OBJECTS OF THE INVENTION

[0009] There is an ongoing need in the industry for providing further stable and purified concentrated leucoindigo salt solutions and indigo made therefrom.

SUMMARY

[0010] Despite the teaching of the addressed prior art, i.e. that concentrated leucoindigo salt solutions may be provided in a molar range of sodium to potassium in the range of from 2.33 : 1 to 1 : 2.33, and that sodium negatively affects the stability of leucoindigo solutions, the inventors of the present disclosure have investigated leucoindigo salt solutions having an increased molar ratio of sodium to potassium. The inventors of the present dislcosure have surprisingly discovered that further stable and concentrated leucoindigo salt solutions may be prepared which meet industrial requirements by increasing the molar ratio of sodium to potassium known from the prior art in the range of from 3 : 1 to 1 : 3 to a molar ratio above 3 : 1. Stable concentrated solutions may be prepared up to a molar ratio of sodium to potassium of 10 : 1, such as from 3.5 : 1 to 10 : 1. Solutions may be obtained having a leucoindigo salt concentration of from 25 to 45 % by weight such as 30 % by weight, based on the total weight of the solution, which are stable at room temperature or at elevated temperature up to 60 °C. This resulting concentration range is sufficient to achieve the desired middle and deep shades in the vat dyeing process. Also the requirements of a reduced wastewater contamination in the dyeing factories may be met.

[0011] The crude leucoindigo salt solutions may be subjected to a purification step such as distillation in order to remove undesired excess aromatic amines, wherein purified and stable concentrated leucoindigo salt solutions may be obtained.

[0012] The disclosure relates to the following items:

1. Method of making an aqueous leucoindigo salt solution, the method comprising step (A):

   (A) subjecting an aqueous composition comprising indigo which contains an aromatic amine in the form of aniline or aniline and N-methylaniline, to reduction, preferably hydrogenation, in the presence of sodium hydroxide and potassium hydroxide in order to generate an aqueous leucoindigo solution comprising said aromatic amine, wherein said leucoindigo is in the form of a mixed sodium and potassium salt, wherein the molar ratio of sodium to potassium is in the range of from above 3 : 1 to 10 : 1, such as 3.5 : 1 to 10 : 1.

   In one aspect, the present disclosure refers to method of making an aqueous leucoindigo salt solution, the method comprising step (A):

   (A) subjecting an aqueous composition comprising indigo which contains an aromatic amine in the form of aniline or aniline and N-methylaniline, to reduction, preferably hydrogenation, in the presence of sodium hydroxide and potassium hydroxide in order to generate an aqueous leucoindigo solution comprising said aromatic amine, wherein said leucoindigo is in the form of a mixed sodium and potassium salt, wherein the molar ratio of sodium to potassium is in the range of from 4:1 to 8:1.

2. Method of purifying an aqueous leucoindigo solution comprising an aromatic amine in the form of aniline or aniline and N-methylaniline, wherein said leucoindigo is in the form of a mixed sodium and potassium salt, wherein the molar ratio of sodium to potassium is in the range of from above 3 : 1 to 10 : 1, such as 3.5 : 1 to 10 : 1, the method comprising step (B):

(B) subjecting the aqueous leucoindigo solution comprising said aromatic amine to a purification step selected from the group consisting of

(a) distillation;
(b) steam distillation;
(c) extraction;
(d) stripping with an inert gas;
(e) subjecting the leucoindigo solution to a purification stream;
(f) or to a combination of two or more thereof.

In another aspect, the present disclosure refers to method of purifying an aqueous leucoindigo solution comprising an aromatic amine in the form of aniline or N-methylaniline or aniline and N-methylaniline, wherein said leucoindigo is in the form of a mixed sodium and potassium salt, wherein the molar ratio of sodium to potassium is in the range of from 4:1 to 8:1, the method comprising step (B):

(B) subjecting the aqueous leucoindigo solution comprising said aromatic amine to a purification step selected from the group consisting of

(a) distillation;
(b) steam distillation;
(c) extraction;
(d) stripping with an inert gas;
(e) subjecting the leucoindigo solution to a purification stream;
(f) or to a combination of two or more thereof.

3. 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 a mixed sodium and potassium salt, wherein the molar ratio of sodium to potassium is in the range of from above 3 : 1 to 10 : 1, such as 3.5 : 1 to 10 : 1, the method comprising at least step (B):

(B) subjecting the aqueous leucoindigo solution comprising said aromatic amine(s) to a purification step selected from the group consisting of

(a) distillation;
(b) steam distillation;
(c) liquid-liquid-extraction;
(d) stripping with an inert gas;
(e) subjecting the leucoindigo solution to a purification stream;
(f) or to a combination of two or more thereof.

In yet another 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 said leucoindigo is in the form of a mixed sodium and potassium salt, wherein the molar ratio of sodium to potassium is in the range of from 4:1 to 8:1, the method comprising at least step (B):

(B) subjecting the aqueous leucoindigo solution comprising said aromatic amine(s) to a purification step selected from the group consisting of

(a) distillation;

(b) steam distillation;

(c) extraction;

(d) stripping with an inert gas;

(e) subjecting the leucoindigo solution to a purification stream;

(f) or to a combination of two or more thereof.

4. Method of item 2 or 3, wherein

(a) distillation is performed using a column provided with trays or packing materials;
(c) extraction is a liquid-liquid-extraction using a centrifugal extractor;
(e) subjecting the leucoindigo solution to a purification stream comprises at least steps (α) to (γ):

(α) providing a liquid stream comprising said aqueous leucoindigo solution comprising said amine(s);
(β) providing a purification stream;
(γ) bringing into contact said liquid stream with said purification stream.

5. Method of item 4, wherein step (γ) comprises steps (γ1) and (γ2), and the method further comprises steps (δ) and (ε):

purification or after the making is set to a range of from 5 to 65 % by weight such as 10 to 60 % by weight or 15 to 55 by weight or 20 to 50 % by weight or 25 to 45 % by weight, based on the total weight of the solution.

18. Aqueous leucoindigo salt solution comprising an aromatic amine in the form of aniline or aniline and N-methylaniline, wherein the concentration of said aromatic amine is above 200 ppm determined according to ISO 14362-1:2017(E), such as 2,000 to 10,000 ppm, wherein the leucoindigo is in the form of a mixed sodium and potassium salt, and wherein the molar ratio of sodium to potassium is in the range of from above 3 : 1 to 10 : 1, such as 3.5 : 1 to 10 : 1.

    In yet another aspect, the present disclosure refers to aqueous leucoindigo salt solution comprising an aromatic amine in the form of aniline or aniline and N-methylaniline, wherein the concentration of aromatic amine is above 200 ppm determined according to ISO 14362-1:2017(E), such as 2,000 to 10,000 ppm, wherein the leucoindigo is in the form of a mixed sodium and potassium salt, and wherein the molar ratio of sodium to potassium is in the range of from 4:1 to 8:1.

19. Aqueous leucoindigo salt solution of item 18, wherein the concentration of the salt in the solution is in the range of from 5 to 65 % by weight such as from 10 to 60 % by weight or 15 to 55 % by weight or 20 to 50 % by weight or 25 to 45 % by weight, based on the total weight of the solution.

20. Aqueous leucoindigo salt solution comprising an aromatic amine in the form of aniline or aniline and N-methylaniline, wherein the concentration of the aromatic amine is below 200 ppm determined according to ISO 14362-1:2017(E), wherein said leucoindigo is in the form of a mixed sodium and potassium salt, and wherein the molar ratio of sodium to potassium is in the range of from above 3 : 1 to 10 : 1, such as 3.5 : 1 to 10 : 1.

