[0013] WO 00/04100 further discloses with reference to WO 94/23114 that a solution of leucoindigo in the form of a sodium salt is stable up to a concentration of 20 % by weight at room temperature.

[0014] WO 00/04100 further discloses that from diluted leucoindigo solutions water may be distilled off in order to concentrate them. E.g., from a solution having a concentration of 25 % by weight of leucoindigo, approx. 44 % by weight water may be distilled off in order to concentrate the solution up to 38 % by weight (Example 4).

[0015] Example 5 of WO 00/04100 discloses that from an aqueous solution containing 20 % by weight leucoindigo about 34 % water are distilled off in order to concentrate the solution to 27 % by weight.

[0016] WO 00/04100 is silent regarding aniline and N-methylaniline concentrations.

OBJECTS OF THE INVENTION

[0017] An increased need exists in the industry for providing concentrated leucoindigo salt solutions which are aniline-free or aniline-free and N-methylaniline-free. Therefore, the problem to be solved by the present invention was to provide. aniline-free leucoindigo salt solutions and aniline-free indigo.

SUMMARY

[0018] The disclosure relates to the following items:

1. In one aspect, the present disclosure refers to method of making an aqueous aniline-free or aniline-free and N-methylaniline-free leucoindigo solution from an aqueous leucoindigo solution comprising aniline or aniline and N-methylaniline, the concentration of aniline or aniline and N-methylaniline being determined according to ISO 14362-1:2017(E), wherein

5. Method of item 4, wherein said vapor stream comprises an inert gas, a gaseous organic solvent which is not miscible with water, or steam, or two or three thereof.

6. Method of any one of items 2 to 5, wherein the device is selected from the group consisting of plate column, packed column, or bubble column, or two or three thereof, or two or more of any of said columns.

7. Method of any one of items 5 to 6, wherein said steam is generated by heating at least a portion of said liquid stream that has been discharged from the device according to step (E).

8. Method of any one of items 2 to 7, wherein steps (A) to (E) are performed simultaneously.

9. In another aspect, the present disclosure refers to stable aqueous leucoindigo solution, wherein said leucoindigo is in the form of an alkali metal salt; wherein the solution is aniline-free or is aniline-free and N-methylaniline-free as determined according to ISO 14362-1:2017(E); and

wherein the concentration of the leucoindigo salt is in a concentration range of from 10 to 45 % by weight based on the total weight of the solution, and wherein the stability of the solution is measured at a temperature of 23 °C; or

wherein the concentration of the leucoindigo salt is in a concentration range of from 45 to 65 % by weight based on the total weight of the solution, and wherein the stability of the solution is measured at a temperature of 60 °C.

10. In yet another aspect, the present disclosure refers to method of making indigo, comprising step (II):

(II) oxidizing the aqueous leucoindigo solution as defined herein.

11. Method of item 10, comprising step (I) prior to step (II):

(l) treating a textile with the leucoindigo solution to be oxidized.

12. In yet another aspect, the present disclosure refers to integrated apparatus, comprising:

a reduction apparatus configured to reduce indigo comprising aniline or aniline and N-methylaniline in order to make an aqueous leucoindigo solution comprising said amine(s), wherein said leucoindigo is in the form of an alkali metal salt; and

a purification apparatus configured to make an aqueous aniline-free or aniline-free and N-methylaniline-free leucoindigo solution from an aqueous leucoindigo solution comprising aniline or aniline and N-methylaniline, the concentration of aniline or aniline and N-methylaniline being determined according to ISO 14362-1:2017(E), wherein said leucoindigo is in the form of an alkali metal salt; said purification apparatus comprising:

(α) first means configured to provide a liquid stream comprising an aqueous leucoindigo solution comprising aniline or aniline and N-methylaniline, wherein said leucoindigo is in the form of an alkali metal salt;

(β) second means configured to provide a purification stream;

(γ) third means comprising a device configured

(γ1) to feed said liquid stream and said purification stream into said device;

(γ2) further configured to bring into contact said liquid stream with said purification stream; and

(γ3) further configured to discharge from the device at least a portion of said purification stream that has contacted said liquid stream, and to

discharge from the device at least a portion of said liquid stream that has been contacted by said purification stream;

(δ) fourth means configured to receive at least a portion of the liquid stream that has been discharged from the device,

13. Integrated apparatus according to item 12, wherein the device is selected from the group consisting of plate column, packed column, and bubble column, or two or three thereof, or more than three of these devices.

14. In yet another aspect, the present disclosure refers to use of a device configured

(γ1) to feed a liquid stream comprising an aqueous leucoindigo solution comprising aniline or aniline and N-methylaniline, wherein said leucoindigo is in the form of an alkali metal salt, and a purification stream into said device;

(γ2) further configured to bring into contact said liquid stream with said purification stream; and

(γ3) further configured to discharge from the device at least a portion of said purification stream that has contacted said liquid stream, and to discharge from the device at least a portion of said liquid stream that has been contacted by said purification stream;

for making an aqueous aniline-free or aniline-free and N-methylaniline-free leucoindigo solution from an aqueous leucoindigo solution comprising aniline or aniline and N-methylaniline, the concentration of aniline or aniline and N-methylaniline being determined according to ISO 14362-1:2017(E), wherein said leucoindigo is in the form of an alkali metal salt.

