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STABILIZED DIAZO COMPOUNDS

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This invention relates to the manufacture of compositions suitable for use in textile printing by a process which comprises precipitation together from an aqueous alkaline solution, of an ice color coupling component, which can be salted out from its aqueous solution and a diazoimino or diazoamino compound formed by the interaction of a diazo compound with the hydrolysis products of glue, gelatine, silk and similar proteid substances (see Plimmer, "Practical Organic and Biochemistry", (1915), p. 359 et seq.).

The manufacture of water-soluble diazoimino compounds from proline (pyrrolidine-2-carboxylic acid) and hydroxy-proline 4-hydroxypyrrolidine-2-carboxylic acid) is described in British specification No. 422,195. It is known (see E. Fischer and Aberhalden, Berichte der deutschen Chem. Gesellschaft, 1904, 37, 3072) that these cyclic imines are present together with other nitrogenous compounds in the hydrolysis products of the aforementioned proteid substances. Isolation of pure proline or hydroxyproline from a mixture of hydrolysis products is at present technically difficult because of the complexity of the operations involved.

It is an object of the invention to use hydrolyzed proteids in the making of dyes and dye compositions. Another object of the invention is a process which avoids the expensive steps of isolating certain proteid substances from the media in which they are found prior to inclusion in dye mixtures. Another object of the invention is to produce proline and oxyproline by the hydrolysis of glue or other animal matters and to isolate by co-precipitation with a complementary dye-forming compound. Another object of the invention is to produce new compositions of matter useful in dyeing. Other objects of the invention will be in part apparent and in part more fully hereinafter described.

We have now found that it is possible to make use of the mixture of compounds obtained by hydrolyzing the described proteid substances, more especially that obtained by hydrolyzing glue or gelatine, in the manufacture of compositions useful in textile printing. For this purpose we have devised a novel method of simultaneous precipitation.

According to the invention we add a diazo compound to an alkaline aqueous solution of an aforementioned proteid hydrolysis mixture, and then add to the solution or suspension obtained a solution of an ice color coupling component which itself may be easily thrown out from its aqueous solution (e. g. of an arylamide of 2:3-hydroxy-naphthoic acid, 2-hydroxycarbazole-3-carboxylic acid, 7-hydroxy-α-naphthocarbazole-6-carboxylic acid, 2-hydroxy-anthracene-3-carboxylic acid or an arylamide of acetoacetic acid), and finally we separate out and dry the desired composition. When the alkali salts of the above coupling components are thrown out in the presence of the diazoamino or diazoimino compounds they collect these upon themselves. The mixture is thus precipitated as a homogeneous semi-solid mass. It is isolated either by decantation of the liquor or by centrifuging. When dry it forms the new composition.

By applying such a composition with the aid of printing assistants to textile material in the known manner and developing in steam containing acetic acid or other volatile organic acid vapor, various fast shades may be produced.

The diazoamino or diazoimino compounds obtained as stated cannot be satisfactorily isolated in the ordinary manner, e. g. by salting out, as they either will not separate or are thrown out as a thin oil which settles slowly and incompletely owing to the dispersing effect of other substances present. But we find that these stabilized diazo compounds, whatever their nature may be can be effectively collected in an easily handled form as above described.

In general we prefer to add an amount of coupling component less than that equivalent to the full combining capacity of stabilized diazo compound present and then, having isolated the semi-solid mass as described, we determined by dye trial the additional amount of arylamide necessary for an optimum balance of reagents. We then mix the determined quantity of dry coupling component with the mass, whereupon the whole is dried.

The determination of the requisite amount of coupling component to be added is carried out by taking a weighed quantity of the material, dissolving in water, thickening and making a print which is developed by acid steam as described in Example I. The developed print is immersed in aqueous 1% caustic soda solution for 15 seconds, steamed in dry steam for one minute and immersed in a solution of a diazo compound, preferably one which will give a contrasting shade to the print. If excess coupling component is present the print is surrounded by a halo of the new color. If no halo appears, a further weighed quantity of the material is taken, mixed with a weighed quantity of the coupling component, dissolved, printed, developed and tested as above.

The process is continued until by trial and error the test shows a slight definite halo, thus indicating a small excess of coupling component. Coupling component, not necessarily as sodium salt, is then added to the bulk of the material in the proportion indicated.

The invention is illustrated but not limited by the following examples. The parts are by weight.

Example I

250 parts of glue are hydrolyzed by boiling for 24 hours with 750 parts of 25% aqueous sulfuric acid. To the solution lime is added until it is neutral, the calcium sulfate is filtered off and the calcium salts in the filtrate are converted to sodium salts by the addition of a small excess of sodium carbonate. After filtering, the solution is concentrated to 600 parts and in it are dissolved 20 parts of anhydrous sodium carbonate after which it is again filtered, if necessary, and cooled to 10°–15° C. A diazo solution prepared in the usual manner from 21.3 parts of 4-chloro-2-toluidine is run in with stirring, the temperature being kept at 20° C. or lower. The diazo reaction rapidly disappears and after 15 minutes the solution is made alkaline to phenol phthalein. 19.7 parts of 2:3-hydroxynaphthoic anilide previously dissolved in 200 parts of water and 7.5 parts of sodium hydroxide are now added and the whole warmed to 50–60° C. for 15 minutes, filtered, cooled to 10° C. and common salt is added until no more will dissolve. A dark oily precipitate is thrown down which slowly sets to a gel or tar on standing. It is collected by decanting off the mother-liquor and dried in vacuo at or below 50° C. If necessary, a further quantity of 2:3-hydroxynaphthoic anilide, as determined by dye or printing trials, is added until the anilide is in a slight excess. The whole is then ground together forming a pale brown powder.

Instead of the 19.7 parts of 2:3-hydroxynaphthoic anilide, 14 parts of acetoacet-ortho-toluidide may be used.

Example II

Glue is hydrolyzed and the hydrolysate extracted with alcohol as described by E. Fischer and Abderhalden, Berichte der deutschen Chem. Gesellschaft, 1904, 37, 3072 et seq.

40 parts of the dried residue from the alcoholic extract are dissolved in 100 parts of water and 15 parts of sodium carbonate and boiled gently until all volatile amines are expelled. The solution is cooled to 10–15° C. and stirred while there is added over 15 minutes the solution obtained by diazotizing 15 parts of 2:5-diethoxy-4-benzoylaminoaniline. When combination is complete the solution is made alkaline to phenol phthalein and then 7 parts of 2:3-hydroxynaphthoic anilide dissolved in 25 parts of water and 2 parts of sodium hydroxide are added and the whole warmed to 50° C., filtered after 30 minutes and cooled to 10° C. To the clear solution is added sufficient solid caustic soda to make a 10% solution, thereupon a black oil separates, which is allowed to settle, collected by decantation and dried in vacuo. It is standardized by dye trials as described in Example I.

Example III

Gelatine is hydrolyzed and treated as described by Kingston and Schryver (Biochemical Journal, 1924, 18, 1070) and the amino acids of those carbamates soluble in alcohol-water (2:1) collected, boiled for 12 hours with 10% aqueous sulfuric acid, then made alkaline with sodium carbonate and boiled until all free amines are expelled. Sufficient of the solution is taken to provide 25 parts of the mixed amino acids formed as a result of this treatment. To this is added at 10°–15° C. a solution made by diazotizing 7.9 parts of 4-chloro-2-anisidine and the solution is kept alkaline by adding aqueous sodium carbonate as necessary. A brown solution is obtained. When on test it is found that free diazo compound is no longer present, the whole is made alkaline to phenol phthalein and a solution of 5 parts of 2:3-hydroxynaphthoic-ortho-anisidide dissolved in 15 parts of water and 1.5 parts of sodium hydroxide is added. The solution is warmed to 50–55° C., filtered after 15 minutes, stirred with 7 parts of green earth and 0.1 part of aluminum powder until the solution is clear golden yellow and again filtered. To the clear solution sufficient solid caustic soda to make a 15% solution is added. The precipitate which results is collected as a honey-like oil by centrifuging, dried in vacuo and standardized by dye trial as described in Example I. Instead of 2:3-hydroxynaphthoic-ortho-anisidide, 8 parts of the para-chloroanilide of carbazole-2:3-hydroxy carboxylic acid may be used.

