

1

3,400,121

2,4,6-TRI-(1-AMINO-SUBSTITUTED AROMATIC)-s-TRIAZINES

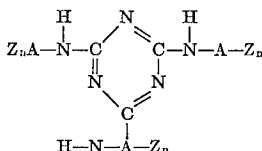
Gerhard Weckler and Siegfried Schiessler, Frankfurt am Main, Germany, assignors to Farbwerke Hoechst Aktiengesellschaft vormals Meister Lucius & Bruning, Frankfurt am Main, Germany, a corporation of Germany

No Drawing. Continuation-in-part of application Ser. No. 303,425, Aug. 20, 1963. This application Mar. 30, 1966, Ser. No. 538,609

3 Claims. (Cl. 260—239.7)

ABSTRACT OF THE DISCLOSURE

Novel compounds have been provided which are symmetrical 2,4,6-triazines of the formula:



in which A is lower alkylene, phenylene or naphthylene, Z is $-\text{SO}_3\text{Y}$, $-\text{OSO}_3\text{Y}$, $-\text{COOY}$ or



Y is hydrogen or a salt-forming cation, and n is an integer from 1 to 3, provided that when Z is $-\text{SO}_3\text{Y}$ and $-\text{COOY}$, n is an integer from 2 to 3.

This application is a continuation-in-part of our application Ser. No. 303,425 filed Aug. 20, 1963 now U.S. Patent 3,278,253.

The present invention relates to improvements in the dyeing of textile materials such as yarns, filaments, fibers and fabrics having a basis of synthetic linear polyamides, as, for example, nylon. More particularly, the present invention relates to an improved process for dyeing yarns, filaments, fibers and fabrics made of, or essentially consisting of, synthetic linear polyamides with acid dyestuffs, complex metal dyestuffs or reactive dyestuffs or mixtures thereof.

It is well known in the art that textile materials made from polyamides can be dyed with various dyestuffs, for example, with acid wool dyestuffs, metal complex dyestuffs or chrome dyestuffs, at temperatures below and above 100°C . However, the dyeings thus produced are not satisfactory, because in most cases it is not possible to level irregularities of the yarn which are mainly caused by variations of the titer and differences in stretching and fixing. These yarn irregularities are distinctly visible after dyeing as streaks, bands or in the form of an unsettled appearance, depending on the type of goods, and they considerably reduce the sales value of the goods.

To by-pass these drawbacks, it has been proposed, in addition to selecting a suitable dyestuff, to retard the dyeing process and to carry it out in the presence of swelling agents in order to augment the penetration into the fiber, and thus to prevent blocking effects. As swelling agents, there have been used, for example, phenols and chlorinated, aromatic substances. These products, however, involve a number of disadvantages. They are, in most cases,

2

not simple to use and they are effective only in high concentrations. In addition, they are partly strongly absorbed by the fibers so that they can be removed later on with difficulty only and may then cause damage to the fibers. Although they reduce streakiness, they do not totally remove the streaks.

Furthermore, attempts have also been made to produce level dyeings through control of the substantivity of the dyestuff by shifting the pH-value of the dyebath during dyeing by the addition of a potentially acid dyeing assistant to the bath. However, this process does not remove or level streakiness of the fabric dyed.

Furthermore, it is known to use surface-active agents in the dyeing of polyamide fibers. Attempts have been made to produce level dyeings by adding cation-active dyeing assistants to the dyebath which are capable of forming complexes with acid wool dyestuffs, and to retard their penetration into the fiber. This process, too, does not yield satisfactory results, because the cation-active products tend to precipitate the acid dyestuffs. Even the addition of non-ionic dispersing agents to the dyebath does not remove the difficulties and does not offer the required reliability. Furthermore, there has been described the use of anion-active products which are added to the dyebath and which are to compete with the dyestuff for the free linking positions of the fibers. However, these products possess either such strong affinity for the polyamide fiber that all linking positions of the fiber are occupied by the dyeing assistant and that the dyebaths cannot be exhausted, or they are well able to retard the penetration of the acid dyestuff into the polyamide fiber in the case of light dyeings, but do not satisfactorily level out the streakiness.

