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Separation by rectification of unsaturated carboxylic acids from solvents

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The present invention relates to a process for the separation by rectification of unsaturated carboxylic acids from solvents in which the acids were absorbed after the synthesis reaction.

15 Unsaturated carboxylic acids of the acrylic acid or methacrylic acid type are at present prepared industrially primarily by heterogeneously catalyzed gas-phase oxidation of the corresponding alkenes, alkanes or the unsaturated aldehydes. Various processes used at present differ primarily in the way the oxidation is conducted and in the process technology for
20 separating off the secondary components unavoidably formed in the process (DE-A 19 62 431, DE-A 29 43 707). In the synthesis, the individual processes differ in whether the reaction gas is circulated and in the type of inert gas added. In the work-up, the difference lies primarily in whether the desired product which comes from the reactors as a hot gas
25 is absorbed in a low-boiling or high-boiling solvent. All these processes have in common that at the end the desired product has to be separated by distillation from the absorbing solvent. This separation is generally carried out by distillation or rectification.

To avoid polymerization during the distillation or rectification,
30 stabilizers such as phenothiazine (PTZ), hydroquinone methyl ether (MeHQ) or hydroquinone (HQ) are used. Nevertheless, polymer formation occurs in the rectification column after a relatively long period of operation and these force regular shutdown and laborious cleaning of the

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plant. This cleaning can be carried out mechanically or by thermal oxidation in a known manner. However, this is very time consuming.

It is an object of the present invention to provide a process by means of which the polymers can be removed in a simple and reliable manner and without requiring a great deal of time.

We have found that this object is achieved by the rectification being interrupted and the rectification column being flushed with a basic solution. The basic solution used is advantageously an aqueous solution of alkali metal and/or alkaline earth metal hydroxide, preferably NaOH, KOH, Ca(OH)_2 or their anhydrous oxides. The compounds dissolved in water here have a concentration of from 0.01 to 30 % by weight, preferably from 0.5 to 10 % by weight. According to an advantageous embodiment of the invention, an essentially neutral alkali metal or alkaline earth metal salt is added to the basic solution in a ratio of from $>0:1$ to 2:1 (weight ratio of neutral salt to hydroxide). Particularly suitable for this purpose are the sulfates, acetates, oxalates, carbonates, hydrogensulfates, hydrogencarbonates or other salts corresponding to the basic compounds. Such an addition enables the solvent behavior of the basic solution to be further improved.

According to a further embodiment of the present invention, alkaline polar organic solvents such as amines or amides, preferably acetamides, particularly preferably monoacetamide (CH_3CONH_2), can be used as solvents in place of alkaline aqueous solutions. Further solvents which can be used for this purpose are monomethylacetamide ($\text{CH}_3\text{CON}(\text{CH}_3)\text{H}$), dimethylacetamide ($\text{CH}_3\text{CON}(\text{CH}_3)_2$) and dimethylformamide ($\text{HCON}(\text{CH}_3)_2$).

The temperatures at which the flushing according to the present invention is carried out are determined by the boiling point of the solvents used, since the solvent action of all the abovementioned solvents increases with rising temperature. The optimum temperature for the



aqueous systems of the alkali metal and alkaline earth metal hydroxides is from $> 80^{\circ}\text{C}$ to about 115°C at atmospheric pressure, preferably from 90°C to 110°C . For the amides described, the optimum use temperature is in each case from 10 to 1°C below the boiling point of the respective substance.

The process of the present invention can be carried out either at regular time intervals or after a certain degree of deposit formation is determined. In each case, a shorter period of interruption of the distillation process is required and, in particular, a considerably simpler and more complete removal of the polymer deposits is achieved.

Further details and advantages of the invention may be found in the experimental examples described below.

Of course, the process of the present invention can be used quite generally in the separation by rectification of unsaturated carboxylic acids, for example also in the pure distillation of crude methacrylic acid to give pure methacrylic acid. It is found to be particularly advantageous to use the process of the present invention preventively, ie. at intervals, before visible deposit formation has occurred. In this way, deposit formation is in fact stopped right at the beginning.

The laboratory experiments gave the following results.

Experiment 1 (reference experiment, according to the prior art)

A Diphyl/acrylic acid mixture was distilled in a glass column (internal diameter 8 cm, 40 bubble cap trays). This mixture was taken from a production plant operating according to a process as described in DE 21 36 396.

The runback was stabilized with phenothiazine. After 238 hours, the column displayed backing up of liquid due to polymer formation. The column was shut down and first flushed with hot water for six hours. Result: the polymer was not removed and had to be removed subsequently by mechanical means. The total cleaning time was a full working day.



Experiment 2 (flushing with alkali according to the present invention)

The procedure was as for Experiment 1, backing up occurred after 212 hours. Flushing with a 5 % strength by weight aqueous NaOH solution at 92°C completely dissolved the polymer after 6 hours of
5 flushing.

Experiment 3 (flushing with alkali/sulfate according to the present invention)

The procedure was as for Experiment 2, backing up occurred after 254 hours. Flushing with an aqueous solution containing 5 % by
10 weight of NaOH and 5 % by weight of Na₂SO₄ at 92°C gave complete removal of the polymer after a flushing time of only 5 hours.

Experiment 4 (flushing with amide according to the present invention)

The procedure was as for Experiment 2, backing up occurred after 205 hours. Flushing with monomethylacetamide at 190°C gave
15 complete removal of the polymer after a flushing time of 6 hours.

Production experiments

The knowledge gained in the laboratory was then used in an industrial plant. The experiments were carried out in an acrylic acid plant operating according to a process as described in DE 21 36 396. This
20 process can be briefly described as follows:

- * heterogeneously catalyzed gas-phase oxidation of propylene and/or acrolein to give acrylic acid
- * separation of the acrylic acid and a part of the secondary components from the reaction gas by countercurrent absorption using a
25 high-boiling solvent
- * separation of a first fraction of low-boiling and middle-boiling components by countercurrent desorption
- * separation by distillation of the acrylic acid and the low-boiling and
30 middle-boiling secondary components from the high-boiling solvent.

The solvent is recirculated to the absorption column.

The pure column arranged at the end of this work-up has a side
offtake for the purified raw acrylic acid. To prevent occurrence of
backing up due to polymer formation and achieve an overall very long
5 operation time, the column was shut down for a short time after a run-
ning time of from 10 to 70 days, preferably from 20 to 50 days, for the
purposes of cleaning according to the process of the present invention.
This ensured very long, reliable operation of the column. The time at
which the column was shut down was determined as a function of
10 throughput and further parameters.

Flushing according to the present invention using a 10 %
strength by weight aqueous NaOH solution at 92°C could be concluded
in 8 hours.

Flushing using a 10 % strength by weight aqueous NaOH so-
15 lution to which 5 % by weight of sodium sulfate (based on the NaOH
solution) had been added and carried out at 92°C could be completed
even more quickly, requiring only 7 hours of flushing time. Comparative
flushing using monomethylacetamide as solvent likewise required a flushing
time of 7 hours at 92°C.

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5 We claim:

1. A process for the separation by rectification of unsaturated carboxylic acids from Solvents in which the acids were absorbed after the synthesis reaction, which comprises interrupting the rectification and flushing the rectification column with a basic solution.
- 10 2. A process as claimed in claim 1, wherein the interruption is carried out at regular time intervals.
3. A process as claimed in claim 1 or 2, wherein the basic solution used is an aqueous solution of alkali metal and/or alkaline earth metal hydroxide, preferably NaOK, KOH, $\text{Ca}(\text{OH})_2$ or their anhydrous oxides.
- 15 4. A process as claimed in claim 3, wherein the basic compounds dissolved in water have a concentration of from 0.01 to 30 % by weight, preferable from 0.5 to 10 % by weight.
5. A process as claimed in any of the preceding claims, wherein a neutral alkali metal or alkaline earth metal salt is added to the basic solution in a ratio of from >0:1 to 2:1 (weight ratio of the neutral salt to
20 hydroxide).
6. A process as claimed in claim 5, wherein the neutral salts added are the sulfates, acetates, oxalates, carbonates or other neutral salts corresponding to the basic compounds.
- 25 7. A process as claimed in any of the preceding claims, wherein flushing is carried out at from 80°C to 115°C, preferably from 90°C to 110°C, and at atmospheric pressure.
8. A process as claimed in claim 1, wherein the basic solutions used are alkaline polar organic solvents.
- 30 9. A process as claimed in claim 8, wherein organic solvents used are amines or amides, preferably acetamides, in particular monoacetamide.

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