

“PROCESS OF PURIFICATION OF LEUCOINDIGO SALT SOLUTIONS AND USE OF AN INERT GAS”

FIELD OF THE INVENTION

[001] The present invention relates to a process for purifying leucoindigo salt solutions. In particular, the process relates to reducing the amounts of aromatic amines by means of stripping. The present invention also relates to the use of an inert gas, in a process of purification of leucoindigo salt solutions, as a gaseous defoamer.

BACKGROUND OF THE INVENTION

[002] Indigo-type dyes are among the oldest dyes used by mankind.

[003] In the past, the indigo dye was extracted exclusively from plants, such as *Indigofera tinctoria* and *Isatis tinctoria*. Only after the discovery of its synthesis route in 1880 by the German chemist Johann Friedrich Wilhelm Adolf von Baeyer and, after BASF made its large-scale manufacturing process viable in 1897, did this dye become one of the most commercialized in the world, being the main responsible for the blue coloring of the jeans type fabric.

[004] Since indigo is insoluble in water, dyeing fabrics with such dye involves reducing indigo to leucoindigo, a greenish solution in which the fabrics to be dyed are impregnated, and subsequent exposure of these fabrics to air, for oxidation of the leucoindigo to indigo, thus restoring the desired blue color.

[005] Due to its synthesis, however, the indigo produced synthetically contains aromatic amines as impurities, such as aniline and N-methyl aniline, which remain in the generated leucoindigo solutions.

[006] In this sense, there is an interest on the part of the industry to remove the aromatic amines from the leucoindigo solutions.

[007] Processes for purifying leucoindigo solutions and/or processes for reducing the aromatic amine content of these solutions have already been described in the prior art.

[008] The international publication WO 2004/024826 refers to processes for the purification of indigo and leucoindigo solutions. However, the concentration of leucoindigo in the final solution decreases as the purification process is carried out.

[009] The international publications WO 2019/030397, WO 2019/030391 and WO 2019/030396 propose methods for extracting aromatic amines from leucoindigo salt solutions by means of purification techniques known by a person skilled in the art, in particular by distillation, with addition of water amounts to the solution to be purified. As they use large amounts of water, there is an increase in mass to be processed, generating economic disadvantages in the process.

[0010] In this sense, the state of the art still lacks a process for the purification of leucoindigo salt solutions containing aromatic amines, which result in leucoindigo salt solutions containing undetectable amounts of said amines and which have an cost-effective process.

[0011] Although there is no conclusive technical explanation of the mechanism that causes the generation of foam when it takes to the boiling of leucoindigo solutions, it is a fact that this generation of foam brings great difficulties, when it does not render unfeasible, processes in which it is necessary boiling such a solution. Such difficulties are mentioned in the international publications WO 2019/030397, WO 2019/030391 and WO 2019/030396 which discuss methods and attempts to purify leucoindigo solutions. Attempts to purify leucoindigo salt solutions containing aromatic amines encountered a problem related to foaming, since the presence of said foam hinders the mass transfer of aromatic amines from the liquid to the gas phase, decreasing efficiency of the

purification process, and even making it impossible to continue removing said amines.

[0012] Still in relation to the problems that the formation of foam in the process can cause, there is an industrially known phenomenon in evaporative processes, the entrainment. Entrainment occurs when part or even all of the product initially loaded in the vessel is transferred, in a liquid state, to the vessel intended to receive the condensate, thus causing loss of yield and productivity, increased process costs, safety problems, and quality problems.

[0013] More particularly, when foaming occurs frequently and without proper control, the process becomes unfeasible.

[0014] Although the state of the art suggests the use of defoamers, such as silicone derivatives, to address the problem related to foaming, these products interfere with the quality and purity of the final product, and impact the solids content of the final solution and the cost of the purification process (see for example Ullmann's Encyclopedia of Industrial Chemistry, fifth edition, 1988, p. 483).

[0015] Furthermore, the inventors of the present application observed that the use of defoamers causes an increase in the insoluble content in the final product, which results in a major problem/ inconvenience for the industry, since the final product has a strict specification to be respected regarding said parameter.

[0016] Thus, there is a need to develop new processes for the purification of leucoindigo salt solutions, containing aromatic amines, by which it is possible to obtain smaller amounts of these amines, without changing the concentration of the leucoindigo salt during the process, and that are economically viable, and also solve the problems observed in the state of the art with respect to foaming in leucoindigo purification processes.

SUMMARY OF THE INVENTION

[0017] Thus, it is an object of the present invention to provide a process for purifying leucoindigo salt solutions, containing aromatic amines, particularly aniline and N-methyl aniline, in which said aromatic amines are reduced to undetectable amounts in the final product.

[0018] In particular, the present invention relates to a process of purifying leucoindigo salt solutions, for the removal of aromatic amines, which comprises the steps of:

- (a) adding to a purification vessel a leucoindigo salt solution having aromatic amines;
- (b) bubbling, with controlled flow rate, an inert gas in the purification vessel, by means of a device submerged on the surface of the stationary mass;
- (c) injecting, with controlled flow rate, an extraction gas stream into the vessel; and
- (d) recovering the purified leucoindigo salt solution from the vessel.

[0019] In a second aspect, the present invention relates to the use of an inert gas, in processes for the purification of leucoindigo salt solutions, as a “gaseous antifoam” which, differently than the teachings of the prior art would lead us to conclude, proves to be extremely effective in eliminating the occurrence of foam during the boiling of the leucoindigo solution and, consequently, enables all the productive processing described herein.

BRIEF DESCRIPTION OF THE FIGURES

[0020] The objectives, technical effects and advantages of the present invention will be apparent to those skilled in the art from the detailed description below which makes reference to the attached figures, which illustrate exemplary, but not limiting, embodiments of the process of the present invention:

- Figure 1 shows a schematic flowchart of the purification process of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0021] The present invention relates to a process of purification of the leucoindigo salt solution, for the removal of aromatic amines, which comprises the steps of:

(a) adding to a purification vessel a leucoindigo salt solution having aromatic amines;

(b) bubbling, with controlled flow rate, an inert gas in the purification vessel, by means of a device submerged on the surface of the stationary mass;

(c) injecting, with controlled flow rate, an extraction gas stream into the vessel; and

(d) recovering the purified leucoindigo salt solution from the vessel;

wherein the purified leucoindigo salt solution, recovered after step (d), has undetectable amounts of aromatic amines.

[0022] Usually, distillation by entrainment is applied when it is intended to extract a substance of interest contained in a "base product" – for example: extraction of essential oils.

[0023] Unlike what is practiced as typical, the purification process of the present invention applies distillation by entrainment for purification of the "base product" (leucoindigo salt solution containing aromatic amines), by removing the unwanted substance (aromatic amines) contained therein.

[0024] In particular, the purification process of the present invention is a process of stripping.

[0025] Aromatic amines are particularly aniline and N-methyl aniline.

[0026] In a preferred embodiment, the purification process of the present invention is carried out in the absence of liquid defoamers, in particular silicone derived defoamers.

[0027] Preferably, steps (b) and (c) of the purification process occur simultaneously.

[0028] The process of the present invention is capable of removing said aromatic amines by both continuous and batch processes, without any loss in production capacity.

[0029] In another preferred aspect, the process of the present invention keeps the concentration and composition of the stationary mass within the reaction vessel constant during purification, without performing one or more dilution steps.

[0030] To keep the concentration and composition of the stationary mass inside the vessel constant during the extraction, continuous and controlled addition of water is performed. Said addition allows the maintenance of an intense and constant rate of evaporation in the medium without affecting the concentration and/or the composition of the leucoindigo solution.

[0031] The salt of the leucoindigo salt solution of step (a) is particularly selected from alkali metal salts, as well as a mixture thereof.

[0032] In a preferred embodiment, the leucoindigo salt is selected from Na, K, or a mixture thereof.

[0033] Still with regard to the mixture of salts of the leucoindigo salt solution, a person skilled in the art would know how to select any of the ranges broadly disseminated in the state of the art. Preferably, the Na:K ratio is 3:1 to 1:3.

[0034] In a preferred embodiment, the leucoindigo salt solution from step (a) has a leucoindigo salt concentration of about 34.5% to 37.0% by weight,

preferably about 35%, relative to the total weight of the solution. The vessel in step (a) preferably has a stirring system.

[0035] In step (b), the inert gas is bubbled in order to promote a homogeneous distribution of this gas throughout the area of the equipment section, thus covering the entire surface of the stationary mass, to inhibit the formation of foam.

[0036] Particularly, the bubbling of step (b) is carried out at a flow rate of 5 to 8 Nm³/h, by means of a device sized and positioned submerged on the surface of the stationary mass in a way that it allows the uniform and constant dispersion of the inert gas flow rate throughout the area of the equipment section. In a particular embodiment, by foreseen an effective uniformity in the distribution, the injection of inert gas is carried out in at least three submerged points on the surface of the leucoindigo salt solution.

[0037] In accordance with an embodiment of the present invention, the purification gas stream of step (c) is selected by taking into account the non-inclusion in the processing of any other foreign substance to the final product – aqueous solution containing purified leucoindigo. Preferably, the purification gas stream of step (c) is live steam.

[0038] In a preferred configuration, the injection of the purification gas stream of step (c) is carried out at a flow rate of 500 to 2000 kg/h, by means of a device submerged in the stationary mass, in order to promote a homogeneous distribution of this gas throughout the area of the equipment section by the bottom of the vessel.

[0039] The process of the present invention, by the use of the purification gas stream of step (c), combined with the continuous and controlled addition of water, eliminates the significant differences between the occupancy rates at the beginning and at the end of it, which are typical when using batch evaporation processes, in which it starts with a highly loaded process vessel but

with a very diluted product, and ends with very little product at the stipulated concentration. In addition to the previous, there is the fact that the direct injection of the purification gas stream in step (c), preferably live steam, a characteristic of distillation techniques by drag, is performed by means of a device submerged in the stationary mass, increasing the productivity of the production process, since it provides better energy efficiency. Furthermore, such configuration allows the process to be carried out with a constant occupancy rate, preferably around 65%, and with a constant concentration of the leucoindigo salt in the leucoindigo salt solution.

[0040] In step (c), the purification gas stream is responsible for the entrainment of impurities (aromatic amines) from the leucoindigo salt solution.

[0041] In an alternative preferred embodiment, the process of the present invention is carried out using vacuum together with the use of inert gas injection and the purification gas stream.

[0042] Preferably, the purified leucoindigo salt solution obtained in step (d) comprises undetectable amounts of aromatic amines. It should be noted, however, that the process of the present invention also makes it possible to obtain a leucoindigo salt solution with any residual levels of aromatic amines, simply by interrupting the purification process when the desired content is reached.

TERMS

[0043] The use of the term “a” or “an” in this specification does not indicate a limited quantity, but the existence of at least (minimum) one of the elements/ components/ items listed. The use of the term “or” indicates any or all of the elements/ components/ items listed. The use of the term “comprise”, “endowed”, “provided” or a similar term indicates that the element/ component/ item listed in view of said term is part of the invention, but it does not exclude other elements/ components/ items not listed.

[0044] As used in the present specification, the expression “at least one” means one or more and therefore includes individual components, as well as mixtures and/or combinations.

[0045] Except in operational examples, or where otherwise indicated, all numbers expressing reaction conditions must be understood as modified in all cases by the term “about”, meaning within +/- 10% of the indicated number.

[0046] As used in this document, all ranges provided must include all specific ranges within and combinations of sub-ranges between the ranges provided. Thus, a range of 1 to 5, for example, specifically includes 1, 2, 3, 4 and 5, as well as subintervals such as 2 to 5, 3 to 5, 2 to 3, 2 to 4, 1 to 4, etc. All ranges and values disclosed herein are inclusive and combinable. For example, any value or point described herein that is within a range described herein can serve as a minimum or maximum value to derive a sub-range, etc.

[0047] The processes of the present invention may comprise, consist of, or consist essentially of the essential elements and limitations of the invention described herein, as well as any additional or optional ingredients, components or limitations described or useful herein.

