in the

ranges of 50 to 600 mbar and of 180 to 265°C, more preferably of 70 to 400 mbar and of 190 to 250°C.

The present invention is not particularly limited with regard to the type of mass transfer elements installed in the divided wall column. Good results are obtained by using suitable mass transfer elements selected from the group consisting of trays, random packings, structured packings and any combinations thereof. It is however, structured packings are particularly suitable as mass transfer elements with the advantages of reducing the column pressure drops and liquid hold-up in the column. It is preferred that the structured packings have a specific surface area in the range of 125 to 750 m<sup>2</sup>/m<sup>3</sup>, and more preferably of in the range of 250 to 500 m<sup>2</sup>/m<sup>3</sup>.

The length of the divided wall in the divided wall section depends on the process conditions and on the mass transfer elements used. In the column of the present invention, the length of the divided wall is approximately 3/5 of the total length of the mass transfer elements portion installed in the divided wall column. It is preferred that the total mass transfer elements portion of the divided wall column has a length between 10,000 and 50,000 mm, and more preferably between 15,000 and 40,000 mm. Under the same process conditions to achieve a high purity meta-phenylenediamine product of 99.9% by weight, the optimum length of the mass transfer elements portion depends particularly on the type of mass transfer elements selected, for example when a structured packing having a specific surface area of 404 m<sup>2</sup>/m<sup>3</sup> is used, the total length of mass transfer elements portion of the divided wall column is approximately 32,000 mm.

In the column of the present invention, the divided wall section is partitioned by the divided wall into a pre-fractionation zone and a main fractionation zone, which each has a different volume, i.e. a different cross-sectional area for each zone. Different processes may be optimized by appropriate selection of the partial cross-sections of the two zones. In a preferred embodiment, the divided wall divides the divided wall section in such a manner that the area of the cross-section of the divided wall section within the divided wall column comprises about 43% of the pre-fractionation zone and about 57% of the main fractionation zone. In another preferred embodiment, the divided wall divides the divided wall section into a pre-fractionation zone and a main fractionation zone, with the cross-sectional area of the divided wall section comprising about 38% of the pre-fractionation zone and about 62% of the main fractionation zone.

Vapor flow from the stripping zone is divided in the pre-fractionation zone and the main fractionation zone in accordance with the cross-sectional area of each zone. The partial cross-sectional areas are set in such a manner that the pressures at the inlet and outlet regions of the pre-fractionation zone are respectively identical with those at the inlet and outlet regions of the

main fractionation zone, which means the total pressure drop of the packings within the pre-fractionation zone are the same as that for the packings within the main fractionation zone.

In accordance with the present invention, the column is equipped with at least one reboiler and at least one condenser. The reboiler can be of any of the types commonly found in the chemical industry, including, but not limited to, falling-film evaporators, forced circulation evaporators, thermosiphon evaporators and etc. However, due to its particular reduced liquid hold-up, a falling film evaporator is preferred to minimize the residence time of the phenylenediamine stream at the bottom of the divided wall column and therefore reduce any unfavorable side-reactions. The condenser can be of any of the types commonly used in the chemical industry including co-current and counter-current condensers.

In certain specific cases, in which cases the overhead product containing a major portion of mixture of ortho and para isomers from the divided-wall column are required to further separations into high purity ortho-phenylenediamine and para-phenylenediamine, the divided wall column may be followed by additional distillation stages, which may include two stages with conventional distillation columns or a single stage with another divided wall column.

