Claims

1. A process for obtaining formic acid by thermal separation of a stream comprising formic acid and a tertiary amine (I) which at a pressure of 1013 hPa abs has a boiling point which is at least 5°C higher than that of formic acid and which has the general formula (Ia)

$$NR^1R^2R^3 \quad (Ia)$$

in which the radicals R^1 to R^3 are selected independently from the group consisting of C_5-C_8-alkyl, in which

(a) a liquid stream comprising formic acid, tertiary amine (I) and water is produced by combining tertiary amine (I) and a formic acid source in the presence of water, where

(i) a formic acid source comprising methyl formate is used and the liquid stream comprising formic acid, tertiary amine (I) and water is obtained therefrom by hydrolysis of methyl formate;
or

(ii) a formic acid source which comprises carbon dioxide is used and the liquid stream comprising formic acid, tertiary amine (I) and water is obtained therefrom by transition metal-catalyzed hydrogenation of carbon dioxide,

and the liquid stream comprising formic acid, tertiary amine (I) and water has a molar ratio of formic acid to tertiary amine (I) of from 0.5 to 5;

(b) water and organic decomposition products of the tertiary amine (I) are separated off from the liquid stream obtained from step (a), with the organic decomposition products of the tertiary amine (I) having been comprised in the tertiary amine (I) fed to step (a) and/or been formed during the course of the process up to the present step (b), and a liquid stream which comprises formic acid and tertiary amine (I) and is depleted in water and organic decomposition products of the tertiary amine (I) is obtained; and

(c) formic acid is removed by distillation from the liquid stream comprising formic acid and tertiary amine (I) obtained from step (b) in a distillation apparatus at a temperature at the bottom of from 100 to 300°C and a pressure of from 30 to 3000 hPa abs;

wherein

(b1) the stream comprising water and organic decomposition products of the tertiary amine (I) which has been separated off in step (b) is separated into two liquid phases;

(b2) the upper liquid phase enriched in organic decomposition products of the tertiary amine (I) is removed; and

(b3) the lower, water-comprising liquid phase is recirculated to step (a).

2. The process according to claim 1, wherein the separation in step (b) is carried out by distillation.

3. The process according to claim 1 or 2, wherein

(i) a formic acid source comprising methyl formate is used and a liquid stream comprising formic acid, tertiary amine (I), water and methanol is obtained therefrom by hydrolysis of methyl formate in step (a); and
(ii) a further stream comprising the methanol formed by dissociation of methyl formate is separated off from the stream obtained from step (a) in step (b).

4. The process according to claim 3, wherein

(i) a further stream comprising unreacted methyl formate is separated off from the stream obtained from step (a) in step (b); and
(ii) the methyl formate which has been separated off is recirculated to step (a).

5. The process according to claim 1 or 2, wherein

(i) a formic acid source which comprises carbon dioxide, hydrogen and a homogeneous catalyst is used in the presence of methanol in step (a) and a liquid stream comprising formic acid, tertiary amine (I), water and methanol is obtained therefrom by homogeneously catalyzed hydrogenation of carbon dioxide; and
(ii) a further stream comprising methanol is separated off from the stream obtained from step (a) in step (b) and the methanol which has been separated off is recirculated to step (a).

6. The process according to any of claims 1 to 5, wherein the tertiary amine (I) to be used in step (a) and the degree of separation in the distillation apparatus

mentioned in step (c) are selected so that two liquid phases are formed in the bottom output from the distillation apparatus mentioned in step (c),

(d) the bottom output from the distillation apparatus mentioned in step (c) is separated into two liquid phases, where the upper liquid phase has a molar ratio of formic acid to tertiary amine (I) of from 0 to 0.5 and the lower liquid phase has a molar ratio of formic acid to tertiary amine (I) of from 0.5 to 4;

(e) the upper liquid phase from the phase separation in step (d) is recirculated to step (a); and

(f) the lower liquid phase from the phase separation in step (d) is recirculated to step (b) and/or (c).

7. The process according to claim 6, wherein in step (e) from 10 to 100% of the upper liquid phase from the phase separation in step (d) is recirculated to step (a).

8. The process according to claim 6, wherein in step (e) from 90 to 100% of the upper liquid phase from the phase separation in step (d) is recirculated to step (a).

9. The process according to any of claims 1 to 8, wherein the liquid stream produced in step (a) has a concentration of formic acid plus tertiary amine (I) of from 1 to 99% by weight, based on the total amount of the stream.

10. The process according to any of claims 1 to 9, wherein the degree of separation in the distillation apparatus mentioned in step (c) is selected so that the molar ratio of formic acid to tertiary amine (I) in the bottom output is from 0.1 to 2.0.

11. The process according to any of claims 1 to 10, wherein tri-n-pentyl amine, tri-n-hexyl amine, tri-n-heptyl amine or tri-n-octyl amine is used as tertiary amine (I).