United States Patent

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[54] **PROCESS FOR DYEING ANIONIC MODIFIED SYNTHETIC FIBERS IN DYE BATHS CONTAINING AN ORGANIC NITROGEN COMPOUND**
9 Claims, No Drawings

[52] **U.S. Cl.** **8/172**
[51] **Int. Cl.** **D06p 5/06**
[50] **Field of Search** ..... 8/166, 172, 92, 94, 178, 179, 177 AB

[56] **References Cited**

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ABSTRACT: Synthetic fibers containing anionic groups, e.g. polyacrylonitrile modified with sulfonic acid groups, are dyed by exhaustion in a dyebath comprising:

A. hydrocarbon chloride solvent;

B. 0.1 to 4% of water based on the solvent;

C. a basic dyestuff soluble in hydrocarbon chloride solvent; and

D. an organic nitrogen compound containing at least 12 carbon atoms, e.g. a fatty amine such as dodecylamine.

PROCESS FOR DYEING ANIONIC MODIFIED SYNTHETIC FIBERS IN DYE BATHS CONTAINING AN ORGANIC NITROGEN COMPOUND

This invention relates to the dyeing of fiber materials and more particularly to the dyeing of anionic groups containing synthetic fiber materials from hydrocarbon chloride solutions containing the dyestuffs in the form of hydrocarbon chloride soluble dye bases or hydrocarbon chloride soluble salts or adducts of the dye bases, furthermore amines, amides and/or amine oxides containing at least 12 carbon atoms and 0.1 to 4 percent by weight of water.

The hydrocarbon chlorides used in the process according to the invention are especially those whose boiling point lies between 40° and 150° C., for example aliphatic hydrocarbon chlorides such as methylene chloride, chloroform, carbon tetrachloride, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, pentachloroethane, 1-chloropropane, 2-chloropropane, 1,2-dichloropropane, 1,1,2,3,3-pentachloropropane, 1-chlorobutane, 2-chlorobutane, 1,4-dichlorobutane, 1-chloro-2-methylpropane, 2-chloro-2-methylpropane, 4-chloro-2-methylpropane, or 1,6-dichlorohexane, and aromatic hydrocarbons such as chlorobenzene and chlorotoluene. Tetrachloroethylene, trichloroethylene and 1,1,1-trichloropropane have proved to be especially satisfactory.

Amines, amides or amine oxides having at least 12 carbon atoms, employed in the process according to the invention include the following: unsubstituted and substituted aliphatic, araliphatic, aromatic, heterocyclic and cyclic mono and polyamines, e.g., fatty amines such as dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, octadecenylamine, as well as ethoxylation and propoxylation products thereof, technical mixtures of fatty amines such as coco fat amine, sperm oil fat amine as well as ethoxylation and propoxylation products thereof; also:

N,N-dimethyl-N-dodecylamine,
N,N-dimethyl-N-hexadecylamine,
N,N-dimethyl-N-octadecenylamine,
Octadecyl hydrazine,
N,N-dimethyl-N-(dodecanoylamino methyl)amine,
N,N-diethyl-N-(beta octadecanoylamino ethyl)-amine,
N,N-dimethyl-N-(gamma octadecanoylamino propyl)amine,
N,N-dimethyl-N-[gamma-(N'-octadecyl carbaminyl) amino propyl]amine,
N,N-dimethyl-N-(gamma octadecylsulfonylamino) propylamine,
N,N-dimethyl-N-(gamma oleoylaminopropyl) amine,
N-methyl-N,N-bis-[gamma-(octadecanoylamino) propyl] amine,
N-methyl-N,N-bis-[gamma-(dodecanoylamino)-propyl] amine,
N-methyl-N,N-bis-[gamma-(oleoylamino) propyl] amine,
N,N-dimethyl-N-(beta octadecyloxy ethyl) amine,
N-methyl-N-beta-hydroxyethyl-N-[(gamma-octadecanoylamino) propyl] amine,
N-methyl-N-beta-hydroxyethyl-N-[gamma-(oleoylamino) propyl] amine,
N-methyl-N-[gamma-(octadecanoylamino) propyl]-N-(beta-octadecanoyl oxyethyl) amine,
N-methyl-N-bis-[beta-octadecenoyloxyethyl] amine,
N-(beta-octadecenoyloxyethyl) amine,
N-beta-oxyethyl-N-(beta-octadecenoyloxyethyl) amine,
N,N-dimethyl-N-[beta-(N'-octadecylcarbaminyl)-oxyethyl] amine,
N,N-bis-(beta-hydroxyethyl)-N-stearylamine,
N-methyl-N-benzyl-N-dodecylamine,
N,N-dimethyl-N-(2-oxy-5 tert butylbenzyl) amine,
N,N-dimethyl-N-[(2-hydroxynaphthyl-1-)methyl] amine,
N,N-dimethyl-N-(4-dodecylphenyl)amine,
N,N-dimethyl-N-(4-dodecanoyl-phenyl) amine,
N-dodecyl morpholine,
N-hexadecyl morpholine,

N-dodecyl piperidine,
N-hexadecyl piperidine,
Hexadecyl pyridine,
N-dodecyl-imidazole,
N-dodecyl benzimidazole,
N-1-(beta-hydroxyethyl)-2-octadecyl imidazoline,
unsubstituted and substituted carboxylic acid amides, e.g., mono and polyfunctional fatty acid amides of mono and polyamines, e.g.,
lauric acid methylamide,
lauric acid dimethylamide,
lauric acid ethylamide,
lauric acid diethyl amide,
tridecyl acid dimethylamide,
tridecyl acid diethyl amide,
tridecyl acid dibutylamide,
myristic acid dimethyl amide,
myristic acid diethyl amide,
palmitic acid diethyl amide,
palmitic acid ethyl amide,
stearic acid ethyl amide,
stearic acid ethanol amide,
oleic acid ethyl amide,
oleic acid ethanol amide,
lauric acid diethanol amide,
tridecyl acid diethanol amide,
myristic acid diethanolamide,
pentadecyl acid diethanol amide,
palmitic acid diethanol amide,
heptadecyl acid diethanol amide,
stearic acid diethanol amide,
oleic acid diethanol amide,
oleic acid propylamide,
oleic acid isopropyl amide,
oleic acid butyl amide,
oleic acid isobutylamide,
oleic acid hydrazide,
N,N-dimethyl-N'-oleoyl hydrazine,
N-oleyl-1,2-diamino ethane,
N-oleoyl-N,N'-dimethyl diamino ethane,
N-oleoyl-1,2-diamino propane
N-oleoyl-N'-dimethyl-propylene diamine-(1,3),
N-stearyl-N'-diethyl propylene diamine-(1,3),
N-palmityl-N'-palmityl-N'-methylpropylene diamine,
or
N-oleyl acetamide,
N-dodecyl phthalic acid imide,
dodecylurea,
octadecylurea,
N-dodecyl-N'-hydroxyethylurea,
N-dodecyl-N'-methylurea,
N-dodecyl-N'-methylol urea,
octadecyldiguanide
N-methyl-carbamic acid octadecyl ester;
unsubstituted and substituted amine oxides e.g., the aliphatic, araliphatic, aromatic, heterocyclic amine oxides:
N,N-dimethyl-N-dodecylamine oxide,
N,N-dimethyl-N-hexadecyl amino oxide,
N,N-dimethyl-N-octadecenyl amino oxide,
N,N-dibutyl-N-dodecylamino oxide,
N-methyl-N-cyclohexyl-N-dodecylamino oxide,
N,N-dimethyl-N-(dodecanoylamino methyl) amino oxide,
N,N-dimethyl-N-(beta-octadecenoylamino ethyl) amino oxide,
N,N-dimethyl-N-(gamma-octadecanoylamino propyl) amino oxide,
N,N-diemthyl-N-[gamma-(N'-octadecyl-carbaminyl) amino propyl] amino oxide,
N,N-dimethyl-N-(gamma-octadecylsulfonylamino propyl) amino oxide,
N,N-dimethyl-N-(gamma-oleoylamino propyl) amino oxide,
N-methyl-N,N-bis-[gamma-(octadecanoylamino) propyl] amino oxide,

N-methyl-N,N-bis-[gamma-(dodecanoylamino) propyl] amino oxide,
N-methyl-N,N-bis-[gamma-(oleoylamino) propyl] amino oxide,
N,N-dimethyl-N-(beta-octadecyloxy ethyl) amino oxide,
N-methyl-N-beta-hydroxyethyl-N-[gamma-(octadecanoylamino) propyl] amino oxide,
N-methyl-N-beta-hydroxyethyl-N-[gamma-(oleoylamino) propyl] amino oxide,
N-methyl-N-[gamma-(octadecanoylamino)-propyl]-N-[beta-(octadecanoyl-oxy)ethyl] amino oxide,
N,N-dimethyl-N-[beta-(N'-octadecylcarbaminyl) oxyethyl] amino oxide,
N,N-bis-(beta-hydroxyethyl)-N-stearyl amino oxide,
N-methyl-N-benzyl-N-dodecyl amino oxide,
N,N-dimethyl-N-(2-oxy-5-tert.butylbenzyl) amino oxide,
N,N-dimethyl-N-[(2-oxynaphthyl-1-)-methyl] amino oxide,
N,N-dimethyl-N-(4-dodecylphenyl) amino oxide,
N,N-dimethyl-N-(4-dodecanoylphenyl) amino oxide,
N-dodecyl morpholine-N-oxide,
N-hexadecyl morpholine-N-oxide,
N-dodecyl piperidine-N-oxide,
N-hexadecyl piperidine-N-oxide,
N-dodecyl imidazole-N-oxide,
N-dodecyl benzimidazole-N-oxide,
N-1-(beta-hydroxyethyl)-2-octadecyl-imidazoline-N-oxide,
1-(beta-octadecanoylamino ethyl)-2-octadecyl imidazoline-N-oxide;

Amine oxides that contain a plurality of amino oxide groups:

N,N-dimethyl-N'-propyl-N'-decyl ethylenediamine-N,N-dioxide,
N,N-diethyl-N'-octadecyl ethylene diamine-N,N'-dioxide,
N,N,N'-triethyl-N'-dodecyl ethylene diamine-N,N'-dioxide,
N,N,N'-tripropyl-N'-tetradecyl-ethylenediamine-N,N'-dioxide,
N,N,N'-trimethyl-N'-decyl-1,3-propylenediamine-N,N'-dioxide,
N,N,N'-trimethyl-N'-hexadecyl-1,3-propylenediamine-N,N'-dioxide,
N,N-diethyl-N'-methyl-N'-dodecyl-1,3-propylenediamine-N,N'-dioxide,
N,N,N'-tris-(beta-hydroxyethyl)-N'-octadecyl-1,3-propylene diamine-N,N'-dioxide,
N,N,N',N'-tetramethyl aminoundecylamine-N,N'-dioxide,
N,N,N',N'-tetramethyl aminomethyl stearylamine-N,N'-dioxide,
2,5-dihydroxy-1,4-bis-(dimethylaminomethyl)benzene-N,N'-dioxide
2,2-bis-(4'-hydroxy-3'-(dimethylamino oxide methyl)-phenyl)-propane,

adipic acid-di-(beta-1-oxide-imidazoline-1-yl-ethyl) ester; the amine oxides that are obtained if in compounds of elevated molecular weight, containing several tertiary amino groups, these tertiary amino groups are completely converted into amine oxide groups by means of hydrogen peroxide in known manner; such compounds are, for example, the condensation products of N-beta-oxyethyl-N-gamma-aminopropyl-N-methylamine or bis-(gamma-aminopropyl)-methylamine and adipic acid or sebacic acid or their esters, the copolymers of 2-vinyl pyridine and ethylene, propylene or dodecylacrylate, the polyurea of bis-(gamma-amino-propyl)-methylamine and hexamethylene diisocyanate or toluene diisocyanate, the polyurethanes of bis-(beta-oxyethyl) methylamine or N-beta-oxyethyl-N-gamma-aminopropyl-N-methylamine and hexamethylene diisocyanate or toluene diisocyanate, the reaction products of alpha, beta-unsaturated carboxylic acids such as acrylic acid, methacrylic acid, crotonic acid, or maleic acid or their esters, with bis-(gamma-aminopropyl)methylamine, and the reaction products of epoxides such as epichlorohydrin, butylene dioxide and diglycidyl ethylene glycol ether with bis (gamma-amino-propyl) methylamine;

furtheron amine oxides which in addition to an amine oxide group or in addition to a plurality of amine oxide groups also contain polyglycol ether groups, e.g.:

1-(dimethylamino-N-oxide)-3,6,9-trioxa-11-(4'-nonylphenoxy)-undecane,
1-(dimethylamino-N-oxide)2-hydroxy-4-oxa-hexadecane,
1-(dimethylamino-N-oxide)3,6,9-trioxa heneicosane,
1-(dimethylamino-N-oxide)-4,7,10,13,16-penta-oxa-19-thia-hentriacontane,

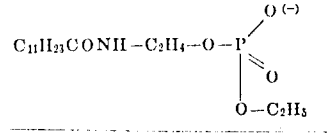
N-monoxides the reaction products of moles ethylene oxide and 1 mole stearylamine and N,N'-dioxides of the reaction products of 5–20 moles ethylene oxide and 1 mole 9-amino-stearylamine or 9-(amino-methyl)stearylamine; also the amine oxides that in addition to one or more amine oxide groups also contain one or more basic nitrogen atoms, e.g.,

N-methyl-N-octadecyl-N-[3-(di-beta-oxyethylamino)-propyl]-amino oxide,
N-methyl-N-octadecyl-N-(3-dimethyl amino)-propyl amino oxide,
N-methyl-N-octadecyl-N-[3-(gamma-aminopropylamino)-propyl]-amino oxide;

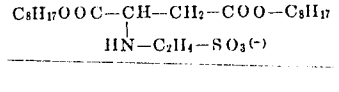
and those amine oxides that are obtainable if in the compounds listed above that contain a plurality of tertiary amino groups, e.g., in condensation products, copolymers, polyureas, polyurethanes, conversion products and reaction products, only a part of the tertiary amino groups are converted to amino oxide groups.

Basic dyes applicable in the process according to the invention are all dyes that contain at least one basic nitrogen atom. They can belong to the most multifarious classes of dyes, e.g., the azo, anthraquinone, azine, oxazine, xanthene, methin, triphenylmethane and phthalocyanine dyes. The dyes must be dissolved in the chlorohydrocarbon solutions either as free dye bases or as salts or adducts of acid esters of inorganic acids or of organic acids. The following anions are employed for the dye salts and dye adducts:

anions of acid esters of inorganic acids such as
dodecyl sulfate
stearyl sulfate
oleyl sulfate
undecylethylene glycol sulfate
oleic acid sulfate
oleic acid butyl ester sulfate
ricinoleic acid ethyl ester sulfate
ricinoleic acid monoethyl glycol ester sulfate
oleic acid ethyl amide sulfate
oleic acid ethanol amide sulfate
oleic acid diethanol amide sulfate
oleic acid diisobutyl amide sulfate
oleic acid anilide sulfate
N-acetyloleyl amino sulfate
tetradecyl triglycol ether sulfate
hexadecyl diglycol ether sulfate
octadecyl pentaglycol ether sulfate
N-oleyl-4-aminobutano-2-sulfate-ion and



anions of organic acids such as
oleic acid-N-dimethyl amide sulfonate



C_{12}–C_{17} paraffin sulfonate
n-butylbenzene sulfonate
n-amylbenzene sulfonate
n-hexylbenzene sulfonate
n-heptylbenzene sulfonate

diisopropylnaphthalene sulfonate
dibutyl naphthalene sulfonate
di-(diisobutyl-methyl)-naphthalene sulfonate
dibutylphenylpolyglycol ether sulfate
n-octylbenzene sulfonate
n-nonylbenzene sulfonate
n-decylbenzene sulfonate
n-dodecylbenzene sulfonate
n-tetradecylbenzene sulfonate
n-hexadecylbenzene sulfonate
n-octadecylbenzene sulfonate
2-ethyl-hexylbenzene sulfonate
2-propyl-heptylbenzene sulfonate
2-butyl-octylbenzene sulfonate
2-amyl-nonylbenzene sulfonate
dodecyl-(6)-benzene sulfonate and
tetrapropylene benzene sulfonate-ion,
also palmitate, stearate, oleate ion.

For the preparation of the dyebaths, the dyes can be added to the hydrocarbon chlorides in the form of free bases or as hydrocarbon chloride soluble dye salts or dye adducts. The hydrocarbon chloride soluble dye salts or dye adducts can however also be produced in the hydrocarbon chlorides from the components, the dye bases and acids, but also by double conversion of dye salts of inorganic acids with salts of organic, acid group containing compounds soluble in hydrocarbon chlorides, e.g., sodium lauryl sulfate, sodium paraffin sulfonate. In this case the dye bases and acids or the dye salts of inorganic acids and the salts of the organic acid group containing compounds soluble in hydrocarbon chlorides are added to the hydrocarbons in such proportion that for each equivalent of the basic dye at least one equivalent of the compounds containing carboxyl, sulfone, sulfate or phosphate groups is present.

The amounts in which the dye bases, dye salts or dye adducts are added to the hydrocarbon chloride dyebaths can vary within wide limits depending on the depth of the shade that is desired; in general amounts from 0.1 to 8 percent by weight based on the weight of the material to be dyed have been found satisfactory.

The amounts in which the amines, amides or amine oxides to be used in the process according to the invention are added to the dye baths depends on the amounts of basic dye employed. In general, it has been found satisfactory to use amines, amides and/or amine oxides and basic dyes in the proportion of 0.1 to 4:1.

It has often been found advantageous if the start was made with the salts of the basic dyes with inorganic acids, when larger amounts of the dye salts must be dissolved, to dissolve or disperse the latter in a hydrotropic solvent and add it to the dyebath in this form. As suitable hydrotropic solvents the following may for example be mentioned: isopropanol, benzyl alcohol, 2-phenoxyethanol, acetonitrile, oxypropionitrile, dimethyl sulfoxide, dimethyl formamide or glycolacetate methyl ether. Only so much hydrotropic solvent is used to dissolve the salts or adducts of the bases that the amount of hydrotropic solvent in the hydrocarbon chloride dyebath is not more than 2 percent by weight based on the weight of the hydrocarbon chloride. In some cases it has proved advantageous to add to the dyebath small amounts of acids, such as formic or acetic acid, especially in those cases where dyestuffs are used which tend in the form of the free base to decomposition through boiling.

It is necessary to add to the hydrocarbon chloride dyebaths, beside the amines, amides or amine oxides, small amounts of water, for example, 0.1–4 percent, preferably 0.1–2 percent by weight. It has been found advantageous for the dispersion of the water also to add emulsifiers to the hydrocarbon chloride solutions in the amount of 0.1–2 percent by weight based on the weight of the hydrocarbon chloride. As emulsifiers preferably nonionogenic compounds are employed; oxyethylation products of fatty alcohols, phenols, fatty acid amides and fatty acids as well as mixtures of these.

By the anionic groups containing synthetic fiber materials to be dyed according to the invention there are to be understood synthetic fiber materials which can be dyed with basic dyestuffs, preferably the commercial polyacrylonitrile containing anionic groups, such as sulfonic acid, sulfimide, carboxyl and/or phosphonic acid groups. Furthermore commercial polyesters, such as polyethylene terephthalate, polycyclohexane-dimethylene terephthalate, heterogeneous polyesters of terephthalic acid, isophthalic acid and ethylene glycol or of terephthalic acid, sulfoisophthalic acid and ethylene glycol, furthermore copolyether-ester fibers from p-hydroxybenzoic acid, terephthalic acid and ethylene glycol which are modified by carboxyl and/or sulfonic acid groups, and commercial polyamides, e.g., polyhexamethylene-diamine adipate, polycaprolactam or poly-ω-amino-undecanic acid modified by sulfonic acid groups.

The dyeing of the anionic groups containing fiber materials from hydrocarbon chloride solutions, which is preferably carried out in closed apparatus, can for example, be achieved by introducing the fiber material at room temperature into the hydrocarbon chloride dyebaths which contain the basic dyestuffs, their salts or acid adducts, the amines, amides and/or amine oxides, the water and optionally the emulsifiers and hydrotropic solvents; the bath is heated to temperatures from 70° to 140° C. and kept at this temperature until the bath is exhausted. After cooling the bath is separated off and the fiber material are freed from adhering solvent by suction or centrifuging and subsequent drying in an air current.

By the process according to the invention, it is possible to dye anionic groups containing synthetic fiber materials from hydrocarbon chlorine solutions with basic dyes in the most varied stages of manufacture, for example as flocks, combed material, yarn, piece goods, gauze material or as ready made articles in deep shades and with excellent uniformity. Colorings with very good abrasion resistance are obtained. The bath exhaustion in the process of the invention is very good.

The dyeing process according to the present invention is distinguished over the dyeing process of the Belgian Pat. No. 703,187 by the use of basic dyestuffs soluble in hydrocarbon chloride solutions. According to the process of the Belgian Patent dyestuffs are used which are insoluble or only sparingly soluble in hydrocarbon chlorides. Compared with the process of the Belgian Patent there are obtained according to the process of the invention dye liquors which are much more stable under the dyeing conditions and which therefore do not yield stains on the textile materials and dyestuff-depositions on the rimps of the dyeing apparatus. Furthermore by the use of the hydrocarbons chloride soluble dyestuff the serious problem of emulsifying aqueous dyestuff solutions in hydrocarbon chloride solutions is avoided. According to the present invention it is possible to prepare the hydrocarbon chloride dye liquors in a simple manner without endangering the personnel.

Parts indicated in the following examples are parts by weight. The structures of the dyes designated by numbers I – XVI are given in the table found at the end of the examples.

The following examples are to further illustrate the invention without limiting it.

EXAMPLE 1

Fifty parts of a fiber yarn of anionically modified polyester are introduced at 22° C. into a dyebath that consists of a mixture of

One part of the reaction product of 1 mole of the dye of formula I with 1 mole of sodium-4-tetradecylbenzene sulfonate
Four parts of oleic acid ethanol amide (technical)
Four parts of the reaction product of 1 mole oleyl alcohol with 20 moles ethylene oxide and 8 parts of water in 983 parts of perchloroethylene.

The bath is heated to 100° C. within 30 minutes with vigorous circulation and is held for one hour at this temperature. After this period the bath is separated off and the yarn freed in an air stream from adhering solvent. A uniform brownish red coloring is obtained.

If one uses as a hydrocarbon chloride instead of the 983 parts perchloroethylene the same quantity of trichloroethylene or 1,1,1-trichloroethane, then one will obtain an equivalent coloring.

EXAMPLE 2

Fifty parts of a fiber yarn of anionic groups containing polyacrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of

one part of the reaction product of 1 mole of the dye of formula I with 1 mole sodium-di-n-butyl-naphthaline sulfonate
four parts of oleic acid diethanolamide (technical)
four parts of a reaction product of 1 mole oleyl alcohol with 20 moles ethylene oxide and
eight parts of water

in 983 parts of perchloroethylene.

Dyeing is carried out as described in example 1. A uniform reddish brown coloring is obtained.

EXAMPLE 3

Fifty parts of a fiber yarn of anionic groups containing polyacrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of

one part of the reaction product of 1 mole of the dye of formula I with 1 mole of sodium-4-tetradecylbenzene sulfonate
four parts of the condensation product of 4 moles stearic acid polyglycerol ester with 1 mole triethylene tetramine
five parts of the reaction product of 1 mole oleyl alcohol with 20 moles ethylene oxide and
10 parts of water

in 980 parts of perchloroethylene.

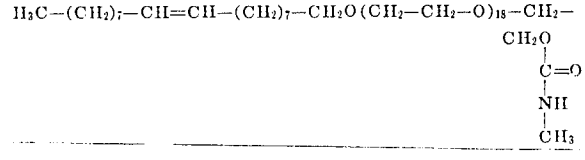
Dyeing is carried out as described in example 1.

A uniform reddish brown coloring is obtained.

EXAMPLE 4

Twenty five parts of knit goods of anionic groups containing acrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of

one part of the reaction product of 1 mole of the dye of formula I with 1 mole of sodium-4-octadecylbenzene sulfonate
four parts of ricinoleic acid amide
four parts of a compound of the formula



two parts of glycol methyl ether and
eight parts of water
in 981 parts of perchloroethylene.

Dyeing is carried out as described in Example 1.

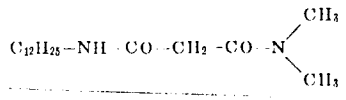
A uniform reddish brown coloring is obtained.

EXAMPLE 5

Fifty parts of a knitting yarn of anionically modified polyester are introduced at 22° C. into a dyebath that consists of a mixture of

one part of the reaction product of 1 mole of dye of formula VII with 1 mole of sodium-diisobutylmethyl-naphthalene sulfonate
five parts of the reaction product of 1 mole oleic acid oxy benzylamide with 20 moles ethylene oxide

five parts of a compound of the formula



and 9 parts of water
in 980 parts of perchloroethylene.

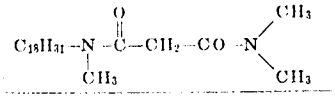
Dyeing is carried out as described in example 1.

A brilliant orange coloring is obtained.

EXAMPLE 6

Fifty parts of a fiber yarn of anionic groups containing polyacrylonitrile are introduced at 22° C. into a dyebath containing a mixture of

one part of formula VIII
0.4 parts of sodium-dodecylbenzene sulfonate
four parts of a compound of the formula



four parts of the reaction product of 1 mole oleyl alcohol with 20 moles ethylene oxide
2 parts of aminoundecanic acid and
8 parts of water
in 980 parts of perchloroethylene.

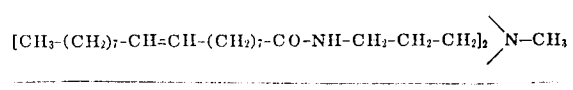
Dyeing is carried out as described in example 1.

A uniform blue-green coloring is obtained.

EXAMPLE 7

Fifty parts of a fabric of anionic groups containing acrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of

one part of dye of formula IX
0.4 parts of sodium-4-dodecylbenzene sulfonate
four parts of a compound of the formula



four parts of the reaction product of 1 mole oleic acid with 7 moles ethylene oxide
four parts of a reaction product of 1 mole phenol with 10 moles ethylene oxide and
seven parts of water
in 980 parts of perchloroethylene.

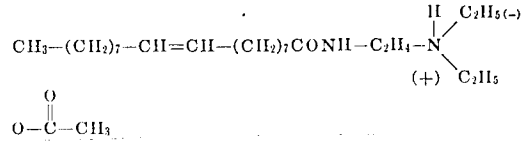
Dyeing is carried out as described in example 1.

A uniform red coloring is obtained.

EXAMPLE 8

Fifty parts of knit goods of anionic groups containing polyacrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of

one part of formula X
0.4 parts of sodium stearyl sulfate
four parts of a compound of the formula



3.6 parts of the reaction product of 1 mole nonyl-phenol with 7 moles ethylene oxide
two parts of the reaction product of 1 mole oleic acid with 20 moles ethylene oxide and
eight parts of water
in 981 parts of perchloroethylene.
Dyeing is carried out as described in example 1.
A uniform red coloring is obtained.

EXAMPLE 9

Fifty parts of a gauze material of anionic groups containing polyacrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of
one part of dye of formula XI
0.4 parts of sodium oleic acid ethanol amide sulfate
five parts of the reaction product of the 1 mole oleylamine with 18 moles ethylene oxide
four parts of N-dodecyl-N'-methylol-urea and
eight parts of water
in 981 parts of perchloroethylene.
Dyeing is carried out as described in example 1.
A uniform yellow coloring is obtained.

EXAMPLE 10

Fifty parts of a gauze material of anionically modified polyester are introduced at 22° C. into a dyebath consisting of a mixture of
one part of dye of formula XII
0.4 parts of sodium-2-butyl-octylbenzene sulfonate
five parts of 3-dimethylamino propyl stearic acid amide acetate
five parts of the reaction product of 1 mole oleyl alcohol with 20 moles ethylene oxide
and 10 parts of water
in 979 parts of trichloroethylene.
Dyeing is carried out as described in example 1.
A uniform orange coloring is obtained.

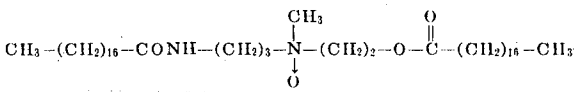
EXAMPLE 11

Fifty parts of a fiber yarn of anionic groups containing polyacrylonitrile (Dralon) are introduced at 22° C. into a dyebath consisting of a mixture of
one part of dye of formula VIII
0.4 parts sodium oleic acid butyl ester sulfate
four parts of the amine oxide of the formula

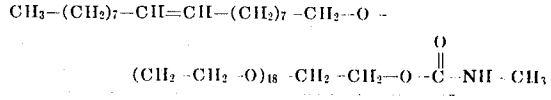
four parts of the reaction product of 20 moles ethylene oxide on 1 mole oleyl alcohol
and 6 parts of water
in 984 parts of perchloroethylene.
Dyeing is carried out as described in example 1.
A clear blue-green coloring is obtained.

EXAMPLE 12

Fifty parts of a fiber yarn of anionically modified polyester (Dacron 64) are introduced at 22° C. into a dyebath consisting of a mixture of
1.5 parts of the dye of formula I
0.7 parts of sodium-N-acetyloleyl amino sulfate
six parts of the amino oxide of the formula



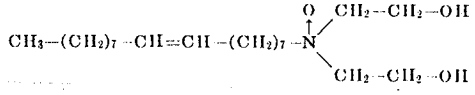
six parts of the compound of the formula



and 8 parts of water
in 984 parts of perchloroethylene.
Dyeing is carried out as in example 1.
A saturated deep reddish brown coloring is obtained.

EXAMPLE 13

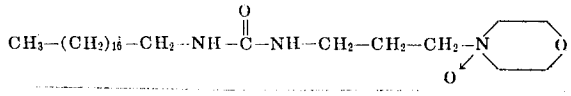
Fifty parts of a fiber yarn of anionic groups containing polyacrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of
1.5 parts of the dye of formula II
0.7 parts of sodium hexadecyldiglycol ether sulfate
4.5 parts of the amine oxide of the formula



five parts of the reaction product of 1 mole oleic acid with 19 moles ethylene oxide
and 4 parts of water
in 980 parts of perchloroethylene.
Dyeing is carried out as described in example 1.
A uniform blue coloring is obtained.

EXAMPLE 14

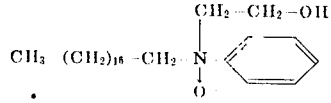
Fifty parts of a fiber yarn of anionic groups containing polyacrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of
one part of the dye of formula III
0.5 parts of the sodium-4-tetradecylbenzene sulfonate
four parts of the amino oxide of the formula



four parts of the reaction product of 20 moles ethylene oxide and 1 mole oleyl alcohol
and 8 parts of water
in 982 parts of perchloroethylene.
Dyeing is carried out as described in example 1.
A uniform wine red coloring is obtained.

EXAMPLE 15

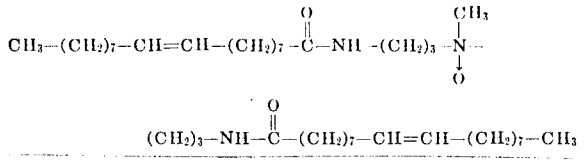
Fifty parts of a fiber yarn of anionically modified polyamide are introduced at 22° C. into a dyebath consisting of a mixture of
one part of the dye of formula IV
0.5 parts of sodium dodecylbenzene sulfonate
four parts of the amino oxide of the formula



2.5 parts of the reaction product of 20 moles ethylene oxide and 1 mole oleyl alcohol and
eight parts of water
in 984 parts of perchloroethylene.
Dyeing is carried out as described in example 1.
A uniform blue coloring is obtained.

EXAMPLE 16

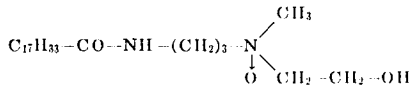
Fifty parts of a fiber yarn of anionic groups containing polyacrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of
one part of dye of formula VIII
0.5 parts of sodium lauryl sulfate
four parts of the amino oxide of the formula



four parts of the reaction product of 1 mole oleyl alcohol with 20 moles ethylene oxide
two parts of the reaction product of 1 mole nonylphenol with 7 moles ethylene oxide
and 9 parts of water
in 980 parts of 1,1,1-trichloropropane.
Dyeing is carried out as described in example 1.
A greenish blue coloring is obtained.

EXAMPLE 17

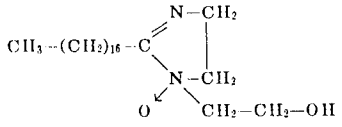
Fifty parts of a fiber yarn of anionic groups containing acrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of
one part of dye of formula XIII
0.2 parts of sodium dodecylbenzene sulfonate
four parts of the amino oxide of the formula



four parts of the reaction product of 1 mole oleyl alcohol with 20 moles ethylene oxide
two parts of the reaction product of 1 mole nonylphenol with 7 moles ethylene oxide
and 9 parts of water
in 980 parts of 1,1,1-trichloropropane.
Dyeing is carried out as described in example 1.
A brilliant green coloring is obtained.

EXAMPLE 18

Fifty parts of a fiber yarn of anionic groups containing polyacrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of
one part of dye of formula X
0.2 parts of ammonium oleyl sulfate
four parts of the amino oxide of the formula



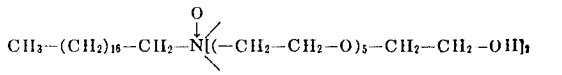
four parts of the reaction product of 1 mole oleyl alcohol with 20 moles ethylene oxide
two parts of the reaction product of 1 mole nonylphenol with 7 moles ethylene oxide
and 9 parts of water
in 980 parts of 1,1,1-trichloropropane.
Dyeing is carried out as described in example 1.
A uniform clear pink coloring is obtained.

EXAMPLE 19

Fifty parts of a fiber yarn of anionic groups containing polyacrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of
one part of dye of formula XIV
0.2 parts of sodium-di-n-butyl-naphthaline sulfonate (1)
four parts of N-octadecyl-morpholine-N-oxide
four parts of the reaction product of 1 mole oleyl alcohol with 20 moles ethylene oxide
two parts of the reaction product of 1 mole nonylphenol with 7 moles ethylene oxide
and 7 parts of water
in 980 parts of 1,1,1-trichloropropane.
Dyeing is carried out as described in example 1.
A uniform yellow coloring is obtained.

EXAMPLE 20

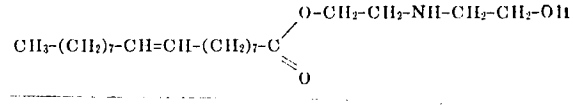
Fifty parts of a fiber yarn of anionic groups containing polyacrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of
one part of dye of formula XII
0.2 parts of sodium-paraffin sulfonate
four parts of the N-oxide of the formula



four parts of the reaction product of 1 mole oleyl alcohol with 20 moles ethylene oxide
two parts of the reaction product of 1 mole nonylphenol with 7 moles ethylene oxide and
seven parts of water
in 982 parts of 1,1,1-trichloropropane.
Dyeing is carried out as described in example 1.
A clear orange coloring is obtained.

EXAMPLE 21

Fifty parts of a fiber yarn of anionically modified polyamide are introduced at 22° C. into a dyebath consisting of a mixture of
one part of dye of formula XV
0.6 parts of sodium paraffin sulfonate
one part of glacial acetic acid
three parts of the compound of the formula

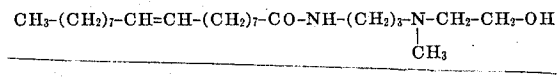


three parts of the reaction product of 1 mole oleyl alcohol with 17 moles ethylene oxide
and 8 parts of water
in 983.4 parts of perchloroethylene.
Dyeing is carried out as described in example 1.
A clear yellow coloring is obtained.

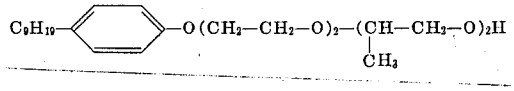
EXAMPLE 22

Fifty parts of a fiber yarn of anionic groups containing polyacrylonitrile are introduced at 22° C. into a dyebath consisting of

one part of the dye of formula I
0.5 parts of sodium lauryl sulfate
two parts of glacial acetic acid
three parts of the compound of the formula



2 parts of the compound of the formula



five parts of water
in 986.5 parts of perchloroethylene.

Dyeing is carried out as in example 1.

A saturated reddish brown coloring is obtained.

EXAMPLE 23

Fifty parts of a fiber yarn of anionic groups containing polyacrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of

one part of dye of formula IX
0.15 parts of 2-butylaminoethanesulfonic acid-(1)
four parts of di-N-2-hydroxyethyl-oleylamine
four parts of a reaction product of 1 mole nonylphenyl with seven moles ethylene oxide and
eight parts of water
in 984 parts of perchloroethylene.

Dyeing is carried out as described in example 1.

A clear brilliant red coloring is obtained.

EXAMPLE 24

Thirty parts of knit goods of anionically modified polyamide (Nylon T 844) are introduced at 22° C. into a dyebath consisting of a mixture of

one part of the dye of formula III
0.5 parts of sodium lauryl sulfate
one part of glacial acetic acid
four parts of dodecyl aniline
two parts of the reaction product of 1 mole oleic acid with 7 moles ethylene oxide
two parts of the reaction product of 1 mole nonylphenol with 10 moles ethylene oxide
two parts of the reaction product of 1 mole oleyl alcohol with 20 moles ethylene oxide and
eight parts of water
in 980 parts of perchloroethylene.

Dyeing is carried out as described in example 1.

A ruby red coloring is obtained.

EXAMPLE 25

Fifty parts of a fiber yarn of anionically modified polyamide are introduced at 22° C. into a dyebath consisting of a mixture of

one part of dye of formula X
0.5 parts of sodium-4-dodecylbenzene sulfonate
three parts of dodecylaniline
three parts of the reaction product of 20 moles ethylene oxide with 1 mole oleyl alcohol and
8.5 parts of water
in 984 parts of perchloroethylene.

Dyeing is carried out as described in example 1.

A clear pink coloring is obtained.

EXAMPLE 26

Fifty parts of a fiber yarn of anionic groups containing polyacrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of

one part of dye of formula VIII
0.5 parts of sodium paraffin sulfonate
four parts of the reaction product of 1 mole oleylamine with 20 moles ethylene oxide
one part of glacial acetic acid and
eight parts of water
in 986 parts of perchloroethylene.

Dyeing is carried out as described in example 1.

A clear greenish-blue coloring is obtained.

EXAMPLE 27

Fifty parts of a fiber yarn of anionic groups containing polyacrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of

one part of dye of formula XIII
0.4 parts of sodium-4-dodecylbenzene sulfonate
four parts of stearylamine
four parts of the reaction product of 1 mole oleyl alcohol with 20 moles ethylene oxide
two parts of glacial acetic acid and
nine parts of water
with 980 parts of perchloroethylene.

Dyeing is carried out as described in example 1.

A clear green coloring is obtained.

EXAMPLE 28

Fifty parts of a fiber yarn of anionically modified polyester are introduced at 22° C. into a dyebath consisting of a mixture of

one part of the dye of formula V
one part of glacial acetic acid
four parts of oleic acid diethanolamide (technical)
four parts of the reaction product of 1 mole oleyl alcohol with 20 moles ethylene oxide and
eight parts of water
in 982 parts of perchloroethylene.

The bath is heated with vigorous circulation to 110° C. within 30 minutes and held at this temperature for 2 hours. The bath is subsequently separated off and the yarn is freed from adhering solvent in an air current.

A clear turquoise coloring is obtained.

EXAMPLE 29

Fifty parts of a fiber yarn of anionic groups containing polyacrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of

0.5 parts of the dye of formula VI
four parts of oleic acid diethanolamide (technical)
four parts of the reaction product of 1 mole oleyl alcohol with 20 moles ethylene oxide
and 8.5 parts of water
in 983 parts of perchloroethylene.

Dyeing is carried out as described in example 1.

A brilliant deep blue coloring is obtained.

EXAMPLE 30

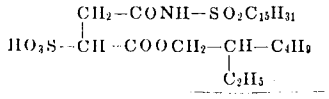
Fifty parts of a fiber yarn of anionic groups containing polyacrylonitrile are introduced at 22° C. into a dyebath consisting of a mixture of

0.5 parts of dye of formula XVI
0.5 parts of oleic acid
four parts of oleic acid diethanol amide
four parts of the reaction product of 1 mole oleyl alcohol with 20 moles ethylene oxide and
eight parts of water
in 983 parts of perchloroethylene.

Dyeing is carried out as described in example 1.

A saturated green coloring is obtained.

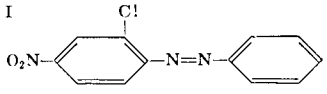
The same saturated green coloring is obtained by using instead of oleic acid 0.5 parts of coco fat acid, sulfuric acid-mono-iso-amyl ester, phosphoric acid-di glycol ester or a compound of the formula



Structures of dyes I–XVI used in the examples.

Number Structure

I



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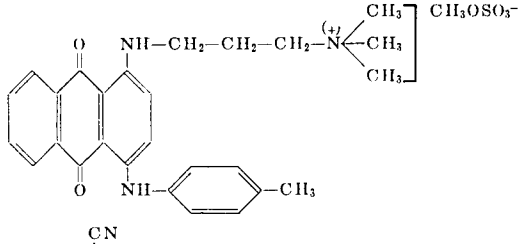

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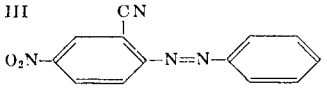

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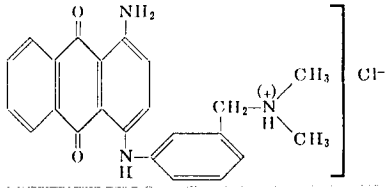

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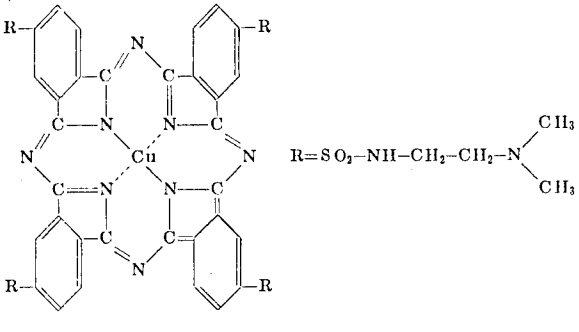

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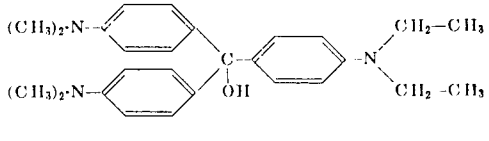

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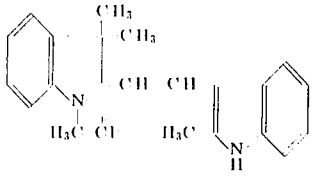
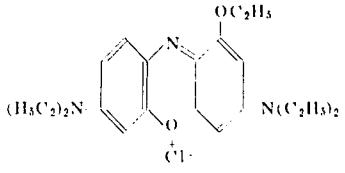


VIII



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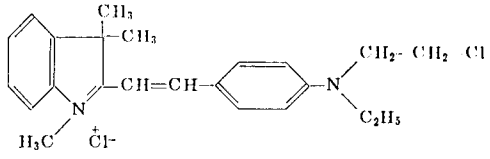
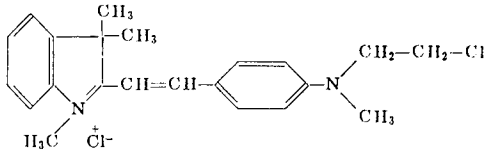
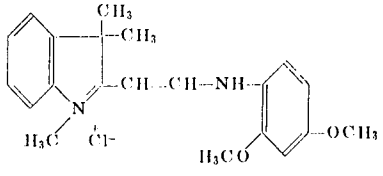


X



XI



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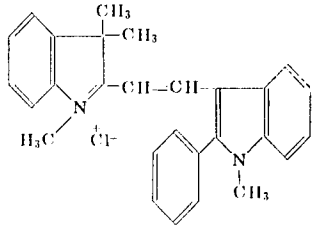

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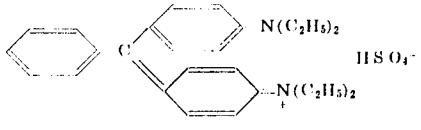

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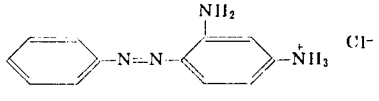
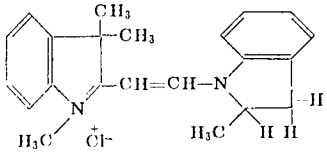
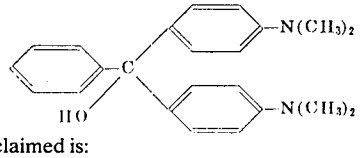


XV



XVI



What is claimed is:

1. A process for dyeing anionic group containing fiber materials selected from the group consisting of polyesters, polyamides and polyacrylonitrile, which comprises dyeing said fiber materials by exhaustion in a dyeing bath comprising

A. a hydrocarbon chloride solvent;
B. 0.1 to 4 percent by weight, based on the hydrocarbon chloride solvent of water;
C. a hydrocarbon chloride soluble basic dyestuff; and
D. an organic nitrogen compound selected from the group consisting of an amine, an amide, an amine oxide, and mixtures thereof, said amine, amide and amine oxide having at least 12 carbon atoms.

2. The process of claim 1, said hydrocarbon chloride soluble basic dyestuff being present in the form of a hydrocarbon chloride soluble dye salt with an acid selected from the group consisting of an organic acid and an acid ester of an inorganic acid.

3. The process of claim 1, said hydrocarbon chloride soluble basic dyestuff being present in the form of a hydrocarbon chloride soluble adduct with an acid selected from the group consisting of an organic acid and an acid ester of an inorganic acid.

4. A process for dyeing anionic group containing fiber materials selected from the group consisting of polyesters, polyamides and polyacrylonitrile, which comprises dyeing said fiber materials by exhaustion in a dyeing bath comprising
A. a hydrocarbon chloride solvent;
B. 0.1 to 4 percent by weight, based on the hydrocarbon chloride solvent of water;
C. a hydrocarbon chloride soluble basic dyestuff;
D. an organic nitrogen compound selected from the group consisting of an amine, an amide, an amine oxide, and mixtures thereof, said amine, amide and amine oxide having at least 12 carbon atoms; and
E. 0.1 to 2 percent by weight, based on the hydrocarbon chloride solvent of an emulsifier.

5. The process of claim 4, said hydrocarbon chloride soluble basic dyestuff being present in the form of a hydrocarbon chloride soluble dye salt with an acid selected from the group consisting of an organic acid and an acid ester of an inorganic acid.

6. The process of claim 4, said hydrocarbon chloride soluble basic dyestuff being present in the form of a hydrocarbon chloride soluble adduct with an acid selected from the group consisting of an organic acid and an acid ester of an inorganic acid.

7. A process for dyeing anionic group containing fiber materials selected from the group consisting of polyesters, polyamides, and polyacrylonitrile, which comprises dyeing said fiber materials by exhaustion in a dyeing bath comprising
A. a hydrocarbon chloride solvent;
B. 0.1 to 4 percent by weight, based on the hydrocarbon chloride solvent of water;
C. a hydrocarbon chloride soluble basic dyestuff;
D. an organic nitrogen compound selected from the group consisting of an amine, an amide, an amine oxide, and mixtures thereof, said amine, amide, and amine oxide having at least 12 carbon atoms; and
E. 0.1 to 2 percent by weight, based on the hydrocarbon chloride solvent of a hydrotropic organic solvent.

8. The process of claim 7, said hydrocarbon chloride soluble basic dyestuff being present in the form of a hydrocarbon chloride soluble dye salt with an acid selected from the group consisting of an organic acid and an acid ester of an inorganic acid.

9. The process of claim 7, said hydrocarbon chloride soluble basic dyestuff being present in the form of a hydrocarbon chloride soluble adduct with an acid selected from the group consisting of an organic acid and an acid ester of an inorganic acid.

* * * * *