FIG. 1 schematically shows the main distillation stage of a divided wall column according to an embodiment of the present invention, which comprises a column shell 1, a condenser 4, a condensate drum 7, a circulation pump 12, a falling film reboiler 14, a substantially fluid tight divided wall 17 extending vertically through the middle part of the column shell 1. The inner space of the column shell 1 is divided by the divided wall 17 into four distinct zones, i.e. a pre-fractionation zone 18 at one side of the divided wall, a rectifying zone 19 above the divided wall 17, a main fractionation zone 20 at the other side of the divided wall 17, and a stripping zone 21 below the divided wall 17, in which column the pre-fractionation zone 18 and the main fractionation zone 20 form the divided wall section. The vapors generated at the bottom of the divided wall column flow upwards through the stripping zone 21 and divide into the pre-fractionation zone 18 and the main fractionation zone 20, counter-currently contacting the liquids flowing downwards from rectifying zone 19, effective for a mass transfer. A multi-component feed stream is then separated via the mass transfer within the four operating zones into three product streams, i.e. an overhead product stream 9, a bottoms product stream 16 and a side-draw product stream 10.

A mixture of isomeric phenylenediamine stream is continuously fed through stream 2 into the pre-fractionation zone 18. The lower-boiling components of having a lower boiling point than that of meta-phenylenediamine concentrate during the distillation in the rectifying zone 19, and

are drawn off through stream 3, which is subsequently condensed in the condenser 4. The condensates flow to the condensate drum 7 through stream 6 and then divide into an overhead product stream 9 withdrawn from the top of the column and into a recycle stream 8, which is fed back to the rectifying zone 19. The uncondensed vapors are removed through stream 5. The higher-boiling components of having a higher boiling point than that of meta-phenylenediamine, are concentrated in the stripping zone 21 and drawn off as a bottom stream 11. The bottom stream 11 is subsequently divided into a bottoms product stream 16, which is withdrawn from the bottom of the column, and a recycle stream 13, which is reboiled in the falling film reboiler 14 and then fed back to the stripping zone 21 through stream 15. A side-draw product of purified meta-phenylenediamine with a purity of at least 99.7% by weight is withdrawn through stream 10 from the main fractionation zone 20.

Alternatively, the distillation process according to the invention may also be performed in two stages comprising a main distillation stage and a secondary distillation stage, wherein the higher-boiling components such as tars in the starting mixture of isomeric phenylenediamine stream are removed from the bottom of the secondary distillation stage and the overhead product substantially free of tars from the secondary distillation stage is fed to the main distillation stage of the divided wall column. One advantage of the two distillation stages is to prevent the structured packings in the divided wall column from blockage by tars, especially when the starting mixture of isomeric phenylenediamine stream contains more than 8% by weight of tars. On the other hand, from the viewpoint of energy consumption such an arrangement of the two distillation stages may result in more energy input than that by using one distillation stage, i.e. the main distillation stage with a divided wall column.

FIG. 2 schematically shows a method for purifying meta-phenylenediamine in accordance with a second embodiment of the present invention. In contrast to the aforementioned first embodiment, this method in accordance with the second embodiment of the present invention comprises a main distillation stage 24, which is a divided wall column as shown and described in FIG. 1, and a secondary distillation stage 26, which is placed upstream of the main distillation stage 24. The secondary distillation stage 26 uses a conventional distillation column without partition, which comprises a column shell 27, a condenser 29, a condensate drum 32, a circulation pump 36, a falling film reboiler 38.

A starting mixture of isomeric phenylenediamine stream is continuously introduced through stream 2 to the inlet of the secondary distillation stage 26. The overhead vapors substantially free of tars are drawn off through stream 28, which is subsequently condensed in the condenser 29. The condensates flow to the condensate drum 32 through stream 31 and then divide into an overhead product stream 34 which is fed to the main distillation stage 24, and into a recycle

stream 33, which is fed back to the top of the column as the reflux. The uncondensed vapors are removed through stream 30. The higher-boiling components of having a higher boiling point than that of meta-phenylenediamine, are drawn off as a bottom stream 35. The bottom stream 35 is subsequently divided into a bottoms product stream 40 comprising large proportions of tars, which is withdrawn from the bottom of the column, and a recycle stream 37, which is reboiled in the falling film reboiler 38 and then fed back to the bottom of the column through stream 39.

In the two-stage process, the main distillation stage with the divided-wall column is performed under similar process conditions to those used in the above-mentioned single-stage process. The secondary distillation stage with the conventional distillation column is preferably carried out under vacuum. The pressure and temperature at the top of the conventional distillation column are preferably in the ranges of 20 to 555 mbar and of 155 to 240°C, and more preferably of 30 to 200 mbar and of 160 to 205°C. The pressure and temperature at the bottom of the conventional distillation column are preferably in the ranges of 35 to 570 mbar and of 180 to 270°C, more preferably of 45 to 230 mbar and of 185 to 235°C.

In accordance with the present invention, the use of a divided-wall column to obtain high purity meta-phenylenediamine from a mixture of isomeric phenylenediamine makes it possible to save one or two distillation stages in comparison with the above-mentioned three-column distillation system. It has advantages that not only the energy consumption and equipment expenditure are significantly reduced, but also the residence time of phenylenediamine stream is less, resulting in a smaller proportion of tars formed due to the exposure to the elevated temperatures.

Subsequently, the present invention is illustrated in more details below with reference to the drawings and the Examples.

## EXAMPLES

The following examples are based on computer simulations (SIMSCI PRO II) using in-house VLE data.

### Example 1a

A main distillation stage with a divided wall column according to an embodiment of the invention as shown in FIG. 1 was performed. Structured packings with a specific surface area of  $404 \text{ m}^2/\text{m}^3$  were used as mass exchange elements in the divided wall column. 26% by weight of the liquid was introduced to the pre-fractionating zone 18 and 74 % by weight of the liquid to the main fractionating zone 20. The rectifying zone 19 had 30 theoretical stages and the stripping zone 21 had 8 theoretical stages. The pre-fractionation zone 18 had 45 theoretical stages above and 18 theoretical stages below the feeding point for the feed stream 2 into the pre-fractionation zone. The main fractionation zone 20 had 45 theoretical stages above and 18 theoretical stages below the withdrawal point of the side-draw stream 10 in the main fractionating zone. The overhead pressure was 50 mbar. The reflux ratio at the withdrawal point of the overhead product stream was 17:1, while the reflux ratio at the withdrawal point of the side-draw product stream was 3.3:1. The pressure and temperature at the bottom of the divided wall column were 82 mbar and 198 °C, respectively.

1919 kg/h of a feed stream 2 composed of 0.46% by weight of water, 1.93% by weight of tars, 0.11% by weight of aniline, 12.88% by weight of ortho-phenylenediamine, 78.98% by weight of meta-phenylenediamine and 5.63% by weight of para-phenylenediamine were fed to the divided wall column, at the 46th stage from the top in the pre-fractionation zone 18. Three product streams were withdrawn from the divided wall column: 376 kg/h of an overhead product stream 9 composed of 0.35% by weight of water, 0.47% by weight of aniline, 65.64% by weight of ortho-phenylenediamine, 4.84% by weight of meta-phenylenediamine and 28.70% by weight of para-phenylenediamine; 200 kg/h of a bottoms product stream 16 composed of 18.56% by weight of tars and 81.44% by weight of meta-phenylenediamine; and 1334 kg/h of a side-draw product stream 10 composed of 99.91% by weight of meta-phenylenediamine, 0.02% by weight of ortho-phenylenediamine and 0.07% by weight of para-phenylenediamine, which stream was withdrawn at the 45th separation stage from the top in the main fractionating zone 20.

### Example 1b to 1c

According to the same manner as that described in Example 1a except for the top pressure setting to 35 mbar (Example 1b) or 190 mbar (Example 1c), a distillation was performed, respectively. 1919 kg/h of a feed stream 2 composed of 0.46% by weight of water, 1.93% by weight of tars, 0.11% by weight of aniline, 12.88% by weight of ortho-phenylenediamine, 78.98% by weight of meta-phenylenediamine and 5.63% by weight of para-phenylenediamine were fed to the divided wall column, at the 46th stage from the top in the pre-fractionating zone 18. Three product streams with substantially the same compositions as those obtained in Example 1a were withdrawn from the divided wall column. The pressure and temperature at the bottom of the divided wall column were 67 mbar and 192°C in Example 1b, while the pressure and temperature at the bottom of the divided wall column were 222 mbar and 230°C in Example 1c.