[0048] In accordance with the present invention, the term “vessel” means a container in which the purification process takes place. Preferably said vessel is a cylindrical, metallic, vertical body, with top and bottom cap, provided with (i) device for homogenizing the solution (example: agitator, pump, etc.), (ii) nozzles for loading and/or unloading a product inside the vessel, (iii) device, internal and/or external, for heating and/or cooling the vessel contents (example: coil, sleeve, etc.), (iv) nozzles for connecting instruments for monitoring and controlling of the purification process (example: pressure gauges, thermometers, etc.).

[0049] As to the term “purification gas stream”, it means any gas that is capable of entraining aromatic amines, especially aniline and N-methyl aniline, but preferably that also entrains other organic substances present in the leucoindigo loaded in the vessel.

[0050] The term “live steam”, within the scope of the present invention, means water in the vapor state, with sufficient caloric amount to promote the heating and/or vaporization of part of the water contained in the stationary mass contained in the vessel, introduced submerged directly in the latter.

[0051] Within the scope of the present invention, “undetectable amounts” of said aromatic amines vary according to the detection methodology (analytical capacity of the method to detect qualitatively – to point out the presence of a substance) used. However, within the scope of the present invention, “undetectable amounts” refer to an aromatic amine content of up to 05 (five) ppm.

[0052] As used in the present application, the term “stationary mass” means all the mass loaded in the vessel, among which are mainly the mass of leucoindigo solution, which remains inside the vessel throughout the purification process.

PURIFICATION VESSEL

[0053] In the purification process of the present invention, no column distillation process is used, which typically corresponds to a vessel associated with a vertical column, filled with plates and/or fillers that allow the control and quality of the steam flow rate through the column when we submit said vessel to temperature conditions above the room temperature.

[0054] When leucoindigo salt solutions having a high concentration of leucoindigo salt are subjected to evaporation, there is a great tendency for

foam generation, and a consequent increase in the possibility of unwanted product entrainment into the vapor phase during the purification process.

[0055] Within the scope of the present invention, the entrainment of the product into the vapor phase during the purification process is a totally unwanted setback, as it generates great losses in productivity and operational risks of all types, such as occupational, environmental and quality. Also, the use of columns enhances the mentioned setbacks, since they are equipped with internal accessories (plates and/or fillings) that will certainly bring complications in the event of a lack of control in the process, which will certainly result in the generation of foam and entrainment.

[0056] Preferably, in the purification vessel of the present invention, mechanisms with countercurrent and/or co-current flow, typical of stripping processes, are not used, but a fixed bed (product – stationary mass) through which passes a gas stream of extraction is used.

[0057] For the inventors of the present application, the maintenance of the product, with high concentration, confined within the vessel during the evaporation process is much more suitable for minimizing entrainment and damage in the process than the movement/ circulation of the product, known to be necessary in processes that recommend flows and counter-flows during evaporation.

INERT GAS (GASEOUS DEFOAMER)

[0058] It has surprisingly been found, contrary to what would be expected by a person skilled in the art, that the use of an inert gas according to the present invention eliminates the occurrence of foam during the process of purifying a leucoindigo salt solution comprising aromatic amines, such as aniline and N-methyl aniline, as well as reducing to a minimum the required amount of one or more liquid defoamers known to a person skilled in the art in the process, making it possible even to not use these liquid defoamers.

[0059] In the context of the present invention, “inert gas” means any gas that is not reactive with the leucoindigo salt solution. In particular, the inert gas of the present invention can be selected from the chemical elements of group VIII of the periodic table, such as helium, neon, argon, krypton, and xenon, or N₂ and H₂ gases.

[0060] The inert gas of step (b) of the present process can be any inert gas known in the art. Preferably, the inert gas is N₂.

[0061] In a preferred embodiment, the inert gas is fed in step (b) at temperatures from -10 °C to 250 °C, at flow rates that can vary from 0.1 L/min to 80 L/min, for a mass of 900 g of leucoindigo salt solution to be purified.

[0062] Preferably, the injection of inert gas, which acts as a defoamer, should be made directly into the product, with controlled flow rate, by means of a device submerged on the surface of the stationary mass, in order to promote a homogeneous distribution of this gas throughout the equipment section area.

[0063] It was noted that the use of an inert gas as a gaseous defoamer has the advantages of:

- Reducing costs;
- Not leaving residual in the final product, obtaining a product with better quality and increasing productivity;
- Reducing the production cycle.

