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Ringel et al.

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[54] **PROCESS FOR DYEING FIBRE MATERIAL CONTAINING NH-GROUPS FROM ORGANIC SOLVENTS**

[75] Inventors: **Paul Ringel,** Leverkusen-Wiesdorf; **Dietrich Hildebrand,** Leverkusen; **Gunter Breidbach,** Cologne-Flittard, all of Germany

[73] Assignee: **Bayer Aktiengesellschaft,** Leverkusen-Bayerwerk, Germany

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[21] Appl. No.: **470,827**

Related U.S. Application Data

[63] Continuation of Ser. No. 859,207, Sept. 18, 1969, abandoned, which is a continuation-in-part of Ser. No. 791,777, Jan. 16, 1969, abandoned.

[30] **Foreign Application Priority Data**

Aug. 2, 1968 Germany 1769902

[52] **U.S. Cl.** ..... **8/169;** 8/162 R; 8/172; 8/173

[51] **Int. Cl.**[2] **D06P 5/04**

[58] **Field of Search** ..... 8/54, 162 R, 169, 173, 8/174, 93, 94, 178 R, 172

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Primary Examiner—Harvey E. Behrend
Assistant Examiner—P. A. Nelson
Attorney, Agent, or Firm—Plumley & Tyner

[57] **ABSTRACT**

Synthetic fibers containing NH-groups, e.g. polyamides are dyed by exhaustion in a dyebath comprising halogenated hydrocarbon and the amine salt or adduct of a dyestuff containing carboxyl and/or sulfonic acid groups.

3 Claims, No Drawings

PROCESS FOR DYEING FIBRE MATERIAL CONTAINING NH-GROUPS FROM ORGANIC SOLVENTS

This application is a continuation of U.S. Pat. Ser. No. 859,207 filed Sept. 18, 1969, now abandoned, which is a continuation-in-part of U.S. Ser. No. 791,777 filed Jan. 16, 1969 now abandoned.

This invention relates to a process for the dyeing of NH-group-containing fibre materials with carboxyl and/or sulfonic acid group containing dyestuffs. The method of this invention is characterized in that the dyeing is done from hydrocarbon chloride solutions that contain amino salts or amino adducts of the dye acids based on an amine containing at least 8 carbon atoms and showing an uninterrupted chain of at least 3 carbon atoms.

The hydrocarbon chlorides preferably employed in the practice of this invention are those whose boiling points lie between 40° and 150° C, e.g. 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, 1,2-dichloropropane, 1-chlorobutane, 2-chlorobutane, 1,4-dichlorobutane, 1-chloro-2-methyl-propane, 2-chloro-2-methylpropane, 4-chloro-2-methyl-propane and aromatic hydrocarbon chlorides such as chlorobenzene and chlorotoluene.

Tetrachloroethylene, trichloroethylene and 1,1,1-trichloropropane have been found especially suitable.

All dyes are suitable for use according to this invention providing they contain 1 to 4 carboxyl and/or sulfonic acid groups. The dyes can belong to the most different dye classes, e.g. to the azo, anthraquinone, phthalocyanine, azine and triphenylmethane dyes and they can also contain reactive groups. These dyestuffs are used in the form of their amine salts and their amine adducts.

As amines containing at least 8 carbon atoms, three of which are in an uninterrupted chain, on which the amine salts or amine adducts of the dyes are based and which are to be used according to the invention, primary, secondary and tertiary monoamines as well as primary, secondary and tertiary polyamines can be employed. As primary, secondary and tertiary monoamines the following may be mentioned:

substituted and unsubstituted aliphatic amines such as
tri-n-propylamine,
2-ethyl-hexylamine,
dodecylamine,
dodecylamine polyglycol ether (with 20 moles ethylene oxide),
hexadecylamine,
hexadecylamine polyglycol ether (with 20 moles ethylene oxide),
octadecylamine,
N-methyl octadecylamine,
N-methyl octadecylamine polyglycol ether (with 10 moles ethylene oxide),
cetylamine,
N,N-dimethyl dodecylamine,
N,N-dimethyl-hexadecylamine,
N,N-dimethyl octadecylamine,
N,N-dibutyl dodecylamine,
N,N-di-2-hydroxyethyl oleylamine,

