

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 February 2002 (14.02.2002)

PCT

(10) International Publication Number
WO 02/12400 A2

(51) International Patent Classification⁷: **C09B 69/10**,
C08L 33/04

Foust; 216 Allison Court, Piney Flats, TN 37686 (US).
PEARSON, Jason, Clay; 116 Pickens Court, Kingsport,
TN 37663 (US). **COOK, Phillip, Michael**; 231 Saddle
Ridge Drive, Kingsport, TN 37664 (US).

(21) International Application Number: PCT/US01/20347

(22) International Filing Date: 27 June 2001 (27.06.2001)

(74) Agent: **BLAKE, Michael, J.**; P.O. Box 511, Kingsport,
TN 37662-5075 (US).

(25) Filing Language: English

(81) Designated States (*national*): CA, JP, MX.

(26) Publication Language: English

(30) Priority Data:
09/633,548 7 August 2000 (07.08.2000) US

(84) Designated States (*regional*): European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE, TR).

(71) Applicant: **EASTMAN CHEMICAL COMPANY**
[US/US]; 100 North Eastman Road, Kingsport, TN 37660
(US).

Published:
— *without international search report and to be republished
upon receipt of that report*

(72) Inventors: **CYR, Michael, John**; 204 Coralwood Drive,
Kingsport, TN 37663 (US). **WEAVER, Max, Allen**; 125
Hill Road, Kingsport, TN 37664 (US). **RHODES, Gerry**,

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: THERMALLY STABLE, ANTHRAQUINONE COLORANTS CONTAINING COPOLYMERIZABLE VINYL GROUPS

(57) Abstract: Disclosed are thermally-stable, anthraquinone colorant compounds (dyes) which contain one or more vinyl groups which render the compounds copolymerizable with reactive vinyl monomers to produce colored, polymeric compositions such as methacrylate polymeric materials. The compounds possess fastness (stability) to ultraviolet (UV) light, good solubility in vinyl monomers, good color strength and excellent thermal stability. Also disclosed are acrylic polymeric materials, i.e., polymers derived from acrylic acid esters, methacrylic acid esters and/or other copolymerizable vinyl compounds, having copolymerized therein one or more of the anthraquinone colorant compounds.



WO 02/12400 A2

- 1 -

THERMALLY STABLE, ANTHRAQUINONE COLORANTS
CONTAINING COPOLYMERIZABLE VINYL GROUPS

Field of the Invention

5 This invention pertains to certain thermally-stable, anthraquinone colorant compounds (dyes) which contain one or more vinyl groups which render the compounds copolymerizable with reactive vinyl monