QUATERNIZED FLUORINDINE COMPOUNDS AND TEXTILE MATERIALS DYED THEREWITH

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22 Claims. (Cl. 8-55)

ABSTRACT OF THE DISCLOSURE

Quaternary salts of fluorindine compounds are useful as dyes for acrylic and modacrylic textile materials.

This invention relates to quaternary salts of compounds of the fluorindine series and their use particularly as dyes for acrylic polymer textile materials.

The compounds are quaternary salts of fluorindines having the general formula

wherein the R groups are the same or different and each represents lower alkyl or substituted lower alkyl and X and Y are the same or different and each represents an ortho-phenylene group, a 1,2-naphthylenylene group, or a 2,3-naphthylenylene group.

The quaternary salts are prepared by quaternizing the above fluorindines so as to obtain either mono-quaternary or di-quaternary salts of the formulas

in which each R₁ represents lower alkyl or benzyl, R, X and Y are as defined above, and Z represents an anion derived from quaternization, e.g., ClO₄, BrO₄, CH₃SO₃O₄, HSO₄O₄, H₂PO₄O₄, etc.

The quaternization of the fluorindine compounds may be carried out in a well-known manner illustrated in the examples below in an inert solvent using the known quaternizing agents. A dialkyl sulfate, an alkyl chloride, an alkyl bromide, an alkyl iodide, an aralkyl chloride, an aralkyl bromide or an alkyl ester of paratoluene sulfonic acid, for example, may be employed. Specific quaternizing agents include, for example, dimethyl sulfate, diethyl sulfate, dipropyl sulfate, dibutyl sulfate, ethyl bromide, ethyl chloride, methyl iodide, ethyl iodide, n-butyl iodide, lauryl iodide, benzyl chloride, benzyl bromide, methyl p-toluene sulfonate, ethyl p-toluene sulfonate, n-propyl p-toluene sulfonate and n-butyl p-toluene sulfonate.

The following are representative fluorindines which are quaternized to obtain the quaternary salts of the invention: fluorindine, 5,12-dimethylfluorindine, 5,12-diethylfluorindine, 5,12-diisopropylfluorindine, 2,5,9,12-tetramethylfluorindine, 3,10-bis(3fluoromethyl)-5,12-dimethylfluorindine, 2,9,12-dibromo-5,12-dimethylfluorindine, 2,9,12-dinitro-5,12-dimethylfluorindine, 5,12-di-(p-cyanobutoxy)fluorindine, 5,12-di-(p-hydroxyethyl)fluorindine, 5,12-di-butylfluorindine, 2,5-dimethyl-12-ethylfluorindine, 2,5-dimethylfluorindine, 12-ethylfluorindine, 2,9-bis(sulfamido)-5,12-diethylfluorindine, 2,9-dimethoxy-5,12-diethylfluorindine, 5,12-dimethyl-dibenzo[b,n]fluorindine.

Fluorindine, itself, is a known compound as is 5,12-diphenylfluorindine. The other fluorindines substituted in at least the 5,12-positions are prepared by reaction of 2,5-dihydroxy-1,4-benzoquinones with the appropriate o-phenylenediamine or o-napthalenediamine in the presence of pyridine or an alkylpyridine as described in our co-filed U.S. patent application No. 499,078 and illustrated in the examples below. In that application the above compounds are named primarily as 5,12-dihydroquinonoxalol[2,3-b]phenazines. The unsymmetrical fluorindines described above where the R groups are different are prepared as described in our above patent application by reaction of a hydroxyquinazinone as illustrated in the examples below.

The quaternized fluorindine compounds are especially useful as dyes for acrylic polymer textile materials such as those containing acrylonitrile units yielding blue and green dyeings having good fastness, for example, light, washing, perspiration, gas (atmospheric) fade, and sublimation. The fluorindines can also be expected to respond favorably to other tests as textile dyes when tested by methods such as described in the A.A.T.C.C. Technical Manual, 1964 Edition. The degree of utility varies, for example, depending upon the textile material being dyed and the formula of the particular fluorindine in use. Thus, all of the quaternary fluorindine compounds will not have the same degree of utility for the same textile material.

The described quaternary fluorindine compounds generally have better light-fastness and wet-fastness properties than do the corresponding non-quaternary fluorindines. They can be expected to show less cross-staining when dyeing mixtures of acrylic fibers with other fibers.

As can be seen from the following examples, the substituents attached to the alkyl or aryl groups R of the above formula, and to the ortho-phenylene groups represented by X and Y can be varied widely and function primarily as auxochrome groups to control the color of the fluorindine compound. Accordingly, the substituted alkyl groups represented by R includes hydroxyalkyl, e.g., hydroxyethyl, polyhydroxyalkyl, e.g., 2,3-dihydroxypropyl; alkoxyalkyl, e.g., methoxyethyl; cyanacyloalkyl, e.g., 3-cyanooctylalkyl; acyloxyalkyl, e.g., acetoxethyl; carboxalkoxyalkyl, e.g., carboxethoxethyl; halogenoalkyl, e.g., chloroethoxy; hydroxyhalogenoalkyl, e.g., hydroxychloroalkyl; chloroethoxy; chloroalkyl, e.g., methylsulfonylalkyl, e.g., methyisulfonfylalkyl; alkyloalkoxyalkyl, e.g., CH₂OOCOCH₃CH₂OOCOCH₃CH₂—carboxyamidoalkyl, e.g., carboxamidoethyl, benzyl, phenoxalkyl, e.g., p-phenoxethyl; alkylsulfonamidoalkyl, e.g.,
3. N-methylsulfonamidoethyl; sulfonamido, alkylsulfonamido e.g. N-methyl sulfonamido; alkylcarboxamidoalkyl, e.g. ethylcarboxamidooethyl; dicarboxamidoalkyl, e.g. β-dicarboxamidoethyl, etc. Substituents on the ortho-phenylene groups represented by X and Y include alkyl e.g. methyl, allyl e.g. methoxy, nitro, amino, cyano, halogen, alkylsulfonyl e.g. methylsulfonyl, alkylsulfonamido e.g. methylsulfonamido, alkanoylamido e.g. aceticamido, alkythio e.g. methylthio, carbamoyl, etc. The compounds where R is alkyl or substituted alkyl may have better affinity than compounds where R is an aryl group such as phenyl.

The following example illustrates one way in which the fluorinide compounds of the invention can be used to dye acrylonitrile polymer textile material. 1 gram of dye is dissolved by warming in 5 cc. of methyl Cellosolve. A 2% aqueous solution of a non-ion surfactant, such as Igepal CA (a polymerized ethylene oxide-alkylphenol condensation product), is added slowly until a fine emulsion is obtained and then the dye mixture is brought to a volume of 200 cc. with warm water. 5 cc. of a 5% aqueous solution of formic acid or acetic acid are added and then 10 grams of fabric mill dyeing acrylonitrile fiber is entered and in the case of Orlon 42 the dyeing is carried out at the boil for one hour. In the case of materials made of Veral acrylic fiber the dyebath temperature should not exceed 90° C. in order to avoid damage to the fiber. The dyed material is then washed well with water and dried.

Representative acrylonitrile homopolymer and copolymer textile materials dyed by the fluorinide compounds, especially the above, 5.12-alkyl and substituted alkyl fluorinides, are characterized by containing at least about 35% combined acrylonitrile units and up to about 95% acrylonitrile units, and modified, for example, by 85-5% of vinyl pyridine units as described in U.S. Patents 2,990,393 (Re. 25,533) and 3,014,008 (Re. 25,539) or modified by 65–5% of vinylpyridilidene units, for example, as described in U.S. Patent 2,970,783, or modified with 65–5% of acrylamide units or acrylamide units as described in U.S. Patents 2,879,253, 2,879,254 and 2,838,470. Similar amounts of the other polymers mentioned above are also useful. A preferred group of the copolymers readily dyable with the fluorinides are the modacylamide polymers such as described in U.S. Patent 2,831,826, composed of a mixture of (A) 70–95% by weight of a copolymer of from 30 to 60% by weight of vinylidene chloride or vinyl chloride and 70–35% by weight of acrylonitrile, and (B) 30–5% by weight of a second polymer from the group consisting of (1) homopolymer of acrylamide monomers of the formula

wherein R₃ is selected from the group consisting of hydrogen and methyl, and R₂ and R₃ are selected from the group consisting of hydrogen and alkyl groups of 1–6 carbon atoms, (2) copolymers consisting of at least two of said acrylamide monomers, and (3) copolymers consisting of at least 50% by weight of at least one of said acrylamide monomers and not more than 50% by weight of a polymerizable monovinyl pyridine monomer.

A particularly efficacious group of modacylamide polymers is an acetoamide soluble mixture of (A) 70–95% by weight of a copolymer of 30–65% by weight of vinylidene chloride and 70–35% by weight of acrylonitrile and (B) 30–5% by weight of an acrylamide homopolymer having the above formula wherein R₁, R₂ and R₃ are as described above. Specific polymers of that group contain 70–95% by weight of (A) a copolymer of from 30–65% by weight of vinylidene chloride and 70–35% by weight of acrylonitrile and (B) 30–5% by weight of a lower N-alkylacylamide polymer such as poly-N-methacrylamide, poly-N-isopropylacrylamide and poly-N-tertarybutylacrylamide. The following examples will serve to illustrate the synthesis and use of the fluorinide compounds.

EXAMPLE 1. 5,12-DIHYDRO -5,12-DIMETHYLQUINOXALO [2,3-b] PHENAZINE (5,12 - DIMETHYLFLUORINDINE)

43 g. (0.22 mole) N-methyl-o-phenylenediamine dihydrochloride and 14 g. (0.1 mole) of 2,5-dihydroxy-1,4-benzoquinones dissolved in 150 ml. of pyridine were heated to a boil and refluxed with stirring for 17 hours. The reaction mixture was then cooled and filtered. The precipitate was washed with hot water, then with acetone and air-dried. The product was a dark powder, soluble in methanol and dilute mineral acids with a clear blue color. The acid solutions give a typical ruby-red fluorescence in ultraviolet light.

Quaternization

A sturr of 5 g. of 5,12-dihydro-5,12-dimethylquinoxalo [2,3-b]phenazine in 25 ml. of dimethylsulfate was stirred for 2 hours. The reaction mixture was then added slowly to slowly to 500 ml. of water at 50° C. The temperature was raised to 95° C. and the solution stirred for 1/2 hour at 95° C. Twenty-five grams of sodium iodide was then added. The mixture was stirred and filtered. The precipitate was washed with water and dried at 60° C. The quaternary iodide thus formed dyed acrylic fibers in bright blue shades with excellent fastness properties. The dye gives a slightly greener shade than the unquaternized material.

EXAMPLE 2. 5,12-DIETHYL-5,12-DIHYDROQUINOXALO [2,3-b] PHENAZINE

18 g. N-ethyl-o-phenylenediamine dihydrochloride and 5.6 g. of 2,5-dihydroxy-1,4-benzoquinone in 75 ml. of pyridine were refluxed, with good agitation for 24 hours. The reaction mixture was then cooled and filtered. The precipitate was washed with warm water until the filtrate came through a clear blue. It was then washed with acetone and air-dried. Yield—15 g. of a black crystalline powder which gave a bright blue solution in dilute mineral acids and methanol.

Quaternization

Five grams of 5,12-dihydro-5,12-diethyquinoxalo [2,3-b]phenazine in 25 ml. of dimethylsulfate was stirred seven hours at 25° C. The reaction mixture was then cooled and filtered. The precipitate was thoroughly washed with ethyl acetate and dried at 60° C. The methosulfate quaternary salt dyed acrylic fibers bright fast blue shades. 6.8 g. (0.02 mole) 5,12-dihydro-5,12-diethylquinoxalo [2,3-b]phenazine in 25 ml. of diethylsulfate was stirred for five hours at 25° C. The reaction mixture was poured into 700 ml. of water and the temperature raised to 95° C. The solution was stirred 1/4 hour at 95° C. and filtered hot. Twenty grams of sodium iodide was added and the reaction mixture was cooled and filtered. The precipitate was recrystallized from water. The resulting 5,12-dihydro-5,12-diethylquinoxalo [2,3-b]phenazinium iodide dye acrylic fibers in fast blue shades. The quaternary salt has the formula:

EXAMPLE 3. 2,5-DIMETHYL-12-ETHYLFLUORINDINE

4.8 g. of 10-ethyl-3-hydroxy-2-phenazinone and 4 g. of 1-N-4-dimethyl-o-phenylenediamine dihydrochloride are added to 25 g. of 3-picoline. The reaction mixture is

3,390,948
heated to 140° C. and stirred at 130-140° C. for two hours removing water as formed. The reaction mixture is cooled and filtered. The precipitate is washed with water, then with dilute (5%) ammonia solution. The filter cake is then thoroughly washed with water and dried at 60° C.

Quaternization

4.77 g. of the above trialkylfluorindine in 80 ml. of dry toluene is heated to 90° C. and 6.66 g. of dimethylsulfate is added over a period of 15 minutes. The temperature is kept at 85-90° C. during the addition and for 15 minutes thereafter. A mixture of 25 ml. of isopropanol and 3 ml. of water is then added slowly and the reaction mixture refluxed for 15 minutes, chilled to 5-10° C. and filtered. The filter cake was washed with cold toluene and dried at 60° C. Yield is 6.5 g. (99.5%). The quaternary dyes acrylic fibers in bright, blue shades with excellent fastness properties.

The compound has the formula

\[ \text{CH}_3 \text{BO}_3 \text{H} \]

Quaternization

The above quaternization was repeated except 5 g. of the trialkylfluorindine in 25 ml. of diethyl sulfate was stirred at room temperature for five hours. The reaction mixture was dissolved in a large excess of diethyl ether, filtered and the filter cake thoroughly washed with ether. The product was dried at 60° C. Yield is 7.15 g. The quaternary ethosulfate dyes acrylic fibers blue shades with properties comparable to the methosulfate quaternary above.

**EXAMPLE 4.**—5,12-DIMETHYL-DIBENZO[b,m] FLUORINDINE

Forty-nine grams of 2-amino-3-methylaminonaphthalene dihydrochloride and 14 g. of 2,5-dihydroxybenzoquinone in 150 ml. of 3-picoline were refluxed with stirring for 3½ hours. The reaction mixture was then cooled and filtered and the product thoroughly washed with warm water. The precipitate was then washed with 3% sodium hydroxide until the filtrate came through colorless. It was then washed with water until alkali-free and dried at 60° C. The material dyes acrylic fibers fast blue shades. Quaternization with dimethylsulfate gave a product which dyes acrylic and modacrylic fibers in fast, blue shades.

Additional fluorindine compounds shown in the following tables, prepared as described in our above patent application, are quaternized in the manner described in the above examples and yield mono-quaternary or di-quaternary fluorindine compounds which dye acrylic, nitrile, polymer fibers to blue shades of good fastness properties. The compounds of this table are symmetrical compounds of the formula:

![Formula](image)

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**TABLE**

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The compounds of this table are unsymmetrical compounds of the formula:

![Formula](image)

**TABLE**

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The invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinafter, and as defined in the appended claims.

What we claim is:

1. A compound having the formula

   \[
   \text{[Diagram]}
   \]

   wherein

   \( X \) and \( Y \) are the same or different and each represents ortho-phenylene; ortho-phenylene substituted with lower alkyl, lower alkoxy, halogen, hydroxy, nitro, amino, lower alkylbifurionyl, lower alkylsulfonamido, lower alkanoylamido, lower alkylthio, carbamoyl, methylcarbamoyl, trifluoromethyl, or sulfamoyl; 1,2-naphthylenyl; or 2,3-naphthylenyl;

   \( R \) represents lower alkyl or lower alkyl substituted with hydroxy, lower alkoxy, lower dialkylamino, cyano, lower alkanoyloxy, or halogen;

   \( R \) represents lower alkyl or benzyl;

   \( m \) and \( n \) each represent 0 or 1, the sum of \( m \) and \( n \) being 1 or 2; and

   \( Z \) represents an anion.
2. A compound having the formula
\[
\begin{array}{c}
\text{X} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{Z} 
\end{array}
\]
wherein
X and Y are the same or different and each represents ortho-phenylene; ortho-phenylene substituted with lower alkyl, trifluoromethyl, halogen, hydroxy, lower alkylsulfonyl, sulfoxamoyl, or nitro; 1,2-naphthylene; or 2,3-naphthylene;
R represents lower alkyl;
R₁ represents lower alkyl;
m and n each represent 0 or 1, the sum of m and n being 1; and
Z represents an anion.

3. A compound according to claim 2 wherein
X and Y each represents ortho-phenylene or ortho-phenylene substituted with lower alkyl;
R₁ represents methyl or ethyl; and
Z represents CH₃SO₃⁻ or C₆H₅SO₄⁻.

4. A compound having the formula
\[
\begin{array}{c}
\text{CH₃} \\
\text{N} \\
\text{N} \\
\text{Z} \\
\text{CH₃} 
\end{array}
\]
wherein Z is an anion.

5. A compound having the formula
\[
\begin{array}{c}
\text{CH₃} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{CF₃} \\
\text{Z} 
\end{array}
\]
wherein Z is an anion.

6. A compound having the formula
\[
\begin{array}{c}
\text{CH₃} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{Z} 
\end{array}
\]
wherein Z is an anion.

7. A compound having the formula
\[
\begin{array}{c}
\text{CH₃} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{NH₂} \\
\text{Z} 
\end{array}
\]
wherein Z is an anion.

8. A compound having the formula
\[
\begin{array}{c}
\text{CH₃CH₂OH} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{Z} 
\end{array}
\]
wherein Z is an anion.

9. A compound having the formula
\[
\begin{array}{c}
\text{H₂N₈SO₃⁻} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{Z} 
\end{array}
\]
wherein Z is an anion.

10. A compound having the formula
\[
\begin{array}{c}
\text{CH₃} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{OCH₃} \\
\text{Z} 
\end{array}
\]
wherein Z is an anion.

11. A compound having the formula
\[
\begin{array}{c}
\text{CH(C₂H₅)} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{Z} 
\end{array}
\]
wherein Z is an anion.

12. A compound having the formula
\[
\begin{array}{c}
\text{CH₃} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{Z} 
\end{array}
\]
wherein Z is an anion.

13. A compound having the formula
\[
\begin{array}{c}
\text{CH₃} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{SO₃⁻NH₂} \\
\text{Z} 
\end{array}
\]
wherein Z is an anion.

14. A compound having the formula
\[
\begin{array}{c}
\text{CH₃} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{Z} 
\end{array}
\]
wherein Z is an anion.

15. A compound having the formula
\[
\begin{array}{c}
\text{CH₃} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{Z} 
\end{array}
\]
wherein Z is an anion.

16. A compound having the formula
\[
\begin{array}{c}
\text{CH₃} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{Z} 
\end{array}
\]
wherein Z is an anion.

75 wherein Z is an anion.
17. A compound having the formula

wherein Z is an anion.

18. A compound having the formula

wherein Z is an anion.

19. A compound having the formula

20. Acrylonitrile polymer textile material dyed with a compound of claim 1.

21. Acrylonitrile polymer textile material dyed with a compound of claim 2.

22. Acrylonitrile polymer textile material dyed with a compound of claim 3.

No references cited.

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