(45) Date of publication and mention of the grant of the patent:
17.08.2016 Bulletin 2016/33

(21) Application number: 08734894.2

(22) Date of filing: 31.03.2008

(54) PROCESS FOR THE PREPARATION OF NITROCELLULOSE SOLUTIONS HAVING A LOW WATER CONTENT

VERFAHREN ZUR HERSTELLUNG VON NITROCELLULOSE-LÖSUNGEN MIT GERINGEM WASSERANTEIL

PROCÉDÉ DE PRÉPARATION DE SOLUTIONS DE NITROCELLULOSE À FAIBLE TENEUR EN EAU

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU MC MT NL NO PL PT RO SE SI SK TR

(30) Priority: 07.04.2007 DE 102007017014

(43) Date of publication of application: 20.01.2010 Bulletin 2010/03

(73) Proprietor: Dow Global Technologies LLC
Midland, MI 48674 (US)

(72) Inventors:
• DRIESEN, Lutz
  29664 Walsrode (DE)

(74) Representative: f & e patent
Fleischer, Engels & Partner mbB, Patentanwälte
Braunsberger Feld 29
51429 Bergisch Gladbach (DE)

(76) References cited:
DE-A1- 3 041 085
US-A- 4 981 555

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention)
The present invention relates to the preparation of nitrocellulose solutions which are free of alcohol or plasticizer proportions and are distinguished by a particularly low water content.

Nitrocelluloses (also referred to below as "NC") which have a low degree of esterification and a nitrogen content of up to 12.6% by mass and are predominantly used in the coating and printing ink industry are introduced onto the market as moist solids having proportions of liquid densensitizers (ethanol, isopropanol, more rarely butanol or water are preferred) of 30 or 35% by mass (including the residual water in the case of alcohols). If the liquid content of the moist product falls below 25% by mass, these so-called industrial nitrocelluloses are then classified as "explosive substances" owing to the increased potential danger (Recommendations on the Transport of Dangerous Goods, 10th edition, of the United Nations, 1997). The residual water content in the product which is alcohol-moist in view of the intended use is from 2 to not more than 8% by mass, based on the moist product. Water-moist NC to which selected plasticizers have been added as desensitizers is plasticized thereby with elimination of water (virtually no longer any fiber structure) and, after thermal treatment, still contains from 1.5 to not more than 3% by mass of residual water in addition to the proportion of from 18 to 20% by mass of plasticizer. In the coating and printing ink industry, the moist NC types obtained as stated in desensitized form are introduced as solids into the formulation batches and dissolved therein. In special formulations, in particular for printing ink production, apart from the residual water said alcohols or plasticizers, as inevitably introduced with a solid NC correspondingly desensitized in each case, are disadvantageous.

However, in order to avoid such impurities, neither the manufacturer of industrial NC nor the coating and printing ink producer can deliver or use anhydrous and non-desensitized (i.e. dry and pure) NC in solid form for safety and legal reasons (for example, considerable effort with regard to safety according to explosives law) and to process it economically to give, for example, alcohol- and plasticizer-free NC solutions (referred to below as finished NC solution) having a low water content. A method conceivable for this purpose would be to convert preferably water-moist solid NC by means of suitable organic solvents into comparatively dilute water-rich and optionally also emulsion-like solutions (referred to below as "crude NC solution") in order, after addition of a preferably solid water binder (for example a molecular sieve), subsequently to remove the water in an appropriate manner from said crude solution. Even if the NC solution thus treated reaches the desired residual water content, a further considerably complicated procedure for purification and regeneration of the molecular sieve and of concentrating the NC solution having a low water content to give the desired finished NC solution follows for economic reasons. A considerable effort comparable with this procedure must be expected if, for example by combined introduction of designated organic NC solvents and organic NC nonsolvents into said crude NC solution, preferably two liquid phases which can be appropriately easily separated are produced, one of which, as low-NC as possible but correspondingly water-enriched, produces the desired dewatering. From economic necessity, the NC-rich phase is then to be concentrated to said finished solution and the solvent is to be substantially recovered from the aqueous phase.

DE 3041085 proposed special NC mixtures with NC solvents and NC nonsolvents, a process for their preparation and the use thereof as additives in polyurethane finishes. According to the invention, water-moist (25% by mass or more water in the solid moist material) nitrocelluloses are preferably used as starting material and are dissolved or at least gelled to a tacky pasty form (elimination of the fiber structure) in batchwise manner in a number of nominated typical organic NC solvents, but preferably in a multiplicity of individual mixtures each consisting of an NC solvent and an organic NC nonsolvent nominated from a number. The resulting (highly) viscous fluid or gel-like pasty products or products rendered solid again by addition of nonsolvent and optionally already shaped are thermally treated (with further addition of NC solvents and/or NC nonsolvents chiefly as entraining agents) for stripping off water. Depending on the chosen starting conditions and objectives, NC solutions having a low water content (about 1% by mass of water), tacky gel-like NC pastes or, particularly preferably, solid moist nitrocellulose moldings (e.g. pellets) can be produced, the residual fluid content of which in each case (at a level of at least 25% by mass for said required desensitization) consists of mixtures, according to the invention, of NC nonsolvents and NC solvents, which mixtures are compatible with PU finishes, and residual water (about 1% by mass). Dryers in combination with rotary evaporators, wherein the procedures for distillation or evaporation of NC batches introduced batchwise which are water-containing but according to the invention have already been pretreated with organic solvents and organic nonsolvents are carried with a mechanical support by rotating apparatus elements in vacuo, are mentioned as a key requirement for the design of the apparatus, in particular for the thermal process steps according to DE 3041085. For the preparation of NC solutions having a low water content according to DE 3041085, the distillation apparatuses used are expressly those evaporators which are equipped with appropriate scraping or scratching tools and should therefore constantly ensure a desired freeing of the heating surface in the evaporator from the adhering product layer. Although the term "thin-film evaporator" is not used for this in the patent, DE 3041085 imparts the technical teaching that rotary thin-film evaporators of known vertical or horizontal design having wiper elements (= scrapers/scratchers) acting on the heating surface, which in turn are mounted on a central shaft in the apparatus and are moved therewith, are the suitable apparatuses. Gravity-driven trickle or falling-film evaporators and also plate-type evaporators which are customary from the group consisting of the plate-type heat exchangers, all...
of which also operate with thin product layers but without any mechanical internals, are likewise not included. However, during the operation thereof, which of course is decisively determined by the existing viscosities of the fluids to be evaporated down, the heating surfaces wetted by the product in a comparatively thin layer must on no account be exposed (dewetted) (cf. also VDI-Wärmeatlas [VDI Heat Atlas], 7th edition 1994, sheet Md6, point 4 or E.G. WORONZOW, "Die minimale Reynoldszahl bei Rieselfilmen [The minimum Reynolds number in trickle films]", BWK 44 (1994) 5, pages 201-205).

[0005] Particularly obvious disadvantages of the invention which have become known with DE 3041085 are, inter alia, the expensive and complex mechanical complexity of the process in terms of apparatus and the energy consumption of the process in batchwise (discontinuous) dissolution, dilution and evaporation procedures of nitrocellulose in conjunction with organic solvents. In addition to this there are considerably complicated safety requirements in technical dimensions in the case of the thermal-mechanical treatment of nitrocellulose and predominantly flammable solvent (mixtures) and in particular the explosive vapors thereof, in order to prevent the admission of atmospheric oxygen, for example in vacuum operation which is preferred according to the invention but complicated.

[0006] It was therefore an object of the present invention to provide an alternative process for the preparation of alcohol- and plasticizer-free NC solutions having a low water content, according to which a range of NC types desired on the market can be reliably processed to give said finished NC solutions and these can be produced and offered in technically feasible (e.g. handleable viscosities) and economically advantageous concentrations and required qualities.

[0007] It was surprisingly found that the concentration methods known per se, as used in plate-type or falling-film evaporators of known designs, are also advantageously suitable for the thermal evaporation and concentration in particular of dilute and comparatively water-rich and consequently optionally also emulsion-like crude NC solutions to the desired clear but thermally sensitive and viscous finished NC solutions. However, it is particularly preferable to operate the entire evaporation process continuously by distillation as a gravity-driven falling-film evaporation with the solution flowing countercurrent to the expelled vapor and without external forced circulation (single pass, no proportionate recirculation) of the solution, a defined part of the solvent used for producing a dilute crude NC solution from preferably water-moist NC performing the function of an entraining agent for the water to be removed in view of the intended use.

[0008] The present invention therefore relates in the preferred embodiments to the one- to three-stage, but preferably two-stage, use of gravity-driven falling-film evaporators of customary design with vertical tube bundle in the jacket space, in order thereby to be able to produce a finished nitrocellulose solution of a quality which meets requirements in a distillative evaporation process gradated according to the invention from a preheated crude nitrocellulose solution provided, by a technically reliable, particularly economical method using simple apparatus. However, in a more general aspect of the present invention also other evaporators than gravity-driven falling-film evaporators may be used for producing the finished nitrocellulose solution. Alternative evaporators are, for example, helical-tube evaporators; plate-type evaporators; and a climbing-film evaporators.

[0009] In general, the subject matter of the invention is a process for the preparation of nitrocellulose solutions having a low water content by a thermal method, comprising the steps of

a) processing or treating a water-moist nitrocellulose having a proportion of water of 25 to 45% by mass, but preferably from 25 to 35% by mass, in or with a solvent, preferably in a stirring container, to give a crude nitrocellulose solution having a proportion of nitrocellulose of 3.5 to 12.5% by mass, but preferably from 4.5 to 9% by mass, and then

b) subjecting, preferably continuously, the crude nitrocellulose solution to an at least partial distillative evaporation process, and

c) taking off, preferably continuously, a finished nitrocellulose solution formed with a proportion of nitrocellulose of from 20 to 35% by mass, but preferably from 25 to 30% by mass, and a residual proportion of water of up to 1% by mass, but preferably up to 0.5% by mass, from the respective last stage of the evaporation process, characterized in that the distillative evaporation process is performed by an evaporator selected from an at least 1-stage, preferably a 1- to 3-stage, and more preferably a 2-stage, falling-film evaporator; a countercurrent falling-film evaporator; a down-draft evaporator; a helical-tube evaporator; a plate-type evaporator; and a climbing-film evaporator.

[0010] In a particularly preferred embodiment the subject matter of the invention is a process as in principle described above, but pursuant to figure 1, characterized in that

a) water-moist nitrocellulose (1) having a proportion of water of 25-45% by mass, but preferably from 25 to 35% by mass, is processed (5) in a slightly water-miscible or water-immiscible solvent (2, 3) customary for nitrocellulose to give a crude nitrocellulose solution (4) having a proportion of nitrocellulose of 3.5 to 12.5% by mass, but preferably from 4.5 to 9% by mass, after which

b) this crude nitrocellulose solution (4) is subjected continuously to a partial distillative evaporation in a 1- to 3-stage, but preferably 2-stage, falling-film evaporation (6, 7) of a design customary in principle, and
In the following, preferred embodiments of the invention are described. The reference signs given below in parenthesis refer to figure 1. However, they are not intended to limit the invention to the process shown in figure 1 but are merely added to facilitate the understanding of the process of the invention.

Within the category of gravity-driven thin-film evaporators, the preferred falling-film evaporator design is divided into countercurrent falling-film evaporators and down-draft evaporators. In both types, heated vertical tube bundles are used for receiving the liquid phase and discharging the latter in the form of a film. A substantial difference is the removal of the vapor produced, which in the first case flows upward countercurrent to the downward-flowing liquid phase and is obtained separately there. In the down-draft evaporator, liquid phase and vapor produced flow downwards (cocurrent) and must be separated after emerging together.

Designs with flow over the heating surfaces which is usually forced by external pumps and hence independently of gravity are helical-tube evaporators having tube coils connected in parallel or in series and plate-type evaporators having a multiplicity of heating surfaces arranged parallel. The first-mentioned permit the concentration of even highly viscous fluids in comparatively thin layers with vapor taken off in the same direction (cocurrent). Plate-type evaporators can carry the resulting vapor phase concurrent and/or countercurrent to the liquid phase.

A further design which can be used for thin-film evaporation comprises so-called climbing (film) evaporators. Also designed as a vertical tube bundle in a heating jacket, the solution to be concentrated is fed into the bottom of the tubes of these apparatuses and, with the onset of vapor evolution, the vapor stream carries a liquid phase so to speak as thin annular layers along the heating surface in an upward direction (cocurrent) for common discharge with subsequent separation.

The above mentioned "solvent", which is preferably a slightly water-miscible or water-immiscible solvent, in which the water-moist nitrocellulose is processed may be any organic solvent, organic non-solvent or mixtures thereof customary for nitrocellulose known by the skilled person. The organic solvent may be, for example, selected from the group comprising ethyl acetate, propyl acetate, butyl acetate, ethylenglycol monomethyl ether acetate, ethylenglycol monothyl ether acetate, methyl ethyl ketone, methyl isobutyl ketone, isophorone, cyclohexanone, nitroethane, and/or nitropropene.

The mentioned organic non-solvent is preferably used as part of a mixture of solvent and non-solvent and may be, for example, selected from the group comprising hexane, heptane, octane solventnaphtha, cyclohexane, methyl cyclohexane, benzene, toluene, and/or xylene. In case of use of mixtures of the above solvents with the non-solvents the ratio of solvent to non-solvent may be in the range of 9:1 to 1:9.

In preferred embodiments of the invention each of the above described processes is characterized in that ethyl acetate is used as solvent (2, 3, 12).

Carrying out the proposed process in particular by means of gravity-driven thin-film evaporation requires flowable NC solutions. In the course of the concentration to a finished NC solution, the viscosity of the liquid phase does of course increase with the NC concentration. However, the solution viscosity is determined to an even greater extent by the average macromolecule chain length introduced by the polymeric NC types evaporated in each case. NC types in demand as coating materials (in particular finishes and paints) or as components therefor are declared as follows for nitrocellulose known by the skilled person. The organic solvent may be, for example, selected from the group comprising hexane, heptane, octane solventnaphtha, cyclohexane, methyl cyclohexane, benzene, toluene, and/or xylene. In case of use of mixtures of the above solvents with the non-solvents the ratio of solvent to non-solvent may be in the range of 9:1 to 1:9.

