

thereof, optionally a part of the distillate from (X) can bypass the washing stages and be led to (Y) and employed to regulate a varying water content in the individual extraction stages.

The virtually quantitative recirculation of the acid used renders possible the use of costly acids such as, for example, methanesulphonic acid, which in turn, owing to its low tendency to corrode, permits the use of economical materials in the apparatus of the process according to the invention.

It has proved useful to define the acid content of the aqueous phase, independent of the varying amine content arising in the aqueous phase of a two-phase system, by means of a so-called "molarity". The molarity is defined as the theoretical concentration of 100% protonated amine (that is, an equal number of acid and amine equivalents) in a volume of aqueous phase theoretically diminished by the proportion of non-protonated amine, according to the formula

$$\text{"molarity"} = \frac{\text{mol of 100\% protonated amine}}{\text{vol. aqu. phase} - \text{vol. unprotonated amine}}$$

The molarity defined in this way can assume values of up to 6 and is purposively varied within this range according to the—here product-related—problem of separation underlying the respective embodiment.

Within an embodiment of the process according to the invention it may also optionally be advantageous to operate the individual processing stages through which the aqueous phase is passed, in particular the extraction stages (2) to (6), with a varying molarity in the aqueous phase, by withdrawing or adding water to the aqueous phase between the individual stages.

This operating range is in practice restricted towards the upper end on the one hand by the increasing tendency of the amine salts to crystallize with increasing concentration, in particular at high degrees of protonation, and on the other hand by the increasing mutual solubility of the phases with one another, in particular at low degrees of protonation.

The degree of protonation expresses the ratio of acid equivalents to amine equivalents.

This range is restricted towards the lower end for economic reasons, owing to the decreasing acid content and therewith the quantitative decline in separation efficiency, that is, for an excellent qualitative separation efficiency which is free from technical problems, with decreasing molarity an increasingly large volume of aqueous phase is necessary for the separation of a given quantity of amine.

In one variant of the process according to the invention, the feed of the starting polyamine mixture (A) from the storage tank (1) takes place by mixing with the flow (B), formed from the stream (E) from the first distillation stage (7.1), consisting of hydrophobic solvent and optionally auxiliary amine, and optionally a partial stream from (S).

In general the content of arylamine, consisting of starting polyamine and auxiliary amine, present in stream (B) after addition of (A) is from 10 to 80 wt. %, preferably from 15 to 60 wt. %.

The content of starting polyamine in stream (B) after addition of (A) is generally from 5 to 60 wt. %, preferably from 10 to 40 wt. %.

In the extractor (3), the stream (B) charged with (A) is passed through counter to the aqueous phase (C).

In general the stream (C) consists of water, a strong protonic acid, auxiliary amine and optionally polyamine. The acid is present in the form of its water-soluble salt together with auxiliary amine and optionally polyamine. The sum of the amine groups of the auxiliary amine and option-

ally polyamine is invariably present in (C) in stoichiometric proportion or in excess, referred to the acid.

The degree of protonation in (C) is generally from 40 to 100%; for aniline, which is preferably used as auxiliary amine, it is preferably from 60 to 100%.

The molarity of the stream (C), which is clearly defined and is measured and controlled within narrow limits for the respective embodiment of the process according to the invention, is purposively varied within a wide range according to the—here product-related—problem of separation underlying the respective embodiment.

In general the aqueous phase (C) passed to the extraction stage (3) of the process according to the invention has a molarity of between 0.5 and 4.5. Within the extraction stage (3), which is preferably operated in multiple stages, the stream (B) charged with (A) and the aqueous phase (C) are passed counter to one another with intimate mixing.

During this process a transition of polyarylamine from the organic phase (B) into the aqueous phase takes place as a rule, optionally in exchange for auxiliary amine in the opposite direction.

In the aqueous phase (H) leaving the extraction stage (3) the acid is present as an aqueous solution of its ammonium salts together with polyamine and optionally auxiliary amine, which solution as a rule contains dissolved free polyamine, that is, not bound in the form of a salt, and optionally free auxiliary amine, that is, not bound in the form of a salt.

The starting polyamine (A) introduced together with the organic phase (B) into the extractor (3) is distributed between the aqueous phase (H) leaving the extractor and the organic phase (D) leaving the extractor (3) (quantitative fractionation).

The quantitative distribution of the individual components of the starting polyamine mixture between the resulting aqueous phase (H) and the resulting organic phase (D) takes place with a surprisingly high selectivity under the conditions of the process according to the invention, so that the resulting product fractions are of another composition, greatly differing from that of the starting polyamine mixture (qualitative fractionation).

For example, starting from the preferably used products of aniline formaldehyde condensation, it was found that from a polyamine component present in two or more isomeric forms in the starting mixture, as a rule the ortho-isomeric form(s) is (are) relatively enriched in the organic phase (D) leaving the separator stage (3); for example, 2,4'-diaminodiphenylmethane relative to 4,4'-diaminodiphenylmethane. Conversely, the resulting aqueous phase (H) is relatively depleted of the 2,4'-isomer, whereas the 4,4'-isomer is relatively enriched.

If several "ortho-isomers" are present in the starting polyamine, for example, 2,2'- and 2,4'-diaminodiphenylmethane, then the "ortho-richer" 2,2'-isomer is more highly enriched in the organic phase (D) as compared with the "ortho-poorer" 2,4'-isomer, which latter is for its part relatively enriched as compared with the "even ortho-poorer" 4,4'-isomer.

The enrichment and depletion effect first found in the compounds of the diaminodiphenylmethane series obtained as products of aniline/formaldehyde condensation was associated purely empirically and descriptively with the measure of ortho- and para-substitution. The characterization, derived therefrom, of products of a process as "ortho-rich" or "ortho-poor" is relative and was expressed by the term "degree of ortho-substitution".

In this connection "degree of ortho-substitution" is defined as the proportion of ortho amino group-methylene