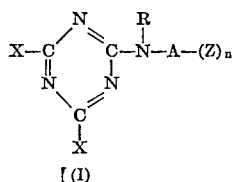
Furthermore, products are described in the literature which are a combination of special, anion-active substances with complex-forming, weakly cation-active surface-active compounds such as polyvinyl pyrrolidone, or hydroxy-ethylated aminophenols.

In many cases these products are capable of levelling out the streakiness occurring with polyamide fibers when dyeing with acid dyestuffs; in the case of difficult dyeings with acid dyestuff combinations, they exhibit retarding effects which are different for each component of the dyestuff combination, so that dyestuff losses and alterations of shade are caused. The full effect of the mixtures is attained at temperatures above 100°C ., so that antioxidants must be used to prevent possible oxidations taking place at these high temperatures. In the dyeing of polyamide fibers with complex metal dyestuffs and reactive dyestuffs, fabric irregularities cannot be levelled out satisfactorily and a strong retardative effect is observed with some dyestuffs. A drawback is also the necessity of exactly adjusting the pH-value of the dyebath for obtaining optimum effects.

It is an object of this invention to provide an improved process for the more complete dyeing of textile materials having a basis of a synthetic linear polyamide with a dyestuff for said material. Another object of this invention is the provision of an aqueous dyebath comprising an acid dyestuff, a complex metal dyestuff, a reactive dyestuff or a mixture thereof and a particularly effective dyeing assistant. Other objects of this invention will be apparent from the following detailed description and claims:

We have found that streak-free dyeings on textile materials having a basis of a synthetic linear polyamide with

acid dyestuffs as well as with complex metal dyestuffs and reactive dyestuffs are obtained, when carrying out the dyeing in the presence of a colorless compound of the formula



anion-active compound. It is preferred to use a ratio of 3 parts by weight of anion-active compound to 1 part by weight of cation-active compound.

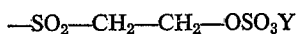
For stabilization, there may be added to the mixtures of anion-active and cation-active compounds, if desired or required, about 0.5–2% of a non-ionic surface-active compound, for example, the product obtained by the addition of 20–40 mols of ethylene oxide to 1 mol of an alkyl phenol having an alkyl radical with about 8–12 carbon atoms.

The dyeing conditions, such as the dyebath temperature, the pH of the dyebath, the proportion of dyestuff in the dyebath and the liquor ratio, may be varied as desired. Thus the dyebath is preferably heated to a temperature of at least 80 to 90° C.; mostly, the dyeing is carried out at the normal boiling point of the dyebath. Augmentation of the dyeing temperature to about 120–130° C. is possible, but is in most cases not necessary to obtain streakless dyeings with good depth of shade. The dyebath should have an acid pH. The pH value may range between about 3 and 6, preferably between 3 and 4.

In comparison with the quantity used of other known assistants, the small quantity of 0.5–3 percent by weight of the anion-active dyeing assistant or of the mixture of anion-active and cation-active substances according to the invention, which gives good results even with deep shades, is a considerable advantage. In many cases, a quantity of only 0.5–2 percent by weight, referred to the weight of the goods, will already be sufficient.

When using the compounds or mixtures according to the present invention, streakless, level dyeings on polyamide fibrous materials will be obtained. Changes of the depth of shade and of the shade itself do not occur or only in a practically insignificant degree. The drawbacks of the known processes are thereby obviated.

Furthermore, when using the products in the dyeing of polyamide fibers with acid wool dyestuffs, good wetting and rubbing fastnesses are obtained. Especially good results will in this case be obtained when using as anion-active compounds of the Formula I such as contain the group $-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{OSO}_3\text{Y}$ (Y having the meaning given in Formula I) and rinsing the goods after dyeing for 1 to 20 minutes at temperatures in the range of 60 and 90° C. with an aqueous alkaline bath in the presence of a high molecular compound containing at least 3 hydroxyl groups. During this treatment in the alkaline medium, there form reactive vinylsulfone groups in the anion-active dyeing assistant which cause cross-linking with the added compounds containing hydroxy groups. This fastness-improving treatment can also be carried out by padding with alkalis and compounds containing hydroxyl groups the dyeings produced on polyamide fabrics in the presence of compounds of the Formula I containing the group



and then further treating the fabric as usual on the stenter at temperatures in the range of 90 and 180° C. for a period from 30 seconds to 10 minutes.

As alkalis for the aftertreatment, there may be used in particular alkali metal hydroxides, alkali metal carbonates and alkali metal bicarbonates, as well as alkali metal salts of organic acids which pass over into hydroxides or carbonates at elevated temperatures. There are mentioned by way of example: sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, and the corresponding bicarbonates, sodium acetate, potassium acetate as well as the sodium or potassium salt of trichloroacetic acid.

The alkalis are generally used in amounts from about 0.3 to 10 percent by weight, preferably 0.3 to 5 percent

quantity should be so chosen as to give a pH of at least by weight, referred to the weight of the goods. The 8. If compounds are used, which pass into alkalies at elevated temperatures, for example, the sodium salt of trichloroacetic acid, one can work under neutral or weakly acid conditions.

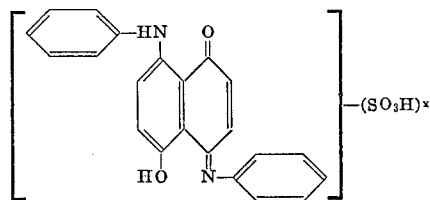
As higher molecular compounds of synthetic origin, with alcoholic hydroxyl groups, there enter into consideration for example, polyvinyl alcohols having K-values from about 10 to 100 (according to Fickentscher, *Cellulosechemie*, tome 13, page 58 (1932)), polyvinyl alcohols which can be either fully hydrolyzed or partly hydrolyzed and have a residual acetyl content of 0–90% as well as polyvinyl acetals containing hydroxyl groups, i.e. partly acetalized polyvinyl alcohols, for example, acetalized with formaldehyde, acetaldehyde, benzaldehyde or other aliphatic or aromatic aldehydes, with an acetalization degree of 0–99% and K-values from 10 to 100. Furthermore, copolymers of monomeric vinyl compounds such as vinyl chloride, acrylic acid esters, methacrylic acid esters, acrylonitrile, styrene, etc. with vinyl esters such as vinyl formiate, vinyl acetate, vinyl propionate, etc., into which hydroxyl groups have been introduced by partial hydrolysis. The proportion of vinyl ester groups in the mentioned copolymers can vary between 0.5 and 99%, the degree of hydrolyzation of the vinyl ester component can vary from about 10 to 100%. Furthermore, there are also suitable resins or partially hydrolyzed graft polymers of vinyl esters with polyethylene glycols, for example, those obtained according to the German specifications 1,081,229 and 1,094,457.

As hydroxyl-containing compounds of natural origin there may be used inter alia carbohydrates such as starches (wheat starch, rice starch, potato starch, etc.) tragacanth, tannine, locust bean flour as well as locust bean flours that are partially etherified with lower mono- or dihydric aliphatic alcohols having 1–4 carbon atoms, modified starch preparations for example, British rubber, sugar, and sugar alcohols, furthermore cellulose esterified with lower carboxylic acids or lower alcohols having 1–4 carbon atoms or etherified cellulose, for example, methyl cellulose, carboxymethyl cellulose, etc.

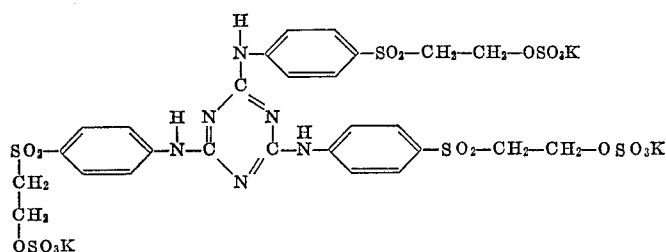
The following examples illustrate the invention, but they are not intended to limit it thereto:

Example 1

100 parts of a polyamide fabric consisting in warp and beam of endless filaments, normally dyeing with streaks only, are dyed in a closed dyeing apparatus for 1 hour at 100° C. with 2 parts of an acid wool dyestuff strongly responding to yarn irregularities and having the general formula



3 parts of acetic acid (30% strength)
3 parts of the compound



1000 parts of water. After having brought the dyebath to the above temperature in the course of 40-50 minutes. After rinsing and drying, there is obtained a streakless, fast, grey dyeing.

An improved fastness can be obtained, when treating the goods in the first rinsing bath with

- 2 parts of sodium trichloroacetate, or
- 2 parts of sodium bicarbonate alone or together with
- 2 parts of tannine for 20 minutes at 60-80° C.

Equally good results are obtained when carrying out the process with 2 parts of a sodium hydroxide solution (32.5%) at 20° C.

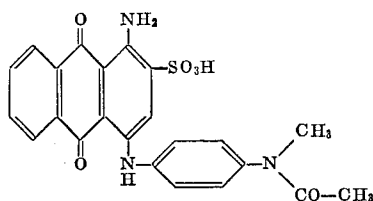
The described aftertreatment can be carried out by padding on a foulard and drying the dyed fabric on a stenter for 5 minutes at 140° C.

In each case, dull colored goods having a convenient handle are obtained.

Example 2

100 parts of the fabric described in Example 1 are dyed as described in Example 1 with a dyebath having the following composition:

- 3 parts of the acid wool dyestuff of the constitution



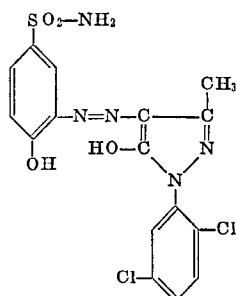
- 0.5 part of a condensation product of 1 mol of stearyl amine and 12 mols of ethylene oxide (30% strength),
- 1.5 parts of 2,4,6-tri-(1-aminobenzene-4-sodium sulfonate)-s-triazine,
- 3 parts of acetic acid (30% strength),
- 1000 parts of water.

When dyeing at a temperature of 100° C., there is already obtained a fast, streakless blue dyeing. Dyeing temperatures of 130° can also be used with good results.

As cation-active compound there can be used instead of 0.5 part of the condensation product of 1 mol of stearylamine and 12 moles of ethylene oxide, with the same success 1 part of polyvinylpyrrolidone.

Example 3

100 parts of the polyamide fabric which can be dyed with streaks only and which is described in Example 1, are dyed with 2 parts of the complex chrome 2:1 dyestuff obtained from 2 molecules of the following compound:



- 3 parts of 2,4,6-tri-(1-aminobenzene-3-potassium sulfonate)-s-triazine,

1 part of the condensation product from 6 mols of formaldehyde, 1 mol of melamine and 1 mol of the product of the addition of 30 mols of ethylene oxide to 1 mol of triethanolamine, prepared by condensation in an acid medium, and subsequently quaternized with dimethyl sulfate,

- 0.75 part of the product of the addition of 30 mols of ethylene oxide to 1 mol of nonyl phenol (30% strength),

3 parts of acetic acid (30% strength),

1000 parts of water, in a closed dyeing apparatus, while bringing the bath to the above temperature of 100° C. in the course of 1 hour, dyeing for 45 minutes at this temperature and finally dyeing for 15 minutes at 120° C.

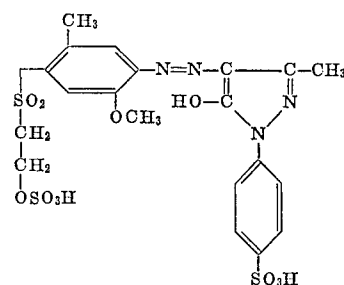
After rinsing and drying, there is obtained a streakless, orange dyeing having good fastness properties.

Instead of the above described cation-active product, there can be used with the same success 1 part of a compound obtained by heating 213 g. of the product of the addition of 616 g. (14 mols) of ethylene oxide to 93 g. (1 mol) aniline with 28.2 g. of phenol and 60 cc. of formaldehyde solution of 30% strength in the presence of 40 cc. of sulfuric acid of 64% strength, while stirring and in the course of 50 minutes, to 100-105° C., adjusting the pH-value of the solution to 9 by adding sodium hydroxide solution, and methylating the condensation product at 50-60° C. by adding 91 g. of dimethyl sulfate, whereupon 291 g. of the quaternary condensation product are obtained in the form of a solution.

Example 4

100 parts of the polyamide fabric described in Example 1 which can be dyed with streaks only are dyed under the conditions described in Example 1 with a dyebath having the following composition:

- 2 parts of the reactive dyestuff of the constitution



- 3 parts of 2,4,6-tri-(1-aminobenzene-3-potassium sulfonate)-s-triazine,

1 part of the condensation product from 12 mols of ethylene oxide and 1 mol of stearylamine (30%),

- 2 parts of acetic acid (30% strength),
- 1000 parts of water.

After rinsing and drying, there is obtained a streakfree fast yellow dyeing corresponding in depth of shade and shade to an untreated dyeing.

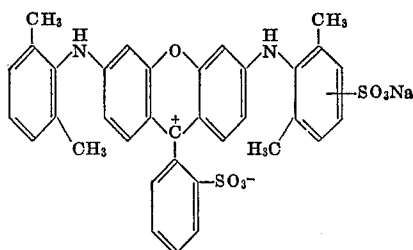
9

Example 5

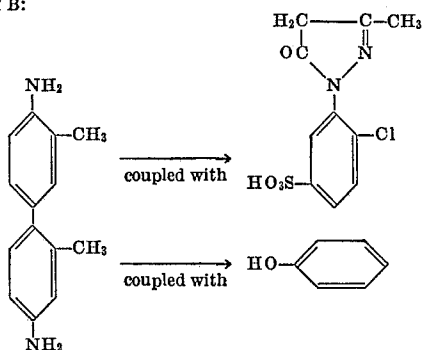
100 parts of the fabric of polyamide described in Example 1, which can be dyed with streaks only, are dyed with a combination of acid dyestuffs of

4 parts of the red dyestuff A
3.6 parts of the yellow dyestuff B
0.05 part of the blue dyestuff C,

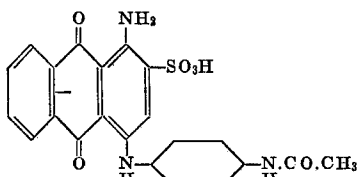
Dyestuff A:



Dyestuff B:



Dyestuff C:



1.6 parts of 2,4,6-tri-(1-aminobenzene-3-potassium sulfonate)-s-triazine,
0.5 part of the condensation product of 12 mols of ethylene oxide and stearyl amine (30%),
3 parts of acetic acid (30% strength), and
1000 parts of water for 1 hour at 100° C., rinsed and dried.

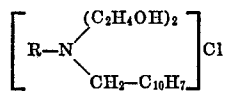
There is obtained a red, streakfree and level dyeing corresponding to an untreated dyeing with regard to depth of shade and shade.

Instead of 1.6 parts of 2,4,6-tri-(1-aminobenzene-3-potassium sulfonate)-s-triazine, there may also be used 1.6 parts of 2,4,6-tri-(1-aminobenzene-2-sodium sulfonate)-s-triazine.

Example 6

100 parts of the fabric described in Example 1 are dyed, after singeing, for 10 minutes at 30° C., with a bath having the following composition:

1000 parts of water,
3 parts of 2,4,6-tri-(1-naphthylamino-3,6-disulfonic acid)-s-triazine,
1 part of the compound

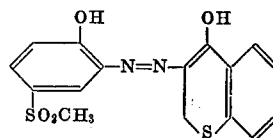


(R meaning soya bean oil)

0.25 part of a nonyl phenol oxethylated with 20 mols of ethylene oxide, and
3 parts of acetic acid (30% strength).

10

To the dyebath are then added through a sieve 3 parts of the complex chrome 2:1 dyestuff of 2 molecules of the following composition



as aqueous solution, the whole is heated within 30 minutes to 100° C. and dyeing is carried out for 60 minutes at this temperature.

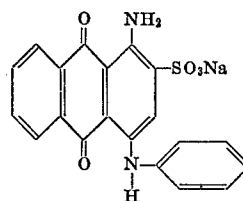
The dyed goods are then rinsed and dried. There is obtained a level grey dyeing.

Without the addition of the dyeing assistant, the nodules formed by the singeing would be dyed deeper owing to their greater affinity for the dyestuff than the fabric.

Example 7

100 parts of the fabric described in Example 1 are dyed for 15 minutes at 30° C. with a bath having the following composition:

1000 parts of water,
3 parts of 2,4,6-tri-(1-aminobenzene-2,4-disulfonic acid)-s-triazine,
1 part of the condensation product of 6 mols of ethylene oxide and 1 mol of laurylamine, and
3 parts of acetic acid (30% strength).
2 parts of the dyestuff of the formula

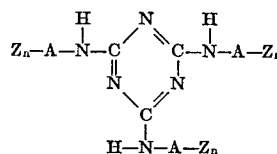


are then added to the dyebath through a sieve, the whole is heated within 40 minutes to the boiling temperature and dyeing is carried out for 60 minutes at 100° C.

After rinsing and drying, there is obtained a level streakfree royal blue dyeing.

We claim:

1. A symmetrical 2,4,6-triazine of the formula

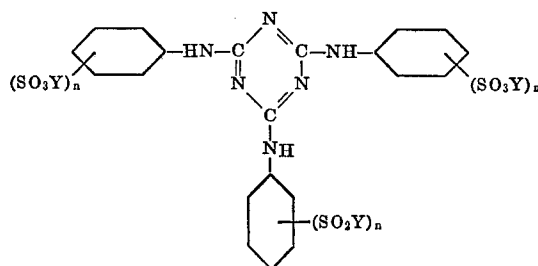


in which A is lower alkylene, phenylene or naphthylene, Z is $-\text{SO}_3\text{Y}$, $-\text{OSO}_3\text{Y}$, $-\text{COOY}$ or



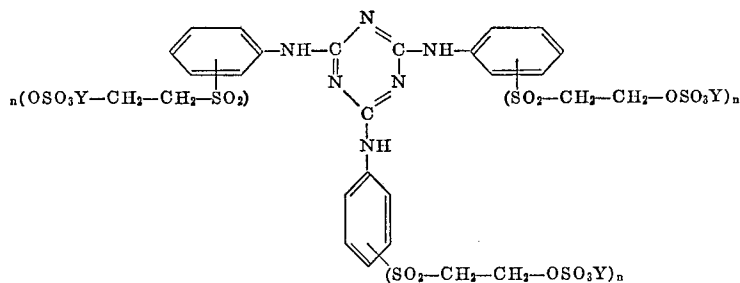
Y is hydrogen or a salt-forming cation, and n is an integer from 1 to 3, provided that when Z is $-\text{SO}_3\text{Y}$ and $-\text{COOY}$, n is an integer from 2 to 3.

2. A symmetrical 2,4,6-triazine of the formula



in which Y is hydrogen or an alkali metal cation and n is 2.

3. A symmetrical 2,4,6-triazine of the formula



in which Y is hydrogen or an alkali metal cation and n is 1 or 2.

References Cited

UNITED STATES PATENTS

2,742,466 4/1956 Randall et al. ----- 260—249.5

OTHER REFERENCES

Beilstein's Handbuch der Organischen Chemie, vol. 26, 4th ed., p. 75, system No. 3889, Erstes Ergänzungs-
werk (1938).

JOHN D. RANDOLPH, *Primary Examiner*.