United States Patent Office 2,819,258 Patented Jan. 7, 1958

2,819,258

PROCESS FOR THE MANUFACTURE OF DIAZOAMINO-COMPOUNDS IN DRY FORM

Max Schmid, Riehen, Eduard Moser, Basel, Albert Bolleter, Muttenz, and Hans Luzi Schucan, Bettingen, Switzerland, assignors to Ciba Limited, Basel, Switzerland, a Swiss firm

No Drawing. Application August 20, 1954
Serial No. 451,297

Claims priority, application Switzerland August 28, 1953

10 Claims. (Cl. 260—140)

It has long been known that certain diazoamino-compounds can be used with advantage for the production of azo-dyestuffs on a suitable substratum. The usual procedure is to apply a mixture of a suitable coupling component with a diazoamino-compound together with one of the usual thickening agents to the substratum to be dyed, especially a textile sheet material to be dyed or advantageously to be printed, and then to steam the substratum to be printed. This procedure has the advantage that the diazoamino-compounds do not couple with the coupling components before the steaming operation, and that coupling takes place during the steaming operation simultaneously with fixation of the dyestuff in a relatively short time.

Most of the known diazoamino-compounds hitherto used are so stable in alkaline media that it is necessary to use an acid medium in which to bring about their splitting and thereby the regeneration of the coupling capacity of the diazo-compounds contained therein. This is desirable for if the diazoamino-compounds were too unstable there would be a risk of their coupling with the coupling component in the printing composition or of their decomposing in another manner, so that the desired effect, namely the formation and fixation of the dyestuff on the substratum would not be satisfactory or might not occur at all. It has therefore generally been considered necessary to use diazoamino-compounds which require at least weakly acid conditions during steaming. The acid reaction may be produced, for example, by using a volatile acid during the steaming process, or by the use of printing pastes which become acid during steaming by the splitting off of a volatile base or which yield an acid reaction during steaming by the hydrolysis of easily hydrolysable esters or amides or other chemical reactions.

In isolated cases other acid development methods are used which can be carried out without any actual steaming operation. However, only in a few cases has this become of practical importance.

Acid steaming involves many difficulties which, for example, when volatile acids are used, include severe corrosion of the apparatus used. Also in other cases, especially when dyestuffs of different classes are used simultaneously, the production of an acid reaction during steaming may interfere with the fixation or impair the tint of the other dyestuff. Attempts have therefore been made to find diazoamino-compounds which do not require an acid reaction for their splitting in order to regenerate the coupling capacity of the diazo-compounds contained therein. The number of diazoamino-compounds of this kind hitherto known is very limited and is far from fulfilling practical requirements.

A great difficulty connected with the production of diazoamino-compounds, which split up in a weakly alkaline medium, is that they can be formed from the corresponding diazo-compounds and amines only with difficulty and in moderate yields.

This invention is based on the observation that diazoamino-compounds which split up easily can be produced in dry form by subjecting to a rapid drying operation a solvent-containing mixture which contains in addition to a diazoamino-compound a free diazo-compound and also as stabilizer a free amine.

As "a rapid drying operation" there is to be understood a process in which the material to be dried is subjected to a raised temperature in the aqueous condition only for a short time, advantageously of the order of a few seconds and preferably in small portions, for instance in the form of fine droplets, although, once the material is dry, it is permissible to leave the material for a longer time at a raised temperature. Accordingly, there are suitable drying or evaporating processes, in which the solution to be subjected to evaporation for drying is continuously exposed in a finely divided state to a powerful source of heat, and advantageously care is taken that the water vapour evolved is continuously and efficiently removed.

Especially advantageous for this purpose is spray drying. The term "spray drying" is used in its ordinary sense to mean a treatment in which the aqueous solution or suspension to be dried is finely sprayed or atomized and simultaneously exposed to a current of warm air. The heat of the current of air is used to evaporate the solvent, especially water. In this manner the air-solvent vapour-dry material system is cooled. For drying aqueous solutions or suspensions to produce a dry preparation it is generally necessary to maintain the outlet temperature of the said system at least at about 70° C., advantageously between 80 and 100° C., and for the same reason it is necessary that the inlet temperature of the air should be above 100° C., advantageously within the range of about 130–180° C., in order to avoid having to heat uneconomically large amounts of air.

Instead of spray drying, there may be used another rapid drying process, for example, a drying process in which the cold solution or suspension is applied in a thin layer to a hot roller or moving band. In this case also it is preferable, on the one hand, by heating to a sufficiently high temperature the moving surface, for example, the roller, and, on the other, by finely distributing the material to be dried, for example, by breaking it up into droplets or by spraying, to take care that a thin uniform film of the material to be dried is formed from which the solvent can be completely distilled in a short time. After the short time the dry layer is completely removed from the hot surface by means of a knife or other suitable apparatus, the material being removed in any event before fresh solution is applied to the place it occupies.

It is surprising that during such rapid drying processes there is at most only a very slight decomposition of the diazo-compound or diazoamino-compound, and even in cases where, owing to an unfavorable equilibrium between the starting materials and the diazoamino-compound being established when the condensation was carried out, a not inconsiderable amount of the temperature-sensitive diazo-compound is still present. The process of this invention is especially advantageous in the case of diazoamino-compounds which, whether owing to their too ready solubility and the consequent difficulty of salting them out or owing to the aforesaid unfavorable equilibrium, cannot be produced at all by other methods or at least cannot be converted into the dry state.

The dry diazoamino-compounds obtained by the process of this invention can be worked up in the usual manner together with suitable coupling components (so-called naphthols) to form valuable preparations and printing pastes. In particular, many preparations can be made which do not require acid steam for develop-

ing the prints and therefore need no addition serving to produce an acid reaction.

The following examples illustrate the invention, the parts and percentages being by weight unless otherwise stated and the relationship of parts by weight to parts by volume being the same as that of the kilogram to the liter:

Example 1

19.4 parts of the hydrochloride of 1-amino-2-methoxy-5-chlorobenzene are dissolved in 45 parts of hydrochloric acid of 10 percent strength, and, after the addition of a small amount of ice, diazotization is carried out at 0–5° C. in a solution of 6.9 parts of sodium nitrite in 25 parts of water. At the same time there is prepared a solution of 19.5 parts of 2-carboxy-phenyl-amino-acetic acid in 400 parts of water with the addition of a sufficient quantity of a sodium hydroxide solution of 30 percent strength to produce a clear solution having a pH value between 7 and 8.2 parts of anhydrous sodium carbonate and 2 parts of sodium bicarbonate are also added, and the whole is cooled by the addition of ice to 0–5° C. The diazo-solution is stirred below the surface for a few minutes, and at the same time a sufficient quantity of a sodium hydroxide solution of 30 percent strength is introduced dropwise to maintain the reaction mixture at a pH value between 9 and 10. The pH value should finally rise to 10.5. The maximum is filtered after the addition of diatomaceous earth to remove a small amount of a precipitate, the residue is washed with a small amount of ice water, and then the clear pale brown filtrate, amounting to about 1000 parts by volume containing in addition to the diazoamino compound the free diazo compound and also as stabilizer free amine, is subjected to spray drying. During the spray drying the inlet temperature of the air is between 140 and 180° C., and the outlet temperature is not lower than 80° C., and not substantially higher than 100° C. There is obtained an orange colored, very fine powder, which has an excellent solubility in water. The yield calculated on the diazoamino-compound used is 85–90 percent of the theoretical yield.

Example 2

17.8 parts of the hydrochloride of 1-amino-2-methyl-5-chlorobenzene are diazotized in the manner described in Example 1. The volume of the diazo-solution is from 150–200 parts by volume. It is coupled in the manner described in Example 1 with a solution of 19.5 parts of 2-carboxy-phenylamino-acetic acid prepared in a similar manner. By filtering the solution containing in addition to the diazoamino compound the free diazo compound and also as stabilizer free amine and working it up in a spray dryer in the manner described in Example 1 there is obtained the corresponding diazoamino-compound in the form of a yellow, very fine powder, which dissolves well in water to give a clear solution. The yield amounts to 85–90 percent of the theoretical yield.

Example 3

In the procedure described in Example 2 the hydrochloride of 1-amino-2-methyl-5-chlorobenzene is replaced by the same quantity of the hydrochloride of 1-amino-2-methyl-4-chlorobenzene, and, before the spray drying, the pH value of the solution is adjusted to 11 by a somewhat larger addition of a sodium hydroxide solution of 30 percent strength. The corresponding diazoamino-compound is obtained in a yield amounting to 85 percent of the theoretical yield, and in the form of a pale yellow, fine powder which dissolves well in water to give a clear solution.

Example 4

12.8 parts of 1-amino-3-chlorobenzene are diazotized in the usual manner in 75 parts of hydrochloric acid of 10 percent strength with 6.9 parts of sodium nitrite in 25 parts of water at 5–10 C. The volume of the diazo-solution amounts to 150–200 parts by volume. This solution is coupled as described in Example 1 with a solution of 19.5 parts of 2-carboxyphenylamino-acetic acid, and the reaction mixture, after being filtered, is subjected to the spray drying operation. The yield amounts to 85–90 percent of the theoretical yield. The product is a fine yellow powder which dissolves well in water to give a clear solution.

Example 5

24.4 parts of 4:4'-diamino-3:3'-dimethoxy-diphenyl are dissolved in a solution of 30 parts of naphthalene sulfonic acid in 110 parts of sulfuric acid of 2 percent strength at 40–50° C. After being cooled to 10° C., the solution is tetrazotized by the addition of 13.8 parts of sodium nitrite in 50 parts of water in such manner that the temperature does not rise above 20° C. The mixture is stirred for a further ½ hour and filtered to remove a small amount of solid constituents. The resulting solution is run into a solution of 47.8 parts of 2-carboxyphenylamino-acetic acid in the form of the disodium salt, 4 parts of anhydrous sodium carbonate and 4 parts of sodium bicarbonate in 800 parts of water. By simultaneously adding a sodium hydroxide solution of 30 percent strength the pH value of the mixture is maintained betwees 9 and 9.5, and is finally 10. The solution is dried in a spray dryer as described in Example 1. The yield amounts to 80–85 percent of the theoretical yield.

Example 6

25.8 parts of 1-amino-2-methoxybenzene-5-sulfonic acid diethylamide are diazotized in 100 parts of water and 30 parts of hydrochloric acid of 30 percent strength at 5–10° C. with 6.9 parts of sodium nitrite in 25 parts of water. The mixture is then filtered to remove a small amount of impurities. At the same time there is prepared a solution of 19.5 parts of 2-carboxyphenyl-amino-acetic acid in 400 parts of water with the addition of a quantity of a caustic potash or caustic soda solution of 30 percent strength that the pH value of the clear solution is between 8 and 9. There are also added 2 parts of anhydrous sodium carbonate and 2 parts of sodium hydrogen carbonate, and the whole is cooled to 0–5° C. The diazo-solution is stirred beneath the surface and at the same time there is added dropwise a sufficient quantity of a caustic potash or caustic soda solution of 30 percent strength to maintain the reaction mixture at a pH value of 9–10. After being filtered, the clear solution containing in addition to the diazoamino compound the free diazo compound and also as stabilizer free amine is dried in a spray dryer in the manner described in Example 2. There is obtained a powder having similar properties and a pale brown color in a yield amounting to 80–85 percent of the theoretical yield.

The filtered solution of the diazoamino-compound obtained as described in this example may also be worked up on a roller dryer. For this purpose the solution is charged into a pressure vessel which is externally cooled to −2° C. The apparatus is as follows:

An externally chromium-plated and polished hollow steel roller is mounted horizontally and freely rotatable. It has a connection for the admission of superheated steam at a maximum of 6 atmospheres' gauge pressure. A brass knife is pressed against the surface of the roller under the action of weights at approximately the level of its axis. At a distance of 20–25 centimeters from the surface of the roller and directed perpendicularly with respect to the centre of the axis, is located a nozzle which is connected to the pressure vessel and is so adjusted that the supply of the solution under 2–5 atmospheres' gauge pressure, and without any special air supply, causes the solution to be finely atomized and sprayed on to the roller. With a roller of 20 centimeters in radius and 20–25 centimeters in length, and at a speed

of rotation of about 6 revolutions per minute, the nozzle and the knife are so adjusted that the planes in which they lie with respect to the roller axis form an angle of 120°. The residence time of the drying material on the roller is then 3–4 seconds when the direction of rotation of the roller is from the nozzle to the knife. The solution is sprayed on to the roller at the rate of 3–4 liters per hour, and the temperature of the surface of the roller is 115–140° C., which corresponds to 2–5 atmospheres' gauge pressure of steam.

The finished diazo-amino-compound is removed from the roller in the form of a pale brown powder and in order to give it a uniform fine grain size it is ground for a short time.

The diazoamino-compound so obtained does not differ in content or yield to any appreciable extent from the product obtained in the spray dryer.

The diazoamino-compounds obtained as described in Examples 1–5 can also be worked up in the same manner and with equal success.

What is claimed is:

1. A process for the manufacture of diazoamino compounds in dry form from an aqueous alkaline solution which contains, in addition to a diazoamino compound, the diazo compound of which is free from sulfonic and carboxylic acid groups, substantially equimolecular proportions of the corresponding free diazo compound and of, as stabilized, the corresponding free amine, wherein the said aqueous solution is subjected to a rapid drying operation of the order of at most a few seconds.