15. Use of item 14, wherein the device is selected from the group consisting of plate column, packed column, and bubble column, or two or three thereof, or two or more of any of said columns.

16. In yet another aspect, the present disclosure refers to method of making indigo, comprising steps (I) and (III):

    (I) performing a method as defined herein.

    (III) oxidizing the leucoindigo solution obtained in step (I).

17. Method of item 16, comprising step (II) prior to step (III):

    (II) treating a textile with the leucoindigo solution obtained in step (I).

18. In yet another aspect, the present disclosure refers to stable aqueous leucoindigo solution, wherein said leucoindigo is in the form of an alkali metal salt; wherein the solution is aniline-free or is aniline-free and N-methylaniline-free as determined according to ISO 14362-1:2017(E); and

    wherein the concentration of the leucoindigo salt is in a concentration range of from 28 to 32 % by weight or 29 to 31 % by weight or in a concentration of 30 % by weight based on the total weight of the solution, and wherein the stability of the solution is measured at a temperature of 23 °C; and

    wherein the salt comprises a mixed sodium and potassium salt or is in the form of a mixed sodium and potassium salt, wherein sodium and potassium are present in a molar ratio of from 2.33 : 1 to 1 : 2.33.

19. In yet another aspect, the present disclosure refers to stable aqueous leucoindigo solution, wherein said leucoindigo is in the form of an alkali metal salt; wherein the solution is aniline-free or is aniline-free and N-methylaniline-free as determined according to ISO 14362-1:2017(E); and

wherein the concentration of the leucoindigo salt is in a concentration range of from 38 to 42 % by weight or 39 to 41 % by weight or in a concentration of 40 % by weight based on the total weight of the solution, and wherein the stability of the solution is measured at a temperature of 23 °C; and

wherein the salt comprises a mixed sodium and potassium salt or is in the form of a mixed sodium and potassium salt, wherein sodium and potassium are present in a molar ratio of from 2.33 : 1 to 1 : 2.33.

[0019] A particular advantage of the method according to the disclosure is that concentrated solution leucoindigo salt solutions may be prepared, preferably in the range of from 10 to 65 % by weight such as 15 to 60 % by weight or 20 to 55 % by weight or 25 to 50 % by weight, which comply with the dyeing requirements in terms of middle and deep shades, and which are aniline-free or aniline-free and N-methylaniline-free. Also the requirements of a reduced wastewater contamination in dyeing factories may be met.

[0020] Moreover, the method does not only provide aniline-free and N-methylaniline-free and high-concentrated leucoindigo solutions and indigo made therefrom, but provides the following additional beneficial advantage:

[0021] As is generally known, purification methods of leucoindigo solutions based on distillation and stripping as described in the prior art above are typically accompanied by foam formation. This foam formation may severely hamper the economical realization at an industrial scale due to modest space yields. Furthermore, foam may result in crusting in the used equipment which also may negatively affect both the process and the quality of the formed product.

[0022] Contrary to this, the inventors of the present disclosure discovered that the method according to the disclosure, respectively the integrated apparatus of the

disclosure and the device used for performing the method, allow reducing foaming to such an extent that an advantageous economical realization at an industrial scale is possible resulting in a high space yield and a product of high quality.

DETAILED DESCRIPTION OF THE INVENTION

[0023] The term “aniline-free” as used in this disclosure defines an aniline concentration below 100 ppm, preferably below 80 ppm, more preferred below 60 ppm, still more preferred below 40 ppm, in particular below 30 ppm or below 20 ppm, and particularly preferred below 10 ppm or below 5 ppm, the concentration being determined according to ISO 14362-1:2017(E).

[0024] The term “aniline-free and N-methylaniline-free” as used in this disclosure defines an aniline concentration and an N-methylaniline concentration below 100 ppm, preferably below 80 ppm, more preferred below 60 ppm, still more preferred below 40 ppm, in particular below 30 ppm or below 20 ppm, and particularly preferred below 10 ppm or below 5 ppm, the concentration being determined according to ISO 14362-1:2017(E).

[0025] **Method according to the invention**

[0026] According to a **first aspect**, the invention relates to a method of making an aqueous aniline-free or aniline-free and N-methylaniline-free leucoindigo solution from an aqueous leucoindigo solution comprising aniline or aniline and N-methylaniline, the concentration of aniline or aniline and N-methylaniline being determined according to ISO 14362-1:2017(E), wherein said leucoindigo is in the form of an alkali metal salt, the method comprising at least steps (A) to (C):

(A) providing a liquid stream comprising said aqueous leucoindigo solution comprising said amine(s);