[0064] Despite the description of the particular embodiments above refer to certain embodiments of the process of purifying leucoindigo salt solutions, having aromatic amines, the present invention may present modifications in its implementation form, so that the scope of protection of the invention is not limited only by the content of the appended claims, including possible equivalent variations therein.

EXAMPLES

[0065] Initially, it should be noted that the process of purifying leucoindigo salt solutions, the object of the present invention, will be described below according to the particular, but not limiting, embodiments, since their embodiments may be carried out in different ways and variations and according to the application desired by the person skilled in the art, with the scope of the invention being defined according to the claims.

EXAMPLE 1

[0066] To obtain a purified leucoindigo salt solution, comprising undetectable amounts of aromatic amines, a purification vessel was loaded with a leucoindigo salt solution having aromatic amines.

[0067] Then, the heating of said leucoindigo salt solution for water evaporation with aromatic amines started, simultaneously to the continuous injection of an inert gas, acting as a gaseous antifoam, and to the continuous replacement of the water, in liquid and/or gaseous form.

[0068] The leucoindigo salt solution obtained has an aniline content of 0 ppm.

[0069] In Figure 1, it is possible to note a block flowchart of Example 1.

TESTS

[0070] To achieve the process of the present invention, the inventors carried out a series of tests of purification methodologies, which obtained unsatisfactory results for obtaining or feasibility of a process of purification of leucoindigo salt solutions, containing aromatic amines, and obtaining a final leucoindigo salt solution with undetectable amounts of said amines

[0071] The following tests illustrate the difficulties in achieving the process of the present invention.

TEST 1

LIQUID/LIQUID EXTRACTION

[0072] In an attempt to purify leucoindigo salt solutions, containing aromatic amines, and obtain a final leucoindigo salt solution with undetectable amounts of said amines, a liquid/liquid extraction test was performed using the cyclohexane solvent.

[0073] After carrying out said extraction, it was observed that the extraction process would not be viable, since it presented low efficiency and did not reach undetectable amounts of aromatic amines. In addition, the extraction process presents a high cost and a higher safety risk, since the solvent to be used is a flammable product), in addition to leaving residual cyclohexane in the final product.

[0074] Furthermore, in addition to the unsatisfactory purification results, an evaporation step would still be necessary to eliminate residual cyclohexane from the final product, which would be necessary for the removal of any other solvent used.

TEST 2

DISTILLATION COLUMN – STRIPPING

[0075] In another attempt to purify leucoindigo salt solutions, containing aromatic amines, and obtain a final leucoindigo salt solution with undetectable amounts of said amines, the stripping purification technique was tested using an unfilled distillation column.

[0076] In this test, it was observed that the production cycle doubles with the use of the distillation column, a fact caused by the heat exchange that causes a great part of the steam (water plus aromatic amines) that comes out of the boiling vessel to condense on the column walls and, at the contrary to what was intended, it returns to the boiling vessel.

[0077] In view of these unfavorable results, it is concluded that the use of a distillation column is not suitable for the purpose of purifying leucoindigo

salt solutions, containing aromatic amines, by stripping of the said leucoindigo salt solution to be purified, it corroborates for this conclusion the fact that the objective of the process of the present invention is not to obtain a vapor phase, later condensed, rich in a product of interest, as in other processes that use a distillation column with or without filling and/or plates, where part of the steam that comes out of the boiling vessel, containing the product of interest, returns to it making the steam increasingly enriched with the product of interest. On the contrary, the use of a distillation column would prove to be much more appropriate if what was desired was to obtain a stream of purified aromatic amines (vapor phase of the distillation process), which would be extracted at the top of the column. In the process of the present invention, the product of interest, which is the purified leucoindigo solution, is contained in the boiling vessel and does not have its aromatic amine content reduced to the desired levels.

[0078] Increasing the cycle reduces productivity and increases process costs.

TEST 3

ADSORBENTS

[0079] The option of using adsorbents such as active carbon and diatomite was also tested. Simple test of addition of active charcoal or diatomite in the proportion of 1 to 2% relative to the mass of leucoindigo salt solution, containing aromatic amines, followed by agitation for 1 to 2 hours, at 25 °C or 100 °C. There was no significant adsorption of aromatic amines by the adsorbents.