Carrying out the proposed process in particular by means of gravity-driven thin-film evaporation requires flowable NC solutions. In the course of the concentration to a finished NC solution, the viscosity of the liquid phase does of course increase with the NC concentration. However, the solution viscosity is determined to an even greater extent by the average macromolecule chain length introduced by the polymeric NC types evaporated in each case. NC types in demand as coating materials (in particular finishes and paints) or as components therefor are declared as follows for nitrocellulose known by the skilled person. The organic solvent may be, for example, selected from the group comprising hexane, heptane, octane solventnaphtha, cyclohexane, methyl cyclohexane, benzene, toluene, and/or xylene. In case of use of mixtures of the above solvents with the non-solvents the ratio of solvent to non-solvent may be in the range of 9:1 to 1:9.
In view of the known prior art, the above gravity-driven or mechanically (oscillating wipers) or hydraulically (pumps) assisted thin-film evaporators, but preferably the countercurrent falling-film evaporators operated according to the invention, offer the best preconditions for economically effective and product-protecting and technically reliable production of comparatively pure and concentrated finished NC solutions from crude NC solutions by a thermal method.

In further preferred embodiments of the invention each of the above described processes may be characterized in that from 40 to 80% by mass, but preferably from 50 to 70% by mass, of the respective predetermined amount to be evaporated altogether from the crude nitrocellulose solution (4) are evaporated in the first stage falling-film evaporator (6).

In further preferred embodiments of the invention each of the above described processes may be characterized in that the falling-film evaporators, in the preferred 2-stage falling-film evaporation the first and second stage falling-film evaporators (6) and (7), operate under identical or individually different pressures in the range from the respective ambient atmospheric pressure increasing up to 2.5 bar, but preferably in the range from 1.1 to 2.2 bar.

In further preferred embodiments of the invention each of the above described processes may be characterized in that the evaporation mixture (9) is conveyed in each case countercurrent to the crude nitrocellulose solution film (4) and is taken off separately from each falling-film evaporator (6, 7).

In further preferred embodiments of the invention each of the above described processes may be characterized in that a condensate mixture (10) preferably subsequently cooled to below 30°C is fed to a separation container (11) for continuous phase separation and water-saturated solvent (3) separated off there is directed back to the stirring container (5) for production of the crude nitrocellulose solution (4).

In further preferred embodiments of the invention each of the above described processes may be characterized in that an amount from 0 to 100% by mass of the fresh solvent (2), but preferably from 50 to 100% by mass thereof and optionally additionally a further portion of water-saturated solvent (12) branched off from the water-saturated solvent quantity (3) in an amount of from 0 to 35% by mass, but preferably from 0 to 25% by mass, are evaporated in the solvent evaporator (14) to give a solvent vapor (13).

In further preferred embodiments of the invention each of the above described processes may be characterized in that the solvent vapor stream (13) is passed into the falling-film evaporators (6, 7), preferably into the two evaporators (V1, V2) in the 2-stage embodiments, as stripping or entraining vapor countercurrent to the liquid phase, but preferably only into the last stage falling-film evaporator (7).

In further preferred embodiments of the invention each of the above described processes may be characterized in that nitrocelluloses required by the coating and printing ink industry, but preferably the nitrocellulose types standardized according to DIN ISO 14 446 and nominated within the ranges E 12 to E 38, M 15 to M 38 and A 15 to A 38 are used as water-moist nitrocellulose (1).

In further preferred embodiments of the invention each of the above described processes may be characterized in that the quantities of heat to be removed from the evaporation mixture (9) and the condensate mixture (10) are utilized for preheating the crude nitrocellulose solution (4) and the fresh solvent stream (2) and optionally the water-saturated solvent stream (12).

The process according to the invention is to be described in more detail with reference to fig. 1: in the actual NC preparation process, it is known that stabilized water-moist nitrocellulose 1 produced in fibrous form (wool) or as particulate shreds or uniformly cut cubes or short pellets, having a proportion of water of 25 to 45% by mass, but preferably from 25 to 35% by mass, is processed, preferably in a stirring container 5, in a slightly water-miscible or water-immiscible fresh solvent 2 customary for nitrocellulose, i.e. as described above, and/or optionally in an already water-saturated solvent 3, but processed in ethyl acetate, to give a crude nitrocellulose solution 4 comprising from 3.5 to 12.5% by mass, but preferably from 4.5 to 9% by mass, of nitrocellulose in the stirring container 5. This crude NC solution 4 is then continuously subjected to a partial distillative evaporation in a 1- to 3-stage falling-film evaporation, but preferably in a 2-stage falling-film evaporation 6 and 7, after which a finished nitrocellulose solution 8 formed with a proportion of nitrocellulose of from 20 to 35% by mass, but preferably from 25 to 30% by mass, and a proportion of residual water of up to 1% by mass, but preferably only up to 0.5% by mass, is continually taken up from the last stage falling-film evaporator, but preferably from the second stage falling-film evaporator 7.
mixture 9, consisting of solvent vapor and steam, is stripped off to the condenser 16 for condensation, and condensate mixture 10 flowing therefrom and subsequently cooled to at least 30°C is passed into the separation container 11 for separation.

[0029] Water-saturated solvent 3 deposited there as a result of separation, but preferably water-saturated ethyl acetate, is directed back to the stirring container 5 for the preparation of the crude NC solution 4 and the water to be removed with the solvent-saturated phase 15 in view of the intended use is likewise discharged from separation container 11. Solvent present therein is then recovered in a simple stripping process. The evaporation mixture 9 is taken off via the top from the falling-film evaporators 6 and 7. In the first and second stage falling-film evaporators 6 and 7, the procedure is carried out with particularly effective countercurrent flow of liquid film and vapor phase in continuous operation.

Omission of said external force circulation of the solution results in additional economic advantages and operational advantages for the falling-film evaporators, in that a comparatively short average residence time of the falling or trickle films on the heating surfaces of both evaporators 6 and 7 makes a substantial contribution to the thermal protection of dissolved NC. Thus, the vacuum operation for boiling point depression and as a consequence thereof very large vapor volume flows of evaporation mixture 9 with their disadvantageous effects in the first and second stage falling-film evaporators 6 and 7 on the countercurrent operation and with regard to the dimensions of the plant can be avoided. In a further process design according to the invention, the cost-efficiency of the process also increases by virtue of the fact that solvent vapor 13 produced in a separate solvent evaporator 14 of suitable customary design is passed as so-called stripping or entraining vapor at the bottom into the tube space, preferably of the last evaporator stage 7. In order to obtain an anhydrous solvent vapor 13 or at least a solvent vapor having a comparatively low water content 13, from 0 to 100% by mass, but preferably from 50 to 100% by mass, of the fresh solvent quantity 2 preferably to be introduced in anhydrous form and finally necessary for the finished NC solution 8 according to the chosen starting conditions, and optionally a portion of water-saturated solvent 12 branched off from the water-saturated solvent quantity 3 in an amount of from 0 to 40% by mass, but preferably from 0 to 25% by mass, of water-saturated solvent 3, are evaporated in the solvent evaporator 14. In an embodiment of the process according to the invention which is particularly advantageous with respect to energy, the heat to be removed from evaporation mixture 9 and that to be removed from finished NC solution 8 is utilized for preheating the crude NC solution 4 to be introduced and the fresh solvent 2 to be freshly introduced and the water-saturated solvent 12 optionally branched off from the water-saturated solvent 3. In addition, in the case of operation with different operating pressures (pressure in evaporator 6 > pressure in evaporator 7), it is very economical in terms of energy to heat the second stage evaporator 7 with the evaporation mixture 9 from the first stage evaporator 6. The process according to the invention is also further improved economically and in particular ecologically by effecting said recovery of the solvent from the solvent-saturated water 15 in a well known manner by means of a stripping column 19 with steam 18 as stripping steam and directing back the resulting mixture 20 of solvent vapor and steam taken from the head of the stripping column 19 into the evaporation mixture stream 9. The sewage 21 is taken from the bottom of the stripping column 19.

[0030] In fig. 1, the meanings are as follows:

1 nitrocellulose, water-moist (SW)
2 solvent, fresh (LP)
3 solvent, water-saturated (LW)
4 crude NC solution (RL)
5 stirring container (B)
6 falling-film evaporator, stage 1 (V1)
7 falling-film evaporator, stage 2 (V2)
8 finished NC solution (FL)
9 evaporation mixture (DG)
10 condensate mixture (KG)
11 separation container (A)
12 solvent, water-saturated (LV)
13 solvent vapor, optionally water-containing (LD)
14 solvent evaporator (V3)
15 water, solvent-saturated (WA)
16 condensation (K)
17 heating medium (HM)
18 steam
19 stripping column
20 mixture of solvent vapor and steam
21 sewage
EP 2 144 936 B1

[0031] The process according to the invention is suitable for the NC types usually demanded by the coating and printing ink industry if these are to be delivered as alcohol- or plasticizer-free finished solutions having a low water content. In particular, the nitrocellulose types (according to DIN ISO 14446) E 12 to E 38, and furthermore M 15 to M 38 and particularly A 15 to A 38 are customary for this purpose.

Examples

[0032] In table 1, examples 1 to 4 show the results of a continuous preparation of finished NC solutions from crude NC solutions produced in each case with water-moist nitrocellulose 1 and ethyl acetate as fresh solvent and/or water-saturated solvent by the process according to the invention.

Table 1

<table>
<thead>
<tr>
<th>Example 1</th>
<th>Example 2</th>
<th>Example 3</th>
<th>Example 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC type (water-moist nitrocellulose)</td>
<td>E 28</td>
<td>E 34</td>
<td>M 34</td>
</tr>
<tr>
<td>Desensitizer Content in % by mass</td>
<td>Water 33.5</td>
<td>Water 35.1</td>
<td>Water 32.1</td>
</tr>
<tr>
<td>Solvent used</td>
<td>Ethyl acetate 100</td>
<td>Ethyl acetate 100</td>
<td>Ethyl acetate 100</td>
</tr>
<tr>
<td>Ma% fresh solvent stream 2 to solvent vapor stream 13</td>
<td>15</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>Ma%solvent stream 3 to solvent stream</td>
<td>NC 7.5 Water 6.3</td>
<td>NC 7.3 Water 6.5</td>
<td>NC 8.0 Water 6.3</td>
</tr>
<tr>
<td>Crude NC solution</td>
<td>Solvent</td>
<td>Solvent</td>
<td>Solvent</td>
</tr>
<tr>
<td>Content in % by mass</td>
<td>NC 30.8 Water 0.4</td>
<td>NC 30.0 Water 0.5</td>
<td>NC 31.5 Water 0.4</td>
</tr>
<tr>
<td>Residue</td>
<td>Solvent</td>
<td>Solvent</td>
<td>Solvent</td>
</tr>
<tr>
<td>Finished NC solution</td>
<td>NC 30.8 Water 0.4</td>
<td>NC 30.0 Water 0.5</td>
<td>NC 31.5 Water 0.4</td>
</tr>
<tr>
<td>Content in % by mass</td>
<td>NC 30.8 Water 0.4</td>
<td>NC 30.0 Water 0.5</td>
<td>NC 31.5 Water 0.4</td>
</tr>
<tr>
<td>Residue</td>
<td>Solvent</td>
<td>Solvent</td>
<td>Solvent</td>
</tr>
</tbody>
</table>

Claims

1. A process for the preparation of nitrocellulose solutions having a low water content by a thermal method, comprising the steps of

   a) processing or treating (5) a water-moist nitrocellulose (1) having a proportion of water of 25 to 45% by mass in or with a solvent (2, 3) to give a crude nitrocellulose solution (4) having a proportion of nitrocellulose of 3.5 to 12.5% by mass, and then
   b) subjecting the crude nitrocellulose solution (4) to an at least partial distillative evaporation process (6, 7), and
c) taking off a finished nitrocellulose solution (8) formed with a proportion of nitrocellulose of from 20 to 35% by mass and a residual proportion of water of up to 1% by mass from the respective last stage (7) of the evaporation process,

   characterized in that the distillative evaporation process is performed by an evaporator selected from an at least 1-stage falling-film evaporator; a countercurrent falling-film evaporator; a down-draft evaporator; a helical-tube evaporator; a plate-type evaporator; or a climbing-film evaporator.

2. The process as claimed in claim 1, characterized in that from 40 to 80% by mass of the respective predetermined amount to be evaporated altogether from the crude nitrocellulose solution (4) are evaporated in the first stage falling-film evaporator (6).

3. The process as claimed in any of the preceding claims, characterized in that the falling-film evaporators, in the preferred 2-stage falling-film evaporation the first and second stage falling-film evaporators (6) and (7), operate under identical or individually different pressures in the range from the respective ambient atmospheric pressure increasing up to 2.5 bar.
4. The process as claimed in any of the preceding claims, characterized in that the evaporation mixture (9) is conveyed in each case countercurrent to the crude nitrocellulose solution film (4) and is taken off separately from each falling-film evaporator (6, 7).

5. The process as claimed in any of the preceding claims, characterized in that a condensate mixture (10) preferably subsequently cooled to below 30°C is fed to a separation container (11) for continuous phase separation and water-saturated solvent (3) separated off there is directed back to the stirring container (5) for production of the crude nitrocellulose solution (4).

6. The process as claimed in any of the preceding claims, characterized in that an amount from 0 to 100% by mass of the fresh solvent (2), but preferably from 50 to 100% by mass thereof and optionally additionally a further portion of water-saturated solvent (12) branched off from the water-saturated solvent quantity (3) in an amount of from 0 to 35% by mass are evaporated in the solvent evaporator (14) to give a solvent vapor (13).

7. The process as claimed in any of the preceding claims, characterized in that the solvent vapor stream (13) is passed into the falling-film evaporators (6, 7) as stripping or entraining vapor countercurrent to the liquid phase, but preferably only into the last stage falling-film evaporator (7).

8. The process as claimed in any of the preceding claims, characterized in that ethyl acetate is used as solvent (2, 3, 12).

9. The process as claimed in any of the preceding claims, characterized in that the nitrocellulose types standardized according to DIN ISO 14 446 and nominated within the ranges E 12 to E 38, M 15 to M 38 and A 15 to A 38 are used as water-moist nitrocellulose (1).

10. The process as claimed in any of the preceding claims, characterized in that the solvent is stripped out with steam from the water phase (15) separated off continuously in the separation container (11) and is directed back in vapor form into the evaporation mixture stream (9).

11. The process as claimed in any of the preceding claims, characterized in that the quantities of heat to be removed from the evaporation mixture (9) and the condensate mixture (10) are utilized for preheating the crude nitrocellulose solution (4) and the fresh solvent stream (2) and optionally the water-saturated solvent stream (12).

Patentansprüche

1. Verfahren zur Herstellung von Nitrocelluloselösungen mit einem niedrigen Wassergehalt durch ein thermisches Verfahren, das die Schritte umfasst:
   a) Bearbeiten oder Behandeln (5) einer wasserfeuchten Nitrocellulose (1) mit einem Wasseranteil von 25 bis 45 Massenprozent in oder mit einem Lösungsmittel (2, 3), um eine Rohnitrocelluloselösung (4) mit einem Anteil an Nitrocellulose von 3,5 bis 12,5 Massenprozent zu ergeben, und dann
   b) Unterziehen der Rohnitrocelluloselösung (4) einem zumindest teilweise destillativen Verdampfungsprozess (6, 7) und
   c) Aufnehmen einer verarbeiteten Nitrocelluloselösung (8), ausgebildet mit einem Anteil von Nitrocellulose von 20 - 35 Massenprozent und einem Restanteil an Wasser von bis zu 1 Massenprozent, aus der jeweils letzten Stufe (7), des Verdampfungsprozesses,
   dadurch gekennzeichnet, dass der destillative Verdampfungsprozess mit einem Verdampfer durchgeführt wird, der ausgewählt ist aus einem wenigstens einstufigen Fallfilmverdampfer, einem Gegenstromfallfilmverdampfer, einem Fallstromverdampfer, einem Wendelrohrverdampfer, einem Plattenverdampfer oder einem Kletterfilmverdampfer.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass 40 bis 80 Massenprozent der jeweiligen vorbestimmten insgesamt zu verdampfenden Menge aus der Rohnitrocelluloselösung (4) im Fallfilmverdampfer (6) der ersten Stufe verdampft werden.

3. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass die Fallfilmverdampfer, in
4. Verfahren wie in einem der vorstehenden Ansprüche beansprucht, **dadurch gekennzeichnet, dass** die Verdampfungsmischung (9) in jedem Fall im Gegenstrom zu dem Film der Rohnitrocelluloselösung (4) geführt wird und getrennt aus jedem Fallfilmverdampfer (6, 7) abgegriffen wird.

5. Verfahren wie in einem der vorstehenden Ansprüche beansprucht, **dadurch gekennzeichnet, dass** die Kondensatmischung (10), vorzugsweise nachfolgend auf unterhalb 30 °C abgekühlt, einem Trennbehälter (11) zur kontinuierlichen Phasentrennung zugeführt wird und das wassergesättigte Lösungsmittel (3), das darin abgetrennt wird, zu dem Rührbehälter (5) zur Herstellung der Rohnitrocelluloselösung (4) zurückgeführt wird.

6. Verfahren wie in einem der vorstehenden Ansprüche beansprucht, **dadurch gekennzeichnet, dass** eine Menge von 0 bis 100 Massenprozent des frischen Lösungsmittels (2), aber vorzugsweise von 50 bis 100 Massenprozent davon, und optional zusätzlich ein weiterer Anteil eines wassergesättigten Lösungsmittels (12), das aus der wassergesättigten Lösungsmittelmenge (3) in einer Menge von 0 bis 35 Massenprozent abgezweigt worden ist, in dem Lösungsmittelverdampfer (14) verdampft werden, um einen Lösungsmittel dampf (13) zu erzeugen.

7. Verfahren wie in einem der vorstehenden Ansprüche beansprucht, **dadurch gekennzeichnet, dass** der Lösungsmittel dampfstrom (13) als Strip- oder Schleppdampf im Gegensatz zur Flüssigphase in die Fallfilmverdampfer (6, 7) eingeleitet wird, vorzugsweise aber nur in den Fallfilmverdampfer (7) der letzten Stufe.

8. Verfahren wie in einem der vorstehenden Ansprüche beansprucht, **dadurch gekennzeichnet, dass** Ethylacetat als Lösungsmittel (2, 3, 12) verwendet wird.

9. Verfahren wie in einem der vorstehenden Ansprüche beansprucht, **dadurch gekennzeichnet, dass** die nach DIN ISO 14 446 standardisierten und innerhalb der Bereiche E 12 bis E 38, M15 bis M38 und A15 bis A38 benannten Nitrocellulosetypen als wasserfeuchte Nitrocellulose (1) eingesetzt werden.

10. Verfahren wie in einem der vorstehenden Ansprüche beansprucht, **dadurch gekennzeichnet, dass** aus der kontinuierlich im Trennbehälter (11) abgetrennten Wasserphase (15) mit Wasserdampf das Lösungsmittel abgestrippt und dampfförmig in den Verdampfungsmischungsstrom (9) zurückgeführt wird.

11. Verfahren wie in einem der vorstehenden Ansprüche beansprucht, **dadurch gekennzeichnet, dass** die von der Verdampfungsmischung (9) und der Kondensatmischung (10) abzuführenden Wärmemengen zur Vorwärmung der Rohnitrocelluloselösung (4) und der frischen Lösungsmittelstroms (2) und wahlweise des mit Wasser gesättigten Lösungsmittelstroms (12) verwendet werden.

Revendications

1. **Un procédé pour la préparation de solutions de nitrocellulose ayant une faible teneur en eau par une méthode thermique, comprenant les étapes consistant :**

   a) à transformer ou traiter (5) une nitrocellulose humidifiée à l’eau (1) ayant une proportion d’eau allant de 25 à 45 % en poids dans ou avec un solvant (2, 3) afin de donner une solution de nitrocellulose brute (4) ayant une proportion de nitrocellulose allant de 3,5 à 12,5 % en poids, et ensuite
   b) à soumettre la solution de nitrocellulose brute (4) à un procédé d’évaporation par distillation au moins partielle (6, 7), et
   c) à soutirer une solution de nitrocellulose finie (8) formée avec une proportion de nitrocellulose allant de 20 à 35 % en poids et une proportion résiduelle d’eau allant jusqu’à 1 % en poids du dernier étage respectif (7) du procédé d’évaporation, **caractérisé en ce que** le procédé d’évaporation par distillation est réalisé par un évaporateur sélectionné parmi un évaporateur à flux descendant à au moins un étage ; un évaporateur à flux descendant à contre-courant ; un évaporateur à courant descendant ; un évaporateur à tube hélicoïdal ; un évaporateur à plaques ; ou un évaporateur à flux ascendant.
2. Le procédé tel que revendiqué dans la revendication 1, caractérisé en ce que de 40 à 80 % en poids de la quantité prédéterminée respective devant être globalement évaporée de la solution de nitrocellulose brute (4) sont évaporés dans l’évaporateur à flux descendant du premier étage (6).

3. Le procédé tel que revendiqué dans n’importe lesquelles des revendications précédentes, caractérisé en ce que les évaporateurs à flux descendant, dans l’évaporation par flux descendant à 2 étages préférée les évaporateurs à flux descendant du premier et du deuxième étage (6) et (7), fonctionnent sous des pressions identiques ou individuellement différentes comprises dans la gamme allant de la pression atmosphérique ambiante respective jusqu’à 2,5 bar.

4. Le procédé tel que revendiqué dans n’importe lesquelles des revendications précédentes, caractérisé en ce que le mélange d’évaporation (9) est emmené dans chaque cas à contre-courant du flux de solution de nitrocellulose brute (4) et est soutiré séparément de chaque évaporateur à flux descendant (6, 7).

5. Le procédé tel que revendiqué dans n’importe lesquelles des revendications précédentes, caractérisé en ce qu’un mélange de condensat (10) de préférence subséquemment refroidi jusqu’à en dessous de 30 °C est introduit dans un récipient de séparation (11) pour une séparation en phase continue et le solvant saturé en eau (3) chassé par séparation de celui-ci est redirigé vers le récipient d’agitation (5) pour la production de la solution de nitrocellulose brute (4).

6. Le procédé tel que revendiqué dans n’importe lesquelles des revendications précédentes, caractérisé en ce qu’une quantité allant de 0 à 100 % en poids du solvant frais (2), mais de préférence de 50 à 100 % en poids de celui-ci et facultativement de plus une portion supplémentaire du solvant saturé en eau (12) provenant de la masse de solvant saturé en eau (3) dans une quantité allant de 0 à 35 % en poids sont évaporées dans l’évaporateur de solvant (14) afin de donner une vapeur de solvant (13).

7. Le procédé tel que revendiqué dans n’importe lesquelles des revendications précédentes, caractérisé en ce que le courant de vapeur de solvant (13) est passé dans les évaporateurs à flux descendant (6, 7) sous forme de vapeur de rectification ou d’entraînement à contre-courant de la phase liquide, mais de préférence seulement dans l’évaporateur à flux descendant du dernier étage (7).

8. Le procédé tel que revendiqué dans n’importe lesquelles des revendications précédentes, caractérisé en que de l’acétate d’éthyle est utilisé comme solvant (2, 3, 12).

9. Le procédé tel que revendiqué dans n’importe lesquelles des revendications précédentes, caractérisé en ce que les types de nitrocellulose normalisés selon DIN ISO 14 446 et listés au sein des gammes E 12 à E 38, M 15 à M 38 et A 15 à A 38 sont utilisés comme nitrocellulose humidifiée à l’eau (1).

10. Le procédé tel que revendiqué dans n’importe lesquelles des revendications précédentes, caractérisé en ce que le solvant est sorti par rectification avec de la vapeur d’eau de la phase aqueuse (15) chassée par séparation en continu dans le récipient de séparation (11) et est redirigé sous forme de vapeur dans le courant de mélange d’évaporation (9).

11. Le procédé tel que revendiqué dans n’importe lesquelles des revendications précédentes, caractérisé en ce que les masses de chaleur devant être retirées du mélange d’évaporation (9) et du mélange de condensat (10) sont utilisées pour préchauffer la solution de nitrocellulose brute (4) et le courant de solvant frais (2) et facultativement le courant de solvant saturé en eau (12).
REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader’s convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- DE 3041085 [0004] [0005]

Non-patent literature cited in the description

- Die minimale Reynoldszahl bei Rieselfilmen [The minimum Reynolds number in trickle films. E.G. WORONZOW. BWK 44. 1994, vol. 5, 201-205 [0004]