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(72) Inventeurs/Inventors:
CHUCK, RODERICK JOHN, CH;
ZACHER, UWE, CH

(73) Propriétaire/Owner:
LONZA AG, CH

(74) Agent: G. RONALD BELL & ASSOCIATES

(54) Titre : PROCEDE DE PREPARATION D'ACIDE NICOTINIQUE
(54) Title: PROCESS FOR PREPARING NICOTINIC ACID

(57) Abrégé/Abstract:
Nicotinic acid is produced from aqueous solutions of ammonium nicotinate by spray-drying. The nicotinic acid may be freed from residual ammonium nicotinate by a thermal post-treatment in a fluidized bed or under reduced pressure. The process is suitable, in particular, for working-up the reaction mixture produced in the oxidation of 3-methylpyridine with atmospheric oxygen, with the ammonia and, if appropriate, the water, being able to be recycled. Nicotinic acid ("vitamin PP") is an important additive for foodstuffs and feedstuffs.

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ABSTRACT

Nicotinic acid is produced from aqueous solutions of ammonium nicotinate by spray-drying. The nicotinic acid may be freed from residual ammonium nicotinate by a thermal post-treatment in a fluidized bed or under reduced pressure. The process is suitable, in particular, for working-up the reaction mixture produced in the oxidation of 3-methylpyridine with atmospheric oxygen, with the ammonia and, if appropriate, the water, being able to be recycled. Nicotinic acid ("vitamin PP") is an important additive for foodstuffs and feedstuffs.

PROCESS FOR PREPARING NICOTINIC ACID

The present invention relates to a process for preparing nicotinic acid from solutions of ammonium nicotinate.

A known process for preparing nicotinic acid is based on the oxidation of 3-methylpyridine (-picoline) with atmospheric oxygen in the presence of water with heterogeneous catalysis. However, this process has the disadvantage that, in a side reaction, some of the 3-methylpyridine is broken down in a sequence of oxidation and hydrolysis steps to form ammonia, which, together with the main product nicotinic acid, forms ammonium nicotinate. The latter, in contrast to the free nicotinic acid, is highly water soluble and thus makes the work-up of the product mixture more difficult, furthermore it represents a loss in yield, if it cannot be converted back to nicotinic acid. The latter is possible, for example, by adding a strong acid, but this results in formation of the ammonium salt of this acid, which must be separated off and disposed of as waste. In addition, it should be noted here that nicotinic acid, as a pyridine derivative, can also react as a base and, with an excess of the strong acid, can form a salt.

An object of the present invention is therefore to provide a process which permits the transformation of ammonium nicotinate to nicotinic acid without adding auxiliaries and without producing waste.

According to the invention, it has surprisingly been found that an aqueous solution of ammonium nicotinate can be converted to nicotinic acid by spray-drying. In this process, the ammonia by-product, together with the water, escapes in the exhaust gas of the spray-dryer.

The spray-drying is preferably carried out at a drying gas temperature (at the inlet) of from 160 to 250°C. A suitable drying gas is air or an inert gas such as nitrogen or argon. The outlet temperature is advantageously kept below 110°C, in order to prevent sublimation of the product.

Preferably, the spray-drying is carried out in a fluidized-bed spray-dryer. Fluidized-bed spray-dryers of this type are available under the name FSD™, for example, from Niro A/S of DK-2860 Søborg/Denmark.

The nicotinic acid obtained after the spray-drying still contains small amounts of ammonium nicotinate, depending on the drying temperature. It has been found that this can be further decreased by a thermal post-treatment in a fluidized bed at from 100 to 200°C, preferably from 130 to 170°C. Any nicotinic acid dust produced in this treatment can be recirculated to the spray-dryer.

As an alternative to this post-treatment in the fluidized bed, post-treatment under reduced pressure (partial vacuum or vacuum) at relatively low temperature can also be carried out. The pressure employed in this case is advantageously below 100 mbar, preferably below 50 mbar. The temperature in this case is expediently from 70 to 150°C, preferably from 80 to 120°C. Particularly good results have been achieved at a pressure of from 10 to 15 mbar, a temperature of from 80 to 90°C and a treatment time of from ½ to 1 hour. At this relatively low temperature, the losses due to sublimation are minimal and a product having excellent transparency, that is no discoloration, is obtained.

Preferably, the process according to the invention is carried out using an ammonium nicotinate solution which was obtained by adding ammonia to the, possibly concentrated, aqueous crude solution from the catalytic oxidation of 3-methylpyridine. This can be achieved, for example, by metering gaseous or aqueous ammonia into an absorption column, to which is fed the gaseous reaction mixture from the oxidation reactor and from which the ammonium nicotinate solution is taken off as bottom product and the excess water is taken off overhead.