TEST 4

SILICONE-BASED DEFOAMER

[0080] As already commented in the present specification, the use of liquid defoamers, particularly silicone-based defoamers, increases the insoluble content in the final, purified leucoindigo salt solution. The higher the dosage of defoamer, the higher the insoluble content.

[0081] In the tests carried out, the continued use of silicone-based defoamer throughout the process of purifying leucoindigo salt solutions, containing aromatic amines, having a content of said aromatic amines of about 4,000 ppm, caused an increase of insoluble matter in the range of 0,1 to 0.5% in the raw material for a range greater than 0.5%, depending on the amount of defoamer dosed.

[0082] In a load of 835 grams of leucoindigo solution, 9.4 g of defoamer was used, which generated an amount of insoluble matter in the aniline-free leucoindigo solution of 1.2%.

[0083] It should be noted that the desired specification for insoluble matter in the final product, after evaporation, is a maximum of 0.5% (data based on a type of defoamer that has high efficiency to eliminate/ avoid foaming in the leucoindigo salt solution).

CLAIMS

1. PROCESS FOR PURIFICATION OF LEUCOINDIGO SALT SOLUTIONS, for the removal of aromatic amines, characterized by comprising the steps of:

(a) adding to a purification vessel a leucoindigo salt solution having aromatic amines;

(b) bubbling, with controlled flow rate, an inert gas in the purification vessel, by means of a device submerged on the surface of the stationary mass;

(c) injecting, with controlled flow rate, an extraction gas stream into the vessel; and

(d) recovering the purified leucoindigo salt solution from the vessel;

wherein the purified leucoindigo salt solution, recovered after step (d), has undetectable amounts of aromatic amines.

2. PROCESS, according to claim 1, characterized by being a process of stripping extraction.

3. PROCESS, according to any one of claims 1 to 2, characterized by the aromatic amines being aniline and N-methylaniline.

4. PROCESS according to any one of claims 1 to 3, characterized by the salt of the leucoindigo salt solution of step (a) being chosen from an alkali metal salt, or a mixture thereof.

5. PROCESS, according to any one of claims 1 to 4, characterized by the bubbling of step (b) being carried out in order to promote a homogeneous distribution of this gas throughout the area of the equipment section.

6. PROCESS, according to claim 5, characterized by the injection of inert gas from step (b) being carried out in at least three points on the surface of the leucoindigo salt solution.

7. PROCESS, according to any one of claims 1 to 6, characterized by the inert gas of step (b) being selected from helium, neon, argon, krypton, xenon, N₂ and H₂.

8. PROCESS according to any one of claims 1 to 7, characterized by the inert gas of step (b) on the surface fed under a flow rate of 5 to 8 Nm³/h.

9. PROCESS according to any one of claims 1 to 8, characterized by the purification gas stream of step (c) on the surface live steam.

10. PROCESS according to any one of claims 1 to 9, characterized by the gas stream of step (c) on the surface fed under a flow rate of 500 to 2,000 kg/h.

11. PROCESS, according to claim 10, characterized by the feeding of the gas stream of step (c) being carried out by means of a device submerged in the stationary mass, in order to promote a homogeneous distribution of such gas throughout the area of the equipment section at the bottom of the vessel.

12. PROCESS, according to claim 1, characterized by a vacuum being used together with steps (b) and (c).

13. PROCESS, according to any one of claims 1 to 12, characterized by being carried out in the absence of liquid defoamers, preferably silicone-derived defoamers.

14. USE OF AN INERT GAS, in a process of purification of leucoindigo salt solutions, characterized by being as a gaseous defoamer.

15. USE, according to claim 14, characterized by the inert gas being injected by means of a device submerged on the surface of the stationary

mass, in order to promote a homogeneous distribution of this gas throughout the area of the equipment section.

16. USE, according to any one of claims 14 to 15, characterized by the injection of inert gas being carried out in at least three points on the surface of the leucoindigo salt solution to be purified.

17. USE, according to any one of claims 14 to 16, characterized by the inert gas being selected from helium, neon, argon, krypton, xenon, N₂ and H₂.