### Example 2

A main distillation stage with a divided wall column coupled with a secondary distillation stage with a conventional distillation were performed as shown in FIG. 2. Structured packings with a specific surface area of 404 m<sup>2</sup>/m<sup>3</sup> were used as mass exchange elements for the divided wall column. 24% by weight of the liquid was introduced to the pre-fractionating zone 18 and 76% by weight of the liquid to the main fractionating zone 20. The rectifying zone 19 had 30 theoretical stages and the stripping zone 21 had 8 theoretical stages. The pre-fractionation zone 18 had 45 theoretical stages above and 18 theoretical stages below the feeding point for the feed stream 2 into the pre-fractionation zone. The main fractionation zone 20 had 45 theoretical stages above and 18 theoretical stages below the withdrawal point of the side-draw stream 10 in the main fractionating zone. The overhead pressure was 50 mbar. The reflux ratio at the withdrawal point of the overhead product stream was 22:1, while the reflux ratio at the withdrawal point of the side-draw product stream was 2.9:1. The pressure and temperature at the bottom of the divided wall column were 82 mbar and 202°C, respectively.

1932 kg/h of a feed stream 2 composed of 0.45% by weight of water, 9.57% by weight of tars, 0.11% by weight of aniline, 11.15% by weight of ortho-phenylenediamine, 76.11% by weight of meta-phenylenediamine and 2.61% by weight of para-phenylenediamine were fed to the secondary distillation stage with a conventional distillation column in a purpose of removing tars before it was introduced to the divided wall column. 1624 kg/h of the overhead product stream 34 from the secondary distillation stage composed of 0.11 % by weight of water, 0.12% by weight of aniline, 12.80% by weight of ortho- phenylenediamine, 84.01% by weight of meta-phenylenediamine and 2.96% by weight of para-phenylenediamine were fed to the divided wall column, at the 46th stage from the top in the pre-fractionating zone 18. Three product streams were withdrawn from the divided wall column: 263 kg/h of an overhead product stream 9 composed of 0.15% by weight of water, 0.64% by weight of aniline, 78.46% by weight of ortho-phenylenediamine, 2.58% by weight of meta-phenylenediamine and 18.17% by weight of para-phenylenediamine; 90 kg/h of a bottoms product stream 16 composed of a major proportion of meta-phenylenediamine and a small amount of tars which was formed during this distillation; and 1265 kg/h of a side-draw product stream 10 composed of 99.93% by weight of meta-phenylenediamine, 0.01% by weight of ortho-phenylenediamine and 0.06% by weight of para-phenylenediamine, which stream was withdrawn at the 45th separation stage from the top in the main fractionating zone 20.

### Example 3a

A main distillation stage with a divided wall column according to an embodiment of the invention as shown in FIG. 1 was performed. Structured packings with a specific surface area of  $350 \text{ m}^2/\text{m}^3$  were used as mass exchange elements in the divided wall column. 23% by weight of the liquid was introduced to the pre-fractionating zone 18 and 77 % by weight of the liquid to the main fractionating zone 20. The rectifying zone 19 had 12 theoretical stages and the stripping zone 21 had 16 theoretical stages. The pre-fractionation zone 18 had 36 separation stages above and 10 separation stages below the feeding point for the feed stream 2 into the pre-fractionation zone. The main fractionation zone 20 had 38 theoretical stages above and 8 theoretical stages below the withdrawal point of the side-draw product stream 10 in the main fractionating zone. The overhead pressure was 50 mbar. The reflux ratio at the withdrawal point of the overhead product stream was 21:1, while the reflux ratio at the withdrawal point of the side-draw product stream was 3:1. The pressure and temperature at the bottom of the divided wall column were 72 mbar and  $194^\circ\text{C}$ , respectively.