The ammonia needed to prepare the ammonium nicotinate solution is, in this case, preferably wholly or partly withdrawn from the spray-drying exhaust gas. For this purpose, for example, the dryer exhaust gas can be cooled

below the dew point and the condensing ammonia water can be separated off and recirculated to the nicotinic acid absorption. Since, as mentioned above, small amounts of ammonia are produced in any case as a by-product in the oxidation of 3-methylpyridine, overall an ammonia excess is produced, so that with sufficient efficiency of the ammonia recycling, in a continuous operation, the feeding of external ammonia can be dispensed with completely.

Likewise, the water present in the spray-drying exhaust gas is preferably completely or partially recirculated to the oxidation reactor. Since, in the oxidation of 1 mol of 3-methylpyridine to nicotinic acid, in the ideal case, 1 mol of water is produced, a small excess of water is produced, which must be discharged from the plant in a suitable manner. Similarly, any unreacted 3-methylpyridine present is advantageously recycled to the oxidation reactor. Furthermore, it is possible to feed pure oxygen instead of air as oxidizing agent in the steady state to a continuous plant for carrying out the process according to the invention and to circulate the drying gas, so that a plant with minimum production of exhaust gas results.

Another advantage of the process according to the invention is that the nicotinic acid thus obtained is free-flowing without additional treatment and virtually has no tendency to clumping even at high temperature and relative humidity. Furthermore, by varying the spray-drying operating parameters, the particle size of the product can be adjusted to a desired value.

In the accompanying drawing, Figure 1 is a flow chart showing diagrammatically, as an example, a continuous plant suitable for carrying out the process according to the invention. Individually, the reference numbers denote the following:

1 fixed-bed reactor together with catalyst

2 absorption column for partial condensation of the reaction mixture

3 neutralization (addition of ammonia)

4 spray-dryer
5 drying gas feed (hot air or inert gas circulation)
6 spray-dryer exhaust gas
7 column for partial condensation of water and ammonia
8 gas recycle to the reactor
9 exhaust gas for exhaust gas treatment
10 exhaust gas treatment (combustion)
11 mixer/preheater
12 product take-off (nicotinic acid)
13 3-methylpyridine feed to the reactor
14 oxygen feed (air) to the reactor
15 water (steam) feed to the reactor
16 ammonia feed to the neutralization
17 ammonia (water) recycle.

The following non-limitative Examples illustrate the procedure of the process according to the invention.

Example 1

15 l/h of an aqueous ammonium nicotinate solution (40% by weight nicotinic acid, 6% by weight ammonia) were sprayed into a fluidized-bed spray-dryer (Niro FSD™-4, diameter 1.2 m, height 2.5 m). The drying gas (nitrogen) inlet temperature was 220°C, and the outlet temperature was 100°C. The internal fluidized-bed temperature was 70°C. This produced a free-flowing product comprising 89% by weight nicotinic acid and 11% by weight ammonium nicotinate having a residual moisture content of 0.05%, a bulk density of 0.4 kg/l and a mean particle size of 451 μm.

Example 2

The spray-dried granules of nicotinic acid obtained in accordance with Example 1 were heated to a maximum temperature of 170°C with air over the course of 45 minutes in a fluidized bed. The granules thus treated had a nicotinic acid content of 99.3% and a bulk density of 0.44 kg/l. It was still free-flowing even after

storage for 48 hours at 50°C and 100% relative humidity.

Example 3

From the condensate of the reaction mixture of the gas-phase oxidation of 3-methylpyridine with air in the presence of water on a fixed-bed catalyst, with addition of ammonia, an approximately 30% strength solution of ammonium nicotinate was produced. This solution was sprayed in a laboratory spray-dryer (Büchi AG, Switzerland). At a drying gas inlet temperature of 250°C and an outlet temperature of 162°C, nicotinic acid having a content of from 99% to 100% was obtained at a nitrogen flow rate of 600 ml/minute.

At an inlet temperature of 200°C and an outlet temperature of 130°C, nicotinic acid having a content of 96.9% was obtained at a nitrogen flow rate of 600 ml/minute.

THE EMBODIMENTS OF THE PRESENT INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for preparing nicotinic acid, wherein an aqueous solution of ammonium nicotinate is spray-dried.

2. A process according to Claim 1, wherein the spray-drying is carried out at a drying gas temperature of from 160 to 250°C.

3. A process according to Claim 1 or 2, wherein the spray-drying is carried out in a fluidized-bed spray-dryer.

4. A process according to any one of Claims 1 to 3, wherein the nicotinic acid produced by the spray-drying is subjected to a thermal post-treatment in a fluidized bed at a temperature from 100 to 200°C.

5. A process according to Claim 4, wherein the temperature of the thermal post-treatment is from 130 to 170°C.

6. A process according to any one of Claims 1 to 3, wherein the nicotinic acid produced by the spray-drying is subjected to a thermal post-treatment under reduced pressure at a temperature from 70 to 150°C.