In yet another aspect, the present disclosure refers to aqueous leucoindigo salt solution comprising an aromatic amine in the form of aniline or aniline and N-methylaniline, wherein the concentration of the aromatic amine is below 200 ppm determined according to ISO 14362-1:2017(E), wherein said leucoindigo is in the form of a mixed sodium and potassium salt, and wherein the molar ratio of sodium to potassium is in the range of from 4:1 to 8:1

21. Aqueous leucoindigo salt solution of claim 20, wherein the concentration of the salt in the solution is in the range of from 5 to 65 % by weight such as from 10 to 60 % by weight or 15 to 55 % by weight or 20 to 50 % by weight or 25 to 45 % by weight, based on the total weight of the solution.

22. In yet another aspect, the present disclosure refers to aqueous leucoindigo solution as defined herein, obtainable by a method as defined herein.

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

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

24. Method of item 23, comprising step (C) prior to step (D):

    (C) treating a textile with the leucoindigo solution as defined in any one of items 20 to 22.

25. 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).

26. Method of item 25, comprising step (II) prior to step (III):

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

DETAILED DESCRIPTION OF THE INVENTION

[0013] The term “aniline-free” as used in this disclosure defines in its broadest meaning an aniline concentration below 200 ppm, or 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).

[0014] The term “aniline-free and N-methylaniline-free” as used in this disclosure defines an aniline concentration and an N-methylaniline concentration below 200 ppm or 100 ppm, preferably below 80 ppm, more preferred below 60 ppm, still more

CLAIMS

1. Method of making an aqueous leucoindigo salt solution, the method comprising step (A):

   (A) subjecting an aqueous composition comprising indigo which contains an aromatic amine in the form of aniline or aniline and N-methylaniline, to reduction, preferably hydrogenation, in the presence of sodium hydroxide and potassium hydroxide in order to generate an aqueous leucoindigo solution comprising said aromatic amine, wherein said leucoindigo is in the form of a mixed sodium and potassium salt, wherein the molar ratio of sodium to potassium is in the range of from 4:1 to 8:1.

2. Method of purifying an aqueous leucoindigo solution comprising an aromatic amine in the form of aniline or N-methylaniline or aniline and N-methylaniline, wherein said leucoindigo is in the form of a mixed sodium and potassium salt, wherein the molar ratio of sodium to potassium is in the range of from 4:1 to 8:1, the method comprising step (B):

   (B) subjecting the aqueous leucoindigo solution comprising said aromatic amine to a purification step selected from the group consisting of

      (a) distillation;

      (b) steam distillation;

      (c) extraction;

      (d) stripping with an inert gas;

      (e) subjecting the leucoindigo solution to a purification stream;

      (f) or to a combination of two or more thereof.

3. 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 a mixed sodium and potassium salt, wherein the molar ratio of sodium to potassium is in the range of from 4:1 to 8:1, the method comprising at least step (B):

(B) subjecting the aqueous leucoindigo solution comprising said aromatic amine(s) to a purification step selected from the group consisting of

(a) distillation;

(b) steam distillation;

(c) extraction;

(d) stripping with an inert gas;

(e) subjecting the leucoindigo solution to a purification stream;

(f) or to a combination of two or more thereof.

4. Method of claim 2 or 3, wherein

(a) distillation is performed using a column provided with trays or packing materials;

(c) extraction is a liquid-liquid-extraction using a centrifugal extractor;

(e) subjecting the leucoindigo solution to a purification stream comprises at least steps (α) to (γ):

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

(β) providing a purification stream;

(γ) bringing into contact said liquid stream with said purification stream.

5. Method of claim 4, wherein step (γ) comprises steps (γ1) and (γ2), and the method further comprises steps (δ) and (ε):

(γ1) feeding said liquid stream and

(γ2) feeding said purification stream

into a device configured to bring into contact said liquid stream with said purification stream;

(δ) discharging from the device at least a portion of said purification stream that has contacted said liquid stream; and

(ε) discharging from the device at least a portion of said liquid stream that has been contacted by said purification stream.