N,N-dimethyl-N-(dodecanoylaminomethyl)amine,
N-methyl-N-2-hydroxyethyl-N-[γ-(octadecanoylamino)-propyl]amine
ε-aminocaproic acid butyl ester,
ε-aminocaproic acid dodecylamide,
ε-aminoundecanic acid butyl ester,
furthermore technical mixtures of fatty amines such as coco fat amine and
sperm oil fat amine, as well as their ethyoxylation and propoxylation products,
substituted and unsubstituted cycloaliphatic amines such as
N,N-dimethyl-cyclohexylamine,
N-ethyl-cyclohexylamine,
N-2-hydroxyethyl-cyclohexylamine,
N,N-bis-(2-dihydroxyethyl)-cyclohexylamine,
N,N-bis-(2-chloroethyl)-cyclohexylamine,
1-cyclohexylamino-propanol-2,
1-cyclohexylamino-propylamine-3,
and dicyclohexylamine,
substituted or unsubstituted araliphatic amines such as benzylamine,
N,N-dimethyl-benzylamine,
N,N-dibenzylamine,
N-methyl-N,N-dibenzylamine,
1-amino-1-phenyl ethane,
1-amino-2-phenyl ethane,
substituted and unsubstituted aromatic amines such as
N-ethyl aniline,
N,N-dimethyl aniline,
N,N-diethyl aniline,
N-propyl aniline,
N,N-dipropyl aniline,
N-butyl aniline,
N-isobutyl aniline,
N-(2-chloroethyl)-N-butyl aniline,
N-2-hydroxyethyl aniline,
N-methyl-N-(2-hydroxyethyl)aniline,
N-butyl-N-(2-hydroxyethyl)aniline,
N,N-bis-(2-hydroxyethyl) aniline,
N-methyl-N-(2-cyanoethyl)aniline,
2-aminotoluene,
2-methylamino toluene,
2-dimethylamino toluene,
2-ethylamino toluene,
3-amino toluene,
3-dimethylamino toluene,
3-ethylamino toluene,
3-butylamino toluene,
3-(N-ethyl-N-hydroxyethyl)amino toluene,
3-[N-bis-(2-hydroxyethyl)] aminotoluene,
3-[N-ethyl-N-(2-dimethylaminoethyl)] aminotoluene,
4-methylaminotoluene,
4-dimethylaminotoluene,
4-ethylaminotoluene,
4-diethylaminotoluene,
N-ethyl-N-benzyl aniline,
3-(N-ethyl-N-benzyl) aminotoluene,
xylidine,
2-iso-propyl aniline,
2-methyl-6-ethyl aniline,
2,6-diisopropyl aniline,
4-dodecyl aniline,
N,N-dimethyl-4-dodecyl-aniline,
5,6,7,8-tetrahydro-naphthylamine-(1),
1-diethylamino-naphthaline,

4,4'-diamino-dicyclohexyl methane, substituted and unsubstituted heterocyclic amines such as
N-propyl morpholine,
N-hexyl morpholine,
N-dodecyl morpholine,
N-hexadecyl morpholine,
N-dodecyl piperidine,
N-hexadecyl piperidine,
N-dodecyl imidazole,
2-dodecyl hydroindole,
N-dodecyl benzimidazole,
2-dodecyl benzimidazole,
1-(beta-hydroxyethyl)-2-octadecyl imidazoline,
1-(beta-octadecanoylaminoethyl)-2-octadecyl imidazoline,