7. A process according to Claim 6, wherein the thermal post-treatment is effected at a pressure below 50 mbar and a temperature from 80 to 120°C.

8. A process according to any one of Claims 1 to 7, wherein the aqueous solution of ammonium nicotinate is a solution produced by adding ammonia to the aqueous crude solution or concentrate thereof obtained in the catalytic oxidation of 3-methyl pyridine in an oxidation reactor.

9. A process according to Claim 8, wherein the ammonia for preparing the ammonium nicotinate solution is wholly or partially withdrawn from the spray-drying exhaust gas.

10. A process according to Claim 8 or 9, wherein the water present in the spray-drying exhaust gas is wholly or partly recycled to the oxidation reactor.

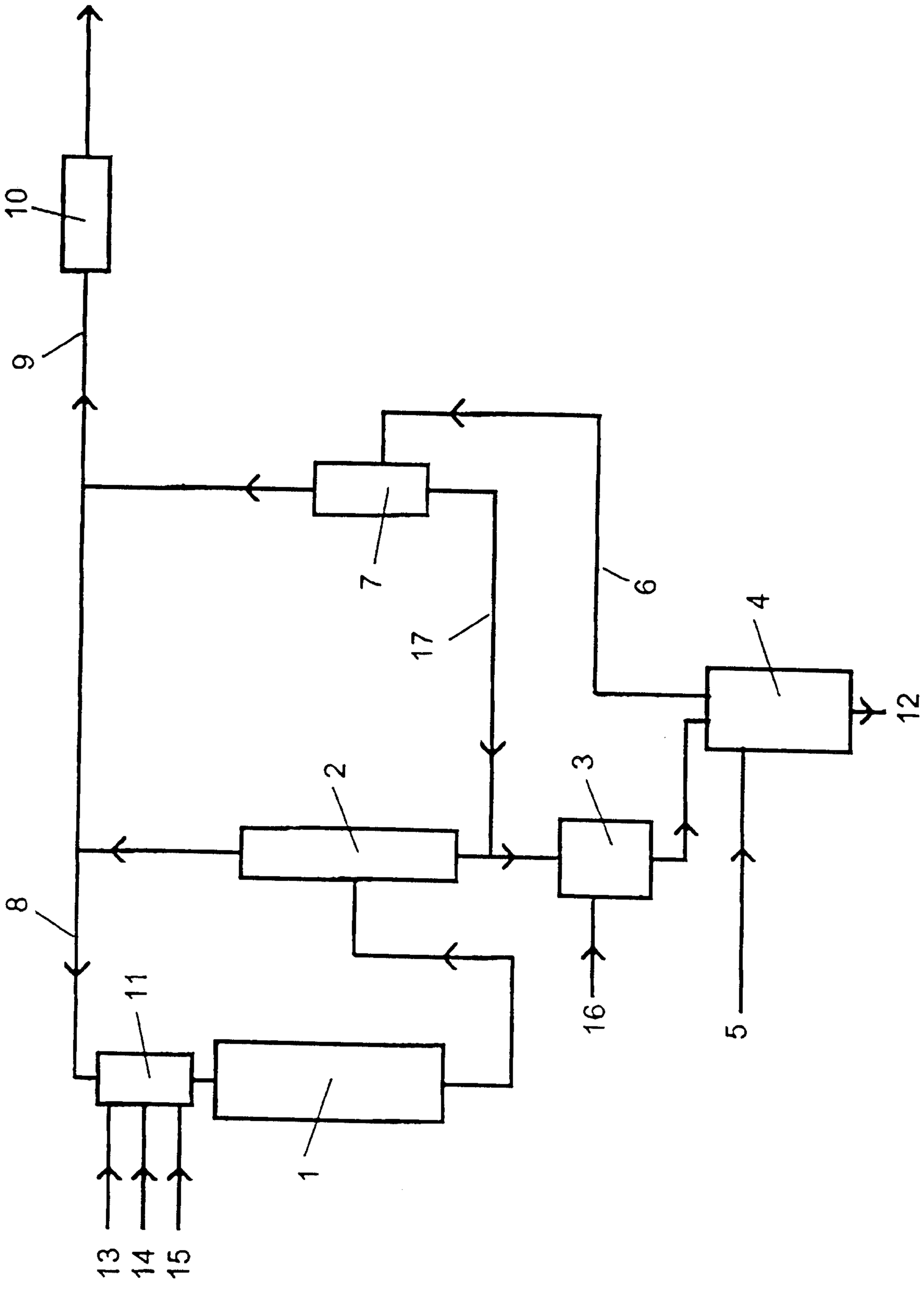

Fig. 1