Example IV

Gelatine is hydrolyzed and worked up through the copper salts of the amino acids as described by Brazier, Biochemical Journal, 1931, 24, 1188 et seq. The copper salts soluble in methyl alcohol are dissolved in water, decomposed by hydrogen sulfide, filtered and made alkaline with sodium carbonate. An amount of solution of at least 10% strength (i. e. concentrated if necessary by evaporation) containing 65 parts of the mixed amino acids is stirred at 10–15° C. while there is run in a diazo solution prepared in the usual manner from 21.3 parts of 5-chloro-2-toluidine, the solution being kept alkaline throughout the addition. The diazo compound rapidly enters into combination. 36 parts of the 4-bromo-2-anisidide of 2:3-hydroxynaphthoic acid are dissolved in 450 parts of warm water and 10 parts of sodium hydroxide and the warm solution is added to the above solution, more caustic alkali is added if necessary and the whole is filtered from any tar-like precipitate and, while still warm, an excess of common salt is added. An oily precipitate is formed which becomes semicrystalline on standing in the cold. It is collected by decantation, dried in vacuo to a brown, easily friable mass and standardized by adding more coupling component as determined by dye or printing trial, as explained in Example I.

Instead of the 4-bromo-2-anisidide the ortho-toluidide of 2:3-hydroxynaphthoic may be employed in the above example.

Example V

8 parts of a composition prepared according to Example I using 2:3-hydroxynaphthoic anilide are dissolved in 25 parts of water at 50–70° C. containing 0.4 part of caustic soda. This is stirred into 75 parts of starch-tragacanth thickening and the paste printed on calico. The print is dried and steamed for two minutes in steam containing the vapors of acetic acid, whereupon the parts printed become bright red. The printed material is now boiled in aqueous soap solution (5 grams per liter) for five minutes and dried. The printed areas now have a bright scarlet shade.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. The process which comprises dissolving glue in an alkaline aqueous solution, subjecting the solution to hydrolysis, adding a diazotized primary arylamine thereto, admixing therewith an ice color coupling component and simultaneously precipitating the coupling component and the diazoimino compound from the solution.

2. The process which comprises dissolving animal matter in an alkaline aqueous solution, subjecting the solution to hydrolysis, adding a diazotized primary arylamine thereto, admixing therewith an ice color coupling component and simultaneously precipitating the coupling component and the diazoimino compound from the solution.

3. Process for the manufacture of dry compositions suitable for use in textile printing which comprises adding an alkaline aqueous solution of an ice color coupling component which can be thrown out from its aqueous alkaline solution to an aqueous solution containing a compound or compounds obtained by the action of a diazo compound on a mixture of amino acids derived from the hydrolysis of a proteid substance, salting out the mixture thus obtained, separating the precipitate and drying it.

4. Process according to claim 3 in which the proteid substance which is hydrolyzed is one of the group consisting of glue and gelatine.

5. The process which comprises stabilizing a diazo compound by combining the compound with an alkaline solution of the compound made by hydrolyzing a proteid substance, whilst maintaining the mixture alkaline, adding a solution of an ice color coupling component which can be thrown out of its aqueous alkaline solution, the amount of said coupling component being less than the equivalent of the full combining capacity of the stabilized diazo compound, separating the composition from the reaction mixture and adding coupling component at least equivalent to the full combining capacity of the stabilized diazo compound.

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