1936 kg/h of a feed stream 2 composed of 0.45% by weight of water, 1.92% by weight of tars, 0.11% by weight of aniline, 10.96% by weight of ortho-phenylenediamine, 83.33% by weight of meta-phenylenediamine and 3.23% by weight of para-phenylenediamine were fed to the divided wall column, at the 37th stage from the top in the pre-fractionating zone 18. Three product streams were withdrawn from the divided wall column: 306 kg/h of an overhead product stream 9 composed of 0.42% by weight of water, 0.57% by weight of aniline, 69.18% by weight of ortho-phenylenediamine, 9.64% by weight of meta-phenylenediamine and 20.19% by weight of para-phenylenediamine; 200 kg/h of a bottoms product stream 16 composed of 18.56% by weight of tars and 81.44% by weight of meta-phenylenediamine; and 1424 kg/h of a side-draw product stream 10 composed of 99.84% by weight of meta-phenylenediamine, 0.03% by weight of ortho-phenylenediamine and 0.13% by weight of para-phenylenediamine, which stream was withdrawn at the 38th separation stage from the top in the main fractionating zone 20.

### Example 3b

According to the same manner as that described in Example 3a, except for trays (Example 3b) used as the mass exchange elements in place of the structured packings, a distillation was performed. 1936 kg/h of a feed stream 2 composed of 0.45% by weight of water, 1.92% by weight of tars, 0.11% by weight of aniline, 10.96% by weight of ortho-phenylenediamine, 83.33% by weight of meta-phenylenediamine and 3.23% by weight of para-phenylenediamine were fed to the divided wall column, at the 37th stage from the top in the pre-fractionating zone 18. Three product streams with substantially the same compositions as those obtained in Example 3a were withdrawn from the divided wall column. The pressure and temperature at the bottom of the divided wall column were 388 mbar and 247°C in Example 3b, respectively.

The invention claimed is:

1. A continuous method for the separation of a mixture of isomeric phenylenediamine said mixture comprising meta-phenylenediamine, ortho-phenylenediamine and para-phenylenediamine by a main distillation stage or by a secondary distillation stage followed by a main distillation stage, in which method the main distillation stage is performed using a divided wall column, wherein a side-draw product having a purity of at least 99.7% by weight of meta-phenylenediamine is obtained.

2. The method of claim 1, wherein the mixture of isomeric phenylenediamine being distilled comprises 75 to 95% by weight of meta-phenylenediamine, 5 to 25% by weight of a mixture of ortho-phenylenediamine and para-phenylenediamine, 0 to 15% by weight of tars, and 0 to 2% by weight of a mixture of water and aniline.

3. The method of claim 1, wherein the divided wall column comprises:

a divided wall provided vertically inside the column shell, defining a divided wall section between an upper undivided section as a rectifying zone for concentrating lower-boiling components of having a lower boiling point than meta-phenylenediamine and a lower undivided section as a stripping zone for concentrating higher-boiling components of having a higher boiling point than meta-phenylenediamine;

a divided wall section arranged between the rectifying zone and the stripping zone having a vertical dividing wall dividing the inner space of the divided wall section into a pre-fractionation zone at one side of the divided wall and a main fractionation zone at the opposite side of the divided wall;

an inlet for the feed of the mixture of isomeric phenylenediamine in the pre-fractionation zone, a side draw outlet for the purified meta-phenylenediamine in the main fractionation zone, an overhead product drawn off from the rectification zone, and a bottoms product from the stripping zone.

4. The method of claim 1, wherein the main distillation stage does not include any other distillation column in addition to the divided wall column.
5. The method of claim 1, wherein the distillation is performed in two distillation stage, i.e. a secondary distillation stage with a de-tarring distillation column prior to the main distillation stage with a divided wall column, wherein the distillation in the secondary distillation stage is performed so that higher-boiling components include tars are removed from the phenylenediamine before it is fed to the main distillation stage.
6. The method of claim 5, wherein overhead product from the secondary distillation stage is introduced into the main distillation stage.
7. The method of claim 1, wherein the overhead product from the main distillation stage is subjected to further distillation to obtain high purity ortho-phenylenediamine and para-phenylenediamine, respectively.
8. The method of claim 1, wherein a pressure and a temperature at the top of the divided wall column are in the ranges of 20 to 555 mbar and 150 to 240°C, respectively.
9. The method of claim 1, wherein a pressure and a temperature at the bottom of the divided wall column are in the ranges of 50 to 600 mbar and of 180 to 265°C, respectively.
10. The method of claim 1, wherein the mass transfer elements are selected from the group consisting of trays, random packings, structured packings and any combinations thereof.

## ABSTRACT

The present invention relates to a method for the separation of meta-phenylenediamine from the ortho-phenylenediamine and para-phenylenediamine by means of distillation, wherein the distillation may be performed in one stage, i.e. a main distillation stage or in two stages, i.e. a secondary distillation stage prior to a main distillation stage. In any case, a divided wall column is used in the main distillation stage.

FIG. 1

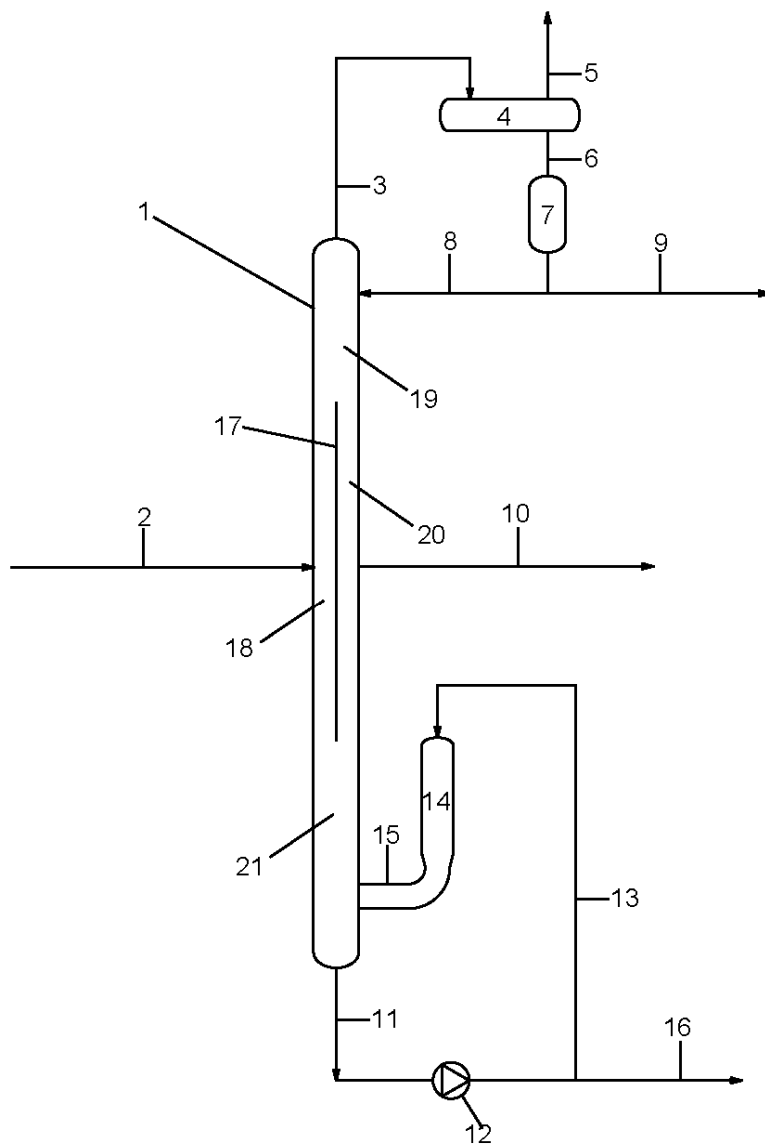


FIG.1

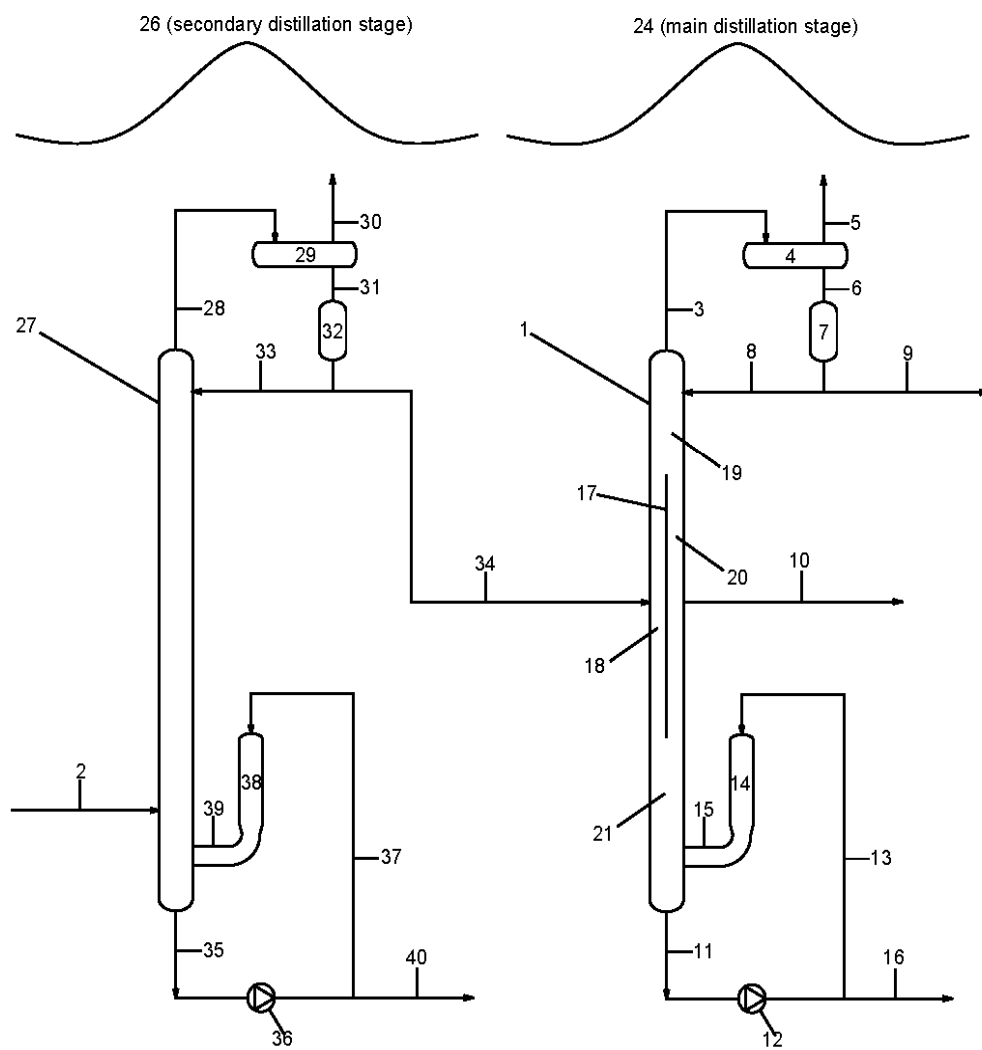


FIG.2