As primary, secondary and tertiary polyamines especially aliphatic polyamines such as the following may be mentioned:
N-dodecyl-N',N'-dimethyl ethylenediamine,
N-dodecyl-N',N'-diethyl ethylene diamine,
N-octadecyl-N',N'-dimethyl ethylene diamine,
N-phenyl-N',N'-dimethyl ethylenediamine,
N-oleyl-N',N'-dimethyl ethylenediamine,
N-oleyl-N',N'-diethyl ethylenediamine,
N-dodecyl-N',N'-dimethyl propylene diamine (1,3),
N-dodecyl-N',N'-diethyl propylene diamine (1,3),
N-oleyl-N',N'-dimethyl propylene diamine (1,3),
N-oleyl-N',N'-diethyl propylene diamine (1,3),
N-dodecyl ethylene triamine,
N-dodecyl ethylene tetramine,
N-octadecyl ethylene tetramine.

When using dye acids containing reactive groups, aturally only those amines may be employed for the ılt formation or adduct formation which contain no ee NH—groups.

The amounts in which the dye amino salts or amino ıdducts to be used according to the invention are ıdded to the hydrocarbon chloride dye baths can vary ithin wide limits depending on the desired depth of olor; usually amounts from 0.1 to 10% by weight ased on the material to be dyed have been found satisıctory.

For preparation of the dye baths the dye amino salts r dye amino adducts to be used according to the inention can be added to the hydrocarbon chlorides as ınished compounds, but the dye amino salts or dye mino adducts can also be produced in the hydrocaron chlorides from their compounds, i.e. the dye acids nd the amines. In this case dye acids and amines are ıdded to the hydrocarbon chlorides in such proportion hat for each carboxyl and sulfonic acid group at least ıne basic amino group is available.

It has often been found advantageous, if the start is nade with finished dye amino salts or adducts to add hese to the hydrocarbon chlorides dissolved in polar ›rganic solvents such as isopropanol, benzyl alcohol, ›henoxyethanol, acetonitrile, hydroxypropionitrile, dinethyl sulfoxide, dimethyl formamide or glycolacetate nethyl ether. Only so much polar organic solvent is ısed to dissolve the dye amino salts or amino adducts ıowever, that the amount of polar organic solvent in he hydrocarbon chloride dye baths never exceeds 1% ›y weight based on the hydrocarbon chlorides.

It has furthermore been found useful, in order to im›rove the receptivity to dyes of the NH group-contain- ing fiber material, especially the natural polyamides such as wool and animal hair, to add to the hydrocarbon chloride dye baths small amounts, e.g. 0.01 to 0.5% by weight of water as well as 0.01 to 0.5% by weight of emulsifiers, based on weight of the hydrocarbon chlorides, to emulsify the water.

As emulsifiers commercial paraffin sulfonates, alkyl benzene sulfonates, fatty alcohol sulfates and oxyethylation products of fatty alcohols, phenols, amines, fatty acid amides and fatty acids and especially mixtures of these compounds have been found useful.

As NH group-containing fiber materials that can be dyed according to the process of this invention, the following may be mentioned: natural polyamides such as wool, animal hair and silk, regenerated protein fibers and synthetic polyamides such as poly-ε-caprolactam, polyhexamethylene diamine adipate or poly-ω-amino undecanic acid, furthermore synthetic polymers that contain amino groups in the side chain provided that these polymers are not dissolved by the hydrocarbon chlorides used.

By means of the dyestuff amino salts or amino adducts soluble in hydrocarbon chlorides that are used according to the invention, it is possible to dye NH group-containing fiber materials in different stages of manufacture, for example as flocks, combed material, yarn, piece goods and ready to wear goods in closed apparatus, for example, in cheese devices, in tubs or paddlers, with a high degree of uniformity and exploitation of the dye and excellent fastness. It is especially to be noted that the baths are well used up and do not only become exhausted to an equilibrium. It is furthermore advantageous that uniform solvents can be used and that in solvent recovery only the water, of which there is only a trace, needs to be removed.

The parts indicated in the following examples are parts by weight, the dyestuff numbers refer to the data in Color Index vol. 3, 2nd edition (1956). The structures of the dyes indicated by numbers I–XII are given in the table at the end of the examples.

EXAMPLE 1

100 Parts of a poly-ε-caprolactam fibre yarn were introduced at 22°C into a dye bath that consisted of a clear solution of
1 part of the dye acid being the basis for dye No. 17,070 and
1 part octadecylamine
in 1,600 parts tetrachloroethylene.

The bath was heated with vigorous circulation to 100°C within 45 minutes and held at this temperature for one hour. At the end of this time, the bath was exhausted. The yarn was removed from the bath, freed by suction from adhering dye liquor and dried without further after treatment. A brilliant scarlet coloring was obtained, with good fastness characteristics.

If instead of using the 1,600 parts tetrachloroethylene as the hydrocarbon chloride, the same amount of methylene chloride, 1,2-dichloroethane, 1,1,1-trichloroethane or trichloroethylene is used, an equally brilliant coloring is obtained, with the same fastness characteristics.

EXAMPLE 2

100 Parts wool knitting yarn were introduced at 22°C into a dye bath that consisted of a clear solution of
1 part of the dye acid that is the basis for dye No. 14690 and
1 part of coco fat amine
in
1600 parts of tetrachloroethylene

7 parts of water
8 parts of a mixture of
30 parts paraffin sulfonate
2.5 parts dodecylbenzene sulfonate
17.5 parts sulfuric acid ester of a sperm oil alcohol
12.0 parts of water and
31.0 parts of ligroin.

The bath was heated with vigorous circulation to 100°C within 45 minutes and held at this temperature for one hour. After this time the bath was exhausted. The fibre material was removed from the bath, freed by suction from the absorbed dye liquor and dried without further after-treatment. A brilliant red coloring with good fastness characteristics was obtained.

If instead of using the 1,600 parts tetrachloroethylene as the hydrocarbon chloride the same amount of trichloroethylene or 1,1,1-trichloroethane was used, an equally brilliant coloring was obtained, with the same fastness characteristics.

EXAMPLE 3

100 Parts wool knitting yarn were introduced at 22°C into a dye bath that consisted of a clear solution of
1 part of the dye acid that is the basis for dye No. 18835 and
1 part of N,N-dimethyl-N-octadecylamine in
1,600 parts of trichloroethylene
7 parts of water and
8 parts of a mixture of
30 parts paraffin sulfonate
2.5 parts dodecylbenzene sulfonate
17.5 parts sulfuric acid ester of a sperm oil alcohol
12.0 parts water and
31.0 parts ligroin.

The bath was heated with vigorous circulation to 85°C within 45 minutes and dyeing was carried out at this temperature for 75 minutes. Then the bath was separated off, the yarn rinsed with fresh trichloroethylene and subsequently dried. A yellow coloring with good fastness characteristics was obtained.

EXAMPLE 4

100 Parts of a knitted material of poly-ε-caprolactam fiber yarn goods were introduced at 22°C into a dye bath that consisted of a clear solution of 2 parts of the dye acid that is the basis for dye No. 35,780 and 2.46 parts of N-3-(dimethylamino-propyl)-stearic acid amide-acetate in 1,600 parts tetrachloroethylene.

The bath was heated with vigorous circulation to 100°C within 45 minutes and held at this temperature for one hour. Subsequently the liquor clinging to the fibre material was removed.

A uniform deep red color was obtained.

EXAMPLE 5

100 Parts of wool knitted goods were introduced at 22°C into a dye bath that consisted of a clear solution of 2 parts of the dye acid that is the basis for dye No. 61,590
and
1.2 parts of N-oleyl-N-diethyl-propylenediamine-(1,3)
in
1000 parts of 1,1,1-trichloropropane
4 parts of water and
5 parts of a mixture of
30 parts of paraffin sulfonate
2.5 parts of dodecylbenzene sulfonate
17.5 parts of sulfuric acid ester of a sperm oil alcohol
12.0 parts of water and
31.0 parts of ligroin.

