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## PROCESS FOR THE DYEING OF FIBROUS MATERIALS

Walter Kling, Ernst Goette, Kurt Heide, and Herbert Gerstner, Chemnitz, Germany, assignors, by mesne assignments, to "Patcheni" Aktiengesellschaft zur Beteiligung an Patenten und sonstigen Erfindungsrechten auf chemische Verfahren, Zurich, Switzerland, a Swiss corporation

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This invention relates to the dyeing of fibrous materials and has for its principal object improvements in dyeing processes of varied character, and in the baths which are employed in dyeing, whereby such processes may be facilitated and greater uniformity and deepening of the color in the finished product may be secured.

It is one of the features of the invention that the field of use of conventional deystuffs is materially extended. For instance, in the dyeing industry it has hitherto been accepted as an axiom that certain dyestuffs may be satisfactorily used only for vegetable fibers, others essentially only for animal fibers. It is now discovered that with the aid of compounds which are capable of giving off surface active cations in dyeing and printing, the power of attraction or affinity of the direct dyes and acid dyes can be so affected that pure cotton dyestuffs can be employed for the dyeing of woolen materials or, alternatively, pure wool dyes can be brought to a state of complete absorption on cotton fibers or artificial silk. Furthermore, by suitable use in the dye bath of these compounds, a material deepening of the dye colors is obtained regardless of the nature of the fiber.

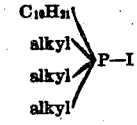
Among the more important compounds which yield surface active cations are the high molecular quaternary ammonium compounds, ammonium salts containing high molecular aliphatic residues, and in particular the compounds derived from heterocyclic nitrogen bases, such as the pyridine bases, these being the most readily accessible. There may be employed, for example dodecyl pyridinium sulphate and the homologues and substitution products thereof, further analogous compounds with unsaturated hydrocarbon residues, for example the corresponding octadecenyl and undecenyl compounds, further substitution products of all these compounds, as well as the corresponding halides. Analogous derivatives of other heterocyclic nitrogen bases such as quinoline and isoquinoline may also be employed.

Less readily accessible but similarly useful are the quaternary ammonium compounds derived from diamines and containing higher alkyl or aliphatic acid residues as well as similar compounds derived from aliphatic tertiary amines, for example triethyl cetyl ammonium iodide or bromide.

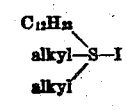
In lieu of the quaternary ammonium compounds, the analogous high molecular phosphonium or sulphonium compounds may be used, for instance decyl phosphonium iodide, dodecyl phosphonium bromide, tetradecyl phosphonium bromide, octadecenyl phosphonium iodide, dodecyl sulphonium iodide, octadecyl sulphonium bromide.

The following compounds have proven satisfactory in addition to those mentioned specifically hereinbefore: tetradecyl, hexadecyl, and octadecyl pyridinium sulfate, undecenyl, dodecyl, tetradecyl, octadecyl, octadecenyl chinolium sulfate, decyl pyridinium bromide, hexadecenyl chinolinium iodide, quaternary ammonium compounds derived from asymmetrical oleyl-diethyl-ethylenediamine by addition of dimethyl sulfate or diethyl sulfate or methyl iodide, heptyl-i-urea bromide, decyl-i-thiourea iodide, hexadecyl-i-thiourea iodide, the addition products of tetradecyl bromide or dodecyl iodide to hexamethylenetetramine, heptyl guanidine, tolyl guanidine, the quaternary ammonium compound prepared by the addition of the dodecyl ether of α-glycerine bromhydrine $C_{11}H_{23}CH_2.O.CH_2CHOH.CH_2Br$ to pyridin, the quaternary ammonium compound formed by the addition of bromine-acetic acid dodecyl ester $BrCH_2.COO.CH_2.C_{11}H_{23}$ to chinoline. The following examples of specific compounds indicate generally the nature of the formulae so far as they are known:

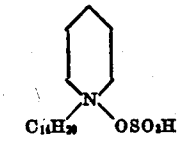
Decyl phosphonium iodide



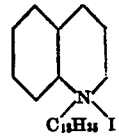

Dodecyl sulphonium iodide



Tetradecyl pyridinium sulphate



Octadecenyl chinolinium iodide



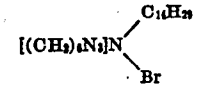
Heptyl isourea bromide

$[H_2N.C(O.C_7H_{15}):NH]Br$

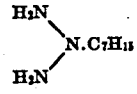
Decyl isothiourea iodide

$[H_2N.C(S.C_{10}H_{21}):NH]I$

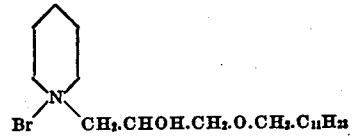
Addition product of tetradecyl bromide to hexamethylene-tetramine



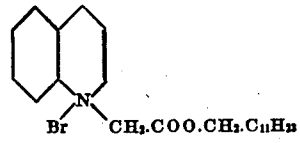
Heptyl guanidine



Addition product of glycerine bromhydrine dodecyl ether to pyridine



Addition product of bromine-acetic acid dodecyl ester of chinoline



These compounds may be added either directly to the dye bath or employed for preliminary treatment of the material to be dyed. Thus an extraordinary deepening of the dye color may be obtained if, for example, a vegetable fibrous material is pretreated with a substance giving off surface active cations in aqueous solution and thereafter dyed with direct dyestuffs. By means of such pretreatment it is not only possible to promote the absorption of direct dyes by vegetable fibers, but the process is even applicable to the satisfactory dyeing of wool and the like by such dyes which normally do not adhere to animal fibers.

For example if an attempt is made to dye wool with 2% Sirius orange G (Schultz, Dye Tables, 7th edition, volume 2, page 198) with the simultaneous employment of 20% sodium chloride in the absence of acid, only a soiling of the fiber occurs, and this can be almost completely removed by washing. On the other hand, if the wool is treated before dyeing with a compound such as hereinbefore described, for instance dodecyl pyridinium sulphate, strong and fast colors can be produced by the subsequent dyeing operation, the operation being facilitated, if necessary, by the further addition of a less quantity of a substance yielding surface active anions, for example a fatty alcohol sulphate or sulphonate. The coloring of the fabric is still further improved if, after the preliminary treatment with dodecyl pyridinium sulphate or an analogous compound, the material is dyed in a dye bath to which has been added a mixture of both types of compound hereinbefore referred to, for instance one part sodium salt of the technical dodecyl sulphuric acid ester and three parts of dodecyl pyridinium sulphate.

In lieu of the fatty alcohol sulphuric acid esters and their salts, which are preferred for the purposes herein indicated as surface active anion yielding compounds, various substitutes may be employed, such as all high molecular aliphatic or cycloaliphatic sulphuric acid esters or true sulphonic acid as well as corresponding phosphoric acid esters. The alkali salts of sulphuric acid esters of the low boiling portions of the alcohols corresponding to the fatty acids of coconut oil, obtainable from the latter by reduction, are particularly satisfactory. Such alcohol mixtures contain principally the alcohols of 6 to 12 carbon atoms.

As applied to the dyeing of animal fibers with acid dyes, the use of quaternary ammonium salts promotes the absorption of the dyes at lower temperatures, for instance 40° C. which is important when sensitive materials are to be dyed. It is also feasible, however, to bring acid dyes to absorption on plant fibers such as cotton or artificial silk, if such fibers are given a preliminary treatment with dodecyl pyridinium sulphate or the like and then dyed either in the normal manner or with the addition to the dye bath of a mixture of dodecyl pyridinium sulphate and fatty alcohol sulphate in which the former predominates.

This process is particularly important in the dyeing of part wool material, since the same dyestuff can be employed to obtain uniform coloring of both types of fiber present in the mixed woven goods. Thus mixed goods of animal and plant fiber can be treated, for instance, with a mixture of wool dye and direct dye after a preliminary treatment of the mixed goods with dodecyl pyridinium sulphate or the like, thereby causing both dyes to be absorbed uniformly by both kinds of fiber.

As an example, by means of Sirius orange C and alizarin blue (pure) B (German Patent 126,392) with admixture of 20% common salt, a greenish coloring of both kinds of fiber of the mixed goods may be secured, whereas without the preliminary treatment the animal fiber would be colored blue and the plant fiber yellow.

The promotion of the absorption of direct dyes by animal fibers is a matter of great importance and may be facilitated by adding to the dye bath a quaternary ammonium compound or the like. The use of such compounds in the silk dyeing industry is also of importance, particularly in dyeing at lower temperatures, such temperatures being frequently necessary in the batik industry because of the low melting point of the waxy masses serving as a reserve.

It is further possible, by a preliminary treatment of acetate silk with dodecyl pyridinium sulphate or similar compounds, to cause direct dye stuffs to adhere to the fibers, such adherence being possible heretofore only through surface saponification of the cellulose acetate. In dyeing with the acid dyes heretofore used for acetate silk, commonly referred to as cellite fast dyes, the preliminary treatment with surface active qua-

ternary ammonium salts results in the establishment of appreciably darker dye shades.

It has also been found that substances capable of giving off surface active cations in aqueous solution are effective equalizing agents in the promotion of level dyeing when basic dyestuffs are employed, the use of such substances rendering superfluous the numerous precautionary measures heretofore adopted for the purpose of obtaining uniform dyeing, considerable simplification of the dyeing procedure resulting. Thus in the case of dyeing with basic dye stuffs on premordanted goods, it has heretofore been necessary to ensure that the mordant should be used in the proper ratio to the strength of the dyestuff, goods too strongly premordanted absorbing the dye too rapidly and consequently promoting uneven dyeing. It was also considered necessary to add the dyestuff in portions to the bath and to begin dyeing in the cold, gradually increasing the temperature. All of these precautionary measures have been found unnecessary, if substances giving off surface active cations such as hereinbefore enumerated are employed.

For example, if we dye artificial silk premordanted with 6% catanol ON (Schultz, Dye Tables, 7th edition, volume 2, page 303) at 70° C. with 0.5 gram malachite green (German Patent 4,332) and fail to employ the special agent defined herein, the dyeing will be wholly uneven. On the contrary, if one gram per liter of dodecyl pyridinium sulphate is added to the dye bath, the dyeing will be quite uniform and so strongly retained that the bath is not extracted and the coloring is correspondingly light. If a smaller quantity of this special agent is employed, or if a second agent giving off surface active anions is subsequently added, for instance the alkali salt of a fatty alcohol sulphuric acid ester, a complete extraction of the dye bath can be effected and a very even coloring obtained.

By suitable treatment of the bath with the proper proportions of the surface active cation and anion yielding substances, which to the extent indicated above oppose each other, the dyeing process may be very accurately controlled and any desired degree or speed of extraction can be obtained, so that the dyeing may be carried out wholly independently of conditions heretofore considered absolutely necessary.

It has also been found that the depth of the color dyed as well as the dyeing throughout of thick materials in the employment of vat dyes can be effectively promoted in accordance with the slop padding process if the fibrous materials are treated with substances giving off surface active cations prior to the slop padding of the dye stuff. As heretofore indicated, such substances as the quaternary higher molecular ammonium compounds and particularly those derived from heterocyclic nitrogen bases, such as pyridine for example, are of special importance in this connection since they are more readily accessible.

*Example I*

Artificial silk is given a preliminary treatment with a solution of three grams per liter of dodecyl pyridinium sulphate in the dye bath proportion of 1:20 at 70° C., centrifuged off, and then slop padded with 1 gram per liter indanthrene blue-green, B powder (Schultz, Dye Tables, 7th edition, volume 2, page 127) with a dye bath ratio of 1:20 and a temperature of 50° C. After twenty minutes it is wound off as uniformly as possible and developed in a fresh bath containing 20 cm. per liter sodium hydroxide 32° Bé. and 5 grams per liter of hydrosulphite at 50° to 60° C. An intense green color is obtained, whereas without such preliminary treatment a materially less intense coloration results.

In the making of aniline black dyes and other oxidation dyes it has been previously the custom to employ boiled and bleached fibrous materials, since it was believed that uniform precipitation of the dye could not be obtained on unsized, unbleached raw materials. It is now found that oxidation dyes can be printed or dyed with excellent results on unsized, unbleached raw materials, provided substances capable of giving off surface active cations are added to the dye baths. For instance to a dye bath containing aniline salt or salts of other suitable aromatic bases such as p-phenylene diamine, or n-amino phenol, special agents of the character hereinbefore described, and particularly quaternary ammonium salts with high molecular aliphatic residues, can be added.

In addition to the excellent wetting and equalizing action of such agents, the fibers are saved and the resistance to tearing exhibited by the goods before treatment is much less adversely affected than if such agents are not employed. These advantages are also derived in some degree by the use of such agents in dyeing and printing on preliminarily bleached materials, although the equalizing action is particularly striking when comparison is made of the action of the dyes on unfinished goods produced with and without the addition of the quaternary ammonium salt or the like.

*Example II*

Piece goods which have not been prewetted or boiled are impregnated on a suitable dye spreading machine with a solution of

| | Grams |
|---|---|
| Aniline chlorhydrate | 100 |
| Aniline | 4–5 |
| Sodium sulphite | 2 |
| Potassium ferrocyanide | 84 |
| Sodium chlorate | 36 |
| Decyl pyridinium sulphate | 2–4 |

per 1.2 liters of the bath

The goods are then dried, briefly steamed, treated with chromate, washed, and dried. An excellent dye color and a deep even black results. Before the steaming or before the impregnation a suitable reserve can be impressed by known methods for the production of patterned goods.

The various other agents hereinbefore indicated can be substituted for the dodecyl pyridinium sulphate employed in the preceding example. Thus the various quaternary compounds which are derived from tertiary heterocyclic bases, such as pyridine and quinoline and their homologues and their derivatives, are particularly satisfactory. Triethyl cetyl ammonium halides and other compounds with 4 alkyl residues, at least one of which is high molecular, and quaternary ammonium salts derived from monoacylated diamines, for example oleyl diethyl ethylene diamine, as well as corresponding phosphonium and sulphonium compounds with high molecular substituents, may be used.

*Example III*

In a single bath which contains

| | Grams |
|---|---|
| Aniline salt | 100 |
| p-Phenylenediamine | 4–8 |
| Ammonium sulphite | 3 |
| Sodium chlorate | 30 |
| Copper sulphate | 3 |
| Dodecyl pyridinium sulphate | 2–4 |

per 1 liter of bath

cotton yarn, not prewetted or boiled, is dyed green, oxidized and washed. The black yarn obtained is very uniform, deep black, proof against rubbing off, does not turn green, and exhibits an excellent degree of fastness.

*Example IV*

A solution consisting of

| | Grams |
|---|---|
| p-Phenylenediamine | 15–20 |
| Sodium sulphoxylate | 1–1.5 |
| Sodium chlorate | 15–20 |
| Ammonium chloride | 15–20 |
| Tartar emetic | 1 |
| Hexadecyl pyridinium chloride | 2– 5 |
| Ammonium vanadate solution 1:1000 | 20 |

per 1 liter of bath

is slop padded on a suitable machine on a nonbleached goods, dried, and finished in unprinted or printed condition in the usual way. The resultant product is a uniform, brown colored or uniformly patterned goods.

In vat dyeing it has heretofore been customary, in order to secure uniformity, to add to the vats ricinoleic soaps, sulphonated oils, Turkey red oil soap, and similar agents. Subsequently, in order to secure in such a process a stronger adherence of the dye, still more dye must be added to the dye bath, since the known leveling means retains a portion of the dye in the bath and prevents its absorption. It is found that by the employment of two different types of surface active substances in the vat dyeing of cotton, artificial silk, linen, wool, and other fibers, results can be obtained which far exceed those secured by prior dyeing processes.

As has been hereinbefore briefly indicated, the addition to the vat of wetting agents which form surface active cations, particularly quaternary ammonium salts containing high molecular aliphatic residues, an extraordinarily strong retentive action is exerted on the vat dye; with the employment of amounts greater than some tenths of a gram per liter, the effect is almost equivalent to reserve action. By then adding wetting agents which form surface active anions, for example by adding suitable amounts of the fatty alcohol sulphates or sulphonates hereinbefore described, the dye retaining action can be advanced or retarded at will. By this process any degree of absorption of the dye originally retained can be secured by properly balancing the action of the two special ingredients; under some conditions complete extraction from the bath can be secured. Since the admixture can be gradually effected, the capillarity of the dye can be made stronger the longer the dyeing is continued.

If desired the process may be carried out by the initial addition of a quaternary, high molecular ammonium salt or the like to a strongly stripping vat bath, a surface active anion yielding substance being thereafter added, for instance the sodium salt of a fatty alcohol sulphuric acid ester, more dyestuff introduced and dyeing continued. It is frequently advantageous to try a parent solution of the quaternary ammonium salt in order to weaken the powerful action and to carry out the proper treatment of the bath. The fatty alcohol sulphate or the like can also be prepared in the form of a parent solution, but this is ordinarily not necessary.

In addition to effective leveling action obtained by this process, there is a marked improvement in the dyeing through the entire depth of very tightly woven goods and highly twisted yarns. The vats last, stay clear, show a very slight bloom, foam, and exhibit at the same time intensive wetting action. The process is particularly advantageous when applied to operations which are generally carried out on machines but which required dyeing in the vat when difficultly leveled dyes were employed owing to the slow movement of the machines.

*Example V*

In the dyeing of indanthrene blue-green FFB powder (Schultz, Dye Tables, 7th edition, volume 2, page 127) in bright color on bleached, mercerized cotton yarn, where the main requirement is uniformity, the following vat dye may be used for the dyeing of 50 kgs. of goods:

| | | |
|---|---|---|
| Water 60° C | liters | 1000 |
| Soda solution 34° Bé | do | 15 |
| Hydrosulphite conc. P | kilograms | 2 |
| A 40% aqueous solution of lauryl pyridinium sulphate | cubic centimeters | 500 |
| Dyestuff in powder form, reduced in the main vat | grams | 250 |

The goods are introduced, soaked for twenty minutes, and then stretched out.

500 ccm. of a 30% aqueous solution of sodium salts of fatty alcohol sulphuric acid esters from the low boiling fractions of the alcohols obtained by reduction of the fatty acids, are then added and dyeing is continued. In order to obtain the standard product, 100 grams of dyestuff are added, reduced in the vat, and complete dyeing follows.

After the addition of the fatty alcohol sulphate, a strong leveling action is invariably observed, which in the present instance is maintained for the purpose of securing better dyeing all the way through, the action being undiminished by further addition of larger quantities of fatty alcohol sulphate. The somewhat higher consumption of dyestuff is an immaterial factor in the total cost.

*Example VI*

Unbleached mercerized cotton yarn is dyed a medium dark color by indanthrene brilliant violet 4 R powder (Schultz, Dye Tables, 7th edition, volume 2, page 128), the goods being treated in four portions of 50 kgs. each.

To the first portion, which is prewetted, the following vat dye is added:

| | | |
|---|---|---|
| Water 60° C | liters | 1000 |
| Soda solution 34° Bé | do | 15 |
| Hydrosulphite conc. powder | kilograms | 3 |
| Indanthrene brilliant violet 4 R powder reduced in the main vat | grams | 500 |
| Lauryl pyridinium sulphate solution as in Example V | cubic centimeters | 500 |

The goods are introduced, soaked for ten minutes, and then stretched out. 1000 ccm. fatty alcohol sulphate solution as in Example V is

added, and the dyeing resumed for thirty minutes more. The bath can then be diluted further by additional quantities of fatty alcohol sulphate. If the remaining portions of the goods are to be dyed in a running bath, the further addition of fatty alcohol sulphate is dispensed with, 200 grams of dyestuff is added, reduced, and the dyeing is finished after thirty minutes.

The second portion of goods, which is still dry, is treated in the dye bath already used, the latter being first heated to 60° C. and 200 ccm. lauryl pyridinium sulphate solution added as in Example V. The bath is thus altered so that the dye no longer penetrates, and the dye bath has been converted into a wetting bath. The goods introduced in this bath is given a preliminary wetting without risk of uneven precipitation, those portions of the goods more strongly wetted being hardly affected by the dye. Wetting is continued for twenty minutes and there is then added to the bath 400 ccm. of a fatty alcohol sulphate solution as described in Example V, the goods being again immersed. Dyeing is now effected since the bath has a dye character. The goods are then stretched, 400 grams of dyestuff, already reduced, are added, and the dyeing continued and completed.

The third and fourth portions of the material are dyed in the same manner as the second portion.

In lieu of the indanthrene dye employed in the preceding examples, indigo and indigoid vat dyes as well as all other vat dyes can be employed both in the hydrosulphite bath and in other vats, the same advantages being obtained.

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent is:

1. A process of dyeing fibrous materials with direct or acid dyes which comprises pretreating the material with a bath containing a substance yielding surface active cations, and thereafter dyeing the material in a dye bath to which is added a smaller quantity of a substance yielding surface active anions.

2. A process of dyeing fibrous materials with direct or acid dyes which comprises pretreating the material with a bath containing a quaternary ammonium compound, and thereafter dyeing the material in a dye bath to which is added a smaller quantity of a higher fatty alcohol sulphate.

3. A process for improving the action of basic dyestuffs which comprises adding to the dye bath a substance yielding surface active cations and a less quantity of a substance yielding surface active anions.

4. A process for improving the dyeing and printing of unsized, unbleached fibrous material with oxidation dyes, which comprises introducing in the dye bath a substance yielding surface active cations.

5. A process of dyeing animal and vegetable fibers in approximately the same shade which comprises treating such material with the dye in the presence of a substance yielding surface active cations and a smaller quantity of a substance yielding surface active anions.

6. A process of dyeing animal and vegetable fibers in approximately the same shade which comprises treating such material with the dye in the presence of a quaternary high molecular ammonium compound and a smaller quantity of a sulphuric acid ester of a higher fatty alcohol.

7. A mixed animal and vegetable fiber impregnated with a substance yielding surface active cations and a smaller quantity of a substance yielding surface active anions and dyed in a uniform shade.

8. The process for dyeing mixed fabrics containing an animal and non-animal fibrous material which comprises treating the mixed fabric with a bath containing an acid dyestuff in the presence of a water soluble cation-active substance containing a tetravalent sulfur hetero atom and an alkyl radical of at least ten carbon atoms.

9. The process for dyeing mixed fabrics containing an animal and non-animal fibrous material which comprises treating the mixed fabric with a bath containing an acid dyestuff in the presence of a water soluble cation-active substance containing a pentavalent phosphorous hetero atom and an alkyl radical of at least ten carbon atoms.

WALTER KLING.
ERNST GOETTE.
KURT HEIDE.
HERBERT GERSTNER.