6. Method of claim 5, wherein the liquid stream and the purification stream are counter-current streams.

7. Method of any one of claims 4 to 6, wherein the purification stream is a vapor stream.

8. Method of claim 7, 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.

9. Method of any one of claims 4 to 8, 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.

10. Method of any one of claims 4 to 9, 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 (ε).

11. Method of any one of claims 4 to 10, wherein steps (α) to (ε) are performed simultaneously.

12. Method of any one of claims 2 to 11, comprising step (A) prior to step (B):

    (A) subjecting an aqueous composition comprising indigo which contains an aromatic amine in the form of aniline or aniline and N-methylaniline, to reduction, preferably hydrogenation, in the presence of sodium hydroxide and potassium hydroxide in order to generate an aqueous leucoindigo solution comprising said aromatic amine, wherein said leucoindigo is in the form of a mixed sodium and potassium salt, wherein the molar ratio of sodium hydroxide to potassium hydroxide is in the range of from 4:1 to 8:1.

13. Method of any one of the preceding claims, wherein the molar ratio of sodium to potassium is in the range or from 5 : 1 to 7 : 1.

14. Method of claim 2 or 3 or any one of claims 4 to 13 as far as depending on claim 2 or 3, wherein the concentration of said aromatic amine in the solution prior to purification or prior to the making is above 200 ppm determined according to ISO 14362-1:2017(E), such as 2,000 ppm to 10,000 ppm.

15. Method of claim 2 or 3 or any one of claims 4 to 14 as far as depending on claim 2 or 3, wherein the distillation performed in step (B) is selected from the group consisting of: distillation at normal pressure, distillation under vacuum and steam distillation, or a combination of two or three thereof.

16. Method of claim 2 or 3 any one of claims 4 to 15 as far as depending on claim 2 or 3, wherein step (B) is performed as long as or as often as required until after purification or after the making the concentration of the aromatic amine in the solution is below 200 ppm determined according to ISO 14362-1:2017(E).

17. Method of claim 2 or 3 or any one of claims 4 to 16 as far as depending on claim 2 or 3, wherein the concentration of the leucoindigo salt in the solution after purification or after the making is set to a range of from 5 to 65 % by weight such as 10 to 60 % by weight or 15 to 55 by weight or 20 to 50 % by weight or 25 to 45 % by weight, based on the total weight of the solution.

18. Aqueous leucoindigo salt solution comprising an aromatic amine in the form of aniline or aniline and N-methylaniline, wherein the concentration of aromatic amine is above 200 ppm determined according to ISO 14362-1:2017(E), such as 2,000 to 10,000 ppm, wherein the leucoindigo is in the form of a mixed sodium and potassium salt, and wherein the molar ratio of sodium to potassium is in the range of from 4:1 to 8:1.

19. Aqueous leucoindigo salt solution of claim 18, wherein the concentration of the salt in the solution is in the range of from 5 to 65 % by weight such as from 10 to 60 % by weight or 15 to 55 % by weight or 20 to 50 % by weight or 25 to 45 % by weight, based on the total weight of the solution.

20. Aqueous leucoindigo salt solution comprising an aromatic amine in the form of aniline or aniline and N-methylaniline, wherein the concentration of the aromatic amine is below 200 ppm determined according to ISO 14362-1:2017(E), wherein said leucoindigo is in the form of a mixed sodium and potassium salt, and wherein the molar ratio of sodium to potassium is in the range of from 4:1 to 8:1.

21. Aqueous leucoindigo salt solution of claim 20, wherein the concentration of the salt in the solution is in the range of from 5 to 65 % by weight such as from 10 to 60 % by weight or 15 to 55 % by weight or 20 to 50 % by weight or 25 to 45 % by weight, based on the total weight of the solution.

22. Aqueous leucoindigo solution as defined in claim 20 or 21, obtainable by a method as defined in claim 16 or claim 17.

23. Method of making indigo, comprising step (D):

    (D) oxidizing the aqueous leucoindigo solution as defined in any one of claims 20 to 22.

24. Method of claim 23, comprising step (C) prior to step (D):

    (C) treating a textile with the leucoindigo solution as defined in any one of claims 20 to 22.

25. Method of making indigo, comprising steps (I) and (III):

    (I) performing a method as defined in any one of claims 1 to 17, preferably claims 16 or 17;

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

26. Method of claim 25, comprising step (II) prior to step (III):

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