The bath was heated to 107°C within 45 minutes and left at this temperature for 45 minutes. Subsequently the bath attached to the fibre material was removed by suction. A uniform deep green coloring with good fastness characteristics was obtained.

EXAMPLE 6

100 Parts silk yarn were introduced at 22° C into a dye bath that consisted of a clear solution of
1 part of the dye acid that is the basis for dye No. 61,135
0.5 parts of N-hexyl-morpholine
in 1600 parts of tetrachloroethylene.

The bath was heated to 80°C within 30 minutes and held at this temperature for 1 hour. After removal by suction and drying, without further after-treatment, a brilliant blue coloring was obtained with the same fastness characteristics as is obtained from an aqueous bath.

EXAMPLE 7

100 Parts of a poly-ε-caprolactam fibre yarn were introduced at 22°C in a dye bath that consisted of a clear solution of 1 part of dye I and
1 part of 1-(beta-hydroxyethyl)-2-octadecyl-imidazoline in 1,600 parts of tetrachloroethylene.

The bath was heated with vigorous circulation to 100°C within 45 minutes and held for 1 hour at this temperature. After removal by suction and drying, without further after treatment a brilliant yellow coloring with good fastness characteristics was obtained.

EXAMPLE 8

100 Parts wool yarn are introduced at 22°C into a dye bath that consists of a clear solution of
1 part of dye II
0.6 parts of N-dodecyl-imidazole
in 1600 parts of tetrachloroethylene.

The bath is heated to 100°C within 45 minutes and kept for 1 hour at this temperature.

After removal of the adhering liquor and drying, without further rinsing, a vivid yellow coloring is obtained whose fastness characteristics are comparable to those obtained by dyeing with the sodium salt of the dye used from acetic acid aqueous solution.

EXAMPLE 9

100 Parts wool knitting yarn are introduced at 22°C into a dye bath that consists of a clear solution of
1 part of dye IV and
1.5 parts of N-dodecyl-morpholine in
1600 parts of tetrachloroethylene
7 parts of water and
8 parts of a mixture of
30 parts of paraffin sulfonate
2.5 parts of dodecylbenzene sulfonate
17.5 parts of sulfuric acid ester of a sperm oil alcohol
and
12.0 parts of water.

Dyeing is accomplished as described in Example 1. A clear red coloring is obtained.

EXAMPLE 10

100 Parts of a polyamide knitted fabric are introuced at 22°C into a dye bath that consists of a clear olution of
1 part of dye III and
1.2 parts of dodecylamine
in 1600 parts of tetrachloroethylene.
The procedure is as described in Example 1 and uniorm red coloring is obtained.

EXAMPLE 11

100 Parts of poly-ε-caprolactam fibre yarn are introuced at 22°C into a dye bath that consists of a clear olution of
1 part of dye IV and
2.3 parts of a reaction product of oleylamine with 20 moles ethylene oxide
in 1,500 parts of trichloroethylene.
The procedure is as described in Example 1. After ompletion of the dyeing process, an after treatment ith fresh trichloroethylene at 50°C for 10 minutes is arried out. A clear blue coloring is obtained.

EXAMPLE 12

100 Parts wool knitting yarn are introduced at 22°C nto a dye bath that consists of a clear solution of
1 part of dye V and
1 part of N,N-dimethyl-stearylamine in
1600 parts of tetrachloroethylene
7 parts of water and
8 parts of a mixture of
30 parts of paraffin sulfonate
2.5 parts of dodecylbenzene sulfonate
17.6 parts of sulfuric acid ester of a sperm oil alcohol
31.1 parts of mineral oil and
12.0 parts of water.
The process is as described in Example 2. A deep yelow coloring with good wet and dry abrasion resistance vas obtained.

EXAMPLE 13

100 Parts of a poly-ε-caprolactam fibre yarn are inroduced at 22°C into a dye bath that consists of a clear olution of
1 part of dye VI and
1.3 parts of N,N-dimethyl oleylamine in
1600 parts of tetrachloroethylene.
The dyeing is carried out as described in Example 1. A clear red coloring with good fastness characteristics s obtained.

EXAMPLE 14

100 Parts poly-ε-caprolactam fibre yarn are introluced at 22°C into a dye bath that consists of a clear olution of
1 part of dye VII
1 part of N,N-di-(2-hydroxyethyl)-oleylamine and
2 parts of glacial acetic acid
in 1600 parts of tetrachloroethylene.
The dyeing is carried out as described in Example 1. A uniform orange coloring with good fastness characteristics is obtained.

EXAMPLE 15

100 Parts of a poly-ε-caprolactam fibre yarn are introduced at 22°C into a bath that consists of a clear solution of
1 part of dye VIII and
0.4 parts of N,N-diethyl-dodecylamine in
1600 parts of tetrachloroethylene.
The dyeing is carried out as described in Example 1. A clear blue coloring with good fastness qualities is obtained.

EXAMPLE 16

100 Parts of a poly-ε-caprolactam fibre yarn are introduced at 22°C into a dye bath that consists of a clear solution of
0.5 parts of dye IX
0.8 parts of N,N-di-(2-hydroxyethyl)-oleylamine and
4 parts of glacial acetic acid
in 1600 parts of tetrachloroethylene.
The dyeing is done as described in Example 1. A uniform, clear red coloring is obtained.

EXAMPLE 17

100 Parts of a poly-ε-caprolactam fibre yarn are introduced at 22°C into a dye bath that consists of a clear solution of
0.5 parts of the dye amino salt prepared from dye X and N,N-diethyl-oleylamine and
4 parts of glacial acetic acid in 1,600 parts of tetrachloroethylene.
The dyeing is achieved as described in Example 1. A clear turquoise coloring is obtained.

EXAMPLE 18

100 Parts wool knitting yarn are introduced at 22°C into a dye bath that consists of a clear solution of
1 part of dye XI
1 part of N,N-dimethyl-stearylamine and
4 parts of glacial acetic acid in 1,600 parts of tetrachloroethylene.
The dyeing is carried out as described in Example 2. A uniform blue coloring is obtained.

EXAMPLE 19

100 Parts wool knitted fabric are introduced at 22°C into a dye bath that consists of a clear solution of 2 parts of the dye amino salt prepared from the dye acid that is the basis for dye No. 26,550 and coco fat amine in
1,600 parts of tetrachloroethylene
8 parts of water and
10 parts of a mixture of
70 parts of paraffin sulfonate
3 parts of dodecyl benzene sulfonate
17 parts of oleylsulfate and
10 parts of a reaction product of 1 mole phenol with 2.7 moles vinyltoluene and 16 moles ethylene oxide.
The dyeing is carried out as described in Example 2. A deep green coloring with good fastness characteristics is obtained.

EXAMPLE 20

The process is as described in Example 19, but instead of the dye amino salt described there, the same amount of a coco fat amino salt of dye XII is used.

A uniform scarlet coloring with good fastness characteristics is obtained.

EXAMPLE 21

100 Parts of a poly-ε-caprolactam fibre yarn are introduced at 22°C into a dye bath that consists of a clear solution of

1 part of the dye amino salt prepared from the dye acid that is the basis for dye No. 50,315 and coco fat amine in 1600 parts of tetrachloroethylene.

The dyeing is carried out as described in Example 1. A deep blue coloring with good fastness characteristics is obtained.

EXAMPLE 22

100 Parts of a coil of textured poly-ε-caprolactam filaments are introduced at room temperature into a clear solution of

1 part of the dye amino salt prepared from the dye acid that is the basis for dye No. 62,105 and N-dodecyl morpholine in

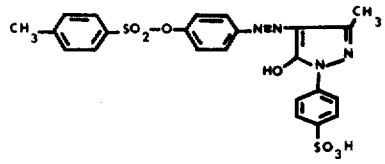
5000 parts of tetrachloroethylene.

The bath is heated with vigorous circulation to 100°C within 35 minutes and kept at this temperature for 45 minutes. Subsequently it is cooled to 45°C, the dye bath separated off and the material rinsed with fresh tetrachloroethylene for 10 minutes at 50°C. A clear blue coloring is obtained.

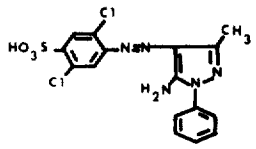
Structures of dyes I-XII used in the examples:

Number — Structure

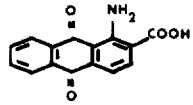
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II

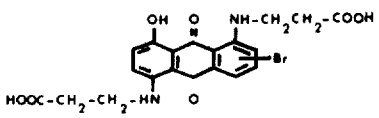


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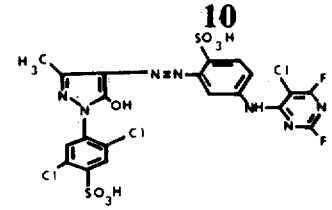
German Auslegeschrift 1,266,272

IV



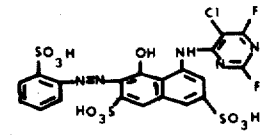
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V



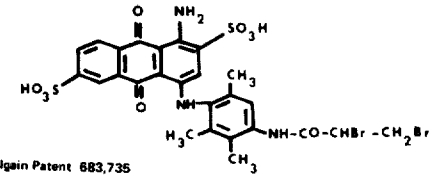
German Auslegeschrift 1,769,172

VI



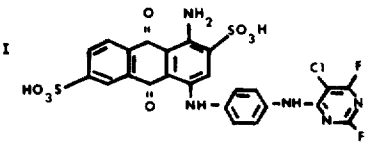
German Auslegeschrift 1,619,530

VII



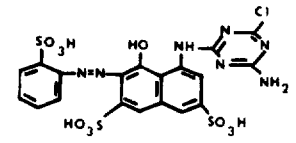
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VIII



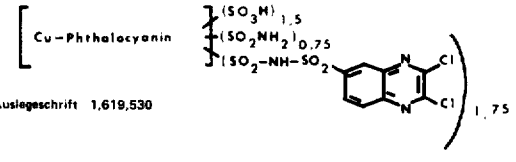
German Offenlegungsschrift 1,769,172

IX



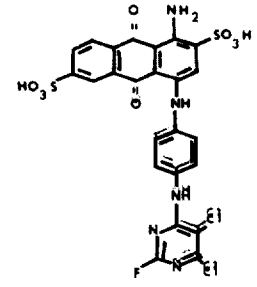
Reactive Red 12
C.I. 18156

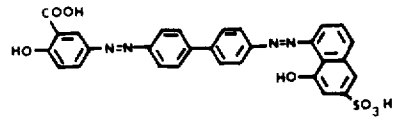
X



German Auslegeschrift 1,619,530

XI





rect Red 1
l. 22310

What is claimed is:

1. A process for dyeing natural or synthetic polyam-e fiber material containing NH-groups comprising the eps of

1. immersing the fiber materials in a dyebath consisting essentially of

a. an organic solvent; said organic solvent consisting of chlorohydrocarbon having a boiling point of 40° to 150°C.;

b. an amine salt of a dyestuff or an amine adduct of a dyestuff; said dyestuff containing 1–4 carboxylic acid or sulfonic acid groups, said amine having at least eight carbon atoms, at least three of which are in an uninterrupted chain; and

c. 0.01 to 0.5% by weight of water based on the weight of the chlorohydrocarbon;

2. dyeing the fiber material until the dyebath is exhausted; and then

3. removing the dyed fiber materials from the exhausted dyebath.

2. The process of claim 1, in which the dyebath additionally contains 0.01 to 0.5% by weight based on the chlorohydrocarbon, of an emulsifier.

3. The process of claim 1 in which said chlorohydrocarbon is tetrachloroethylene, trichloroethylene, or 1,1,1-trichloropropane.

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