2. A process for the manufacture of diazoamino compounds in dry form from an aqueous alkaline solution containing, in addition to a diazoamino compound, the diazo compound of which is free from sulfonic and carboxylic acid groups, substantially equimolecular proportions of the corresponding free diazo compound and of, as stabilizer, the corresponding free amine, wherein small portions of said solution are suddenly heated to the drying temperature for at most a few seconds.

3. A process for the manufacture of diazoamino compounds in dry form from an aqueous alkaline solution containing, in addition to a diazoamino compound, the diazo compound of which is free from sulfonic and carboxylic acid groups, substantially equimolecular proportions of the corresponding free diazo compound and of, as stabilizer, the corresponding free amine, wherein the droplets of said solution are suddenly heated to the drying temperature for at most a few seconds.

4. A process for the manufacture of diazoamino compounds in dry form from an aqueous alkaline solution containing, in addition to a diazoamino compound which dissociates in a non acid medium and the diazo compound of which is free from sulfonic and carboxylic acid groups, substantially equimolecular proportions of the corresponding free diazo compound and of, as stabilizer, the corresponding free amine, wherein small portions of said solution are suddenly heated to the drying temperature for at most a few seconds.

5. A process for the manufacture of diazoamino compounds in dry form from an aqueous alkaline solution which contains in addition to a diazoamino compound which dissociates in a non-acid medium and the diazo compound of which is free from sulfonic and carboxylic acid groups, substantially equimolecular proportions of the corresponding free diazo compound and of, as stabilizer, the corresponding free amine, wherein small portions of said solution are suddenly heated to a temperature from 70 to 180° C. for at most a few seconds.

6. A process for the manufacture of diazoamino compounds in dry form, which comprises applying for at most a few seconds in small portions to a roller at a temperature between 115 and 140° C., an aqueous alkaline solution which contains, in addition to a diazoamino compound which dissociates in a non-acid medium and the diazo compound of which is free from sulfonic and carboxylic acid groups, substantially equimolecular proportions of the corresponding diazo compound and of, as stabilizer, the corresponding free amine.

7. A process for the manufacture of diazoamino compounds in dry form from an aqueous alkaline solution which contains, in addition to a diazoamino compound which dissociates in a non-acid medium and the diazo compound of which is free from sulfonic and carboxylic acid groups, substantially equimolecular proportions of the corresponding free diazo compound and of, as stabilizer, the corresponding free amine, wherein fine droplets of said solution are applied for at most a few seconds to a roller at a temperature between 115 and 140° C.

8. A process for the manufacture of diazoamino compounds in dry form from an aqueous alkaline solution which contains, in addition to a diazoamino compound which dissociates in a non-acid medium and is derived from a diazo compound suitable for the production of ice colors and from 2-carboxyphenylamino-acetic acid, substantially equimolecular proportions of the corresponding free diazo compound and of, as stabilizer, free 2-carboxyphenylamino-acetic acid, wherein the said solution is applied in fine droplets to a roller at a temperature between 115 and 140° C.

9. A process for the manufacture of diazoamino compounds in dry form from an aqueous alkaline solution which contains, in addition to a diazoamino compound which dissociates in a non-acid medium and the diazo compound of which is free from sulfonic and carboxylic acid groups, substantially equimolecular proportions of the free diazo compound and of, as stabilizer, the corresponding free amine, wherein the said solution is spray-dried by means of air heated to 140–180° C., the drying time being of the order of at most a few seconds.

10. A process for the manufacture of diazoamino compounds in dry form from an aqueous alkaline solution which contains a diazoamino compound which dissociates in a non-acid medium and is derived from a diazo component suitable for the production of ice colors and from 2-carboxyphenylamino-acetic acid and substantially equimolecular proportions of the corresponding free diazo compound and of free 2-carboxyphenylamino-acetic acid, wherein said solution is spray-dried by means of air heated to 140–180° C., the drying time being of the order of at most a few seconds.

References Cited in the file of this patent

UNITED STATES PATENTS

1,979,327	Holmes et al.	Nov. 6, 1934
2,071,492	Boehmer	Feb. 23, 1937
2,124,594	Schmelzer	July 26, 1938
2,263,616	Dahlen	Nov. 25, 1941
2,574,597	Salvin et al.	Nov. 13, 1951
2,675,374	Petitcolas et al.	Apr. 13, 1954

FOREIGN PATENTS

1,049,221	France	Aug. 12, 1953

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,819,258 January 7, 1958

Max Schmid et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 19, for "and 8.2 parts" read -- and 8. 2 parts --; column 5, line 28, for "stabilized" read -- stabilizer --.

Signed and sealed this 27th day of May 1958.

(SEAL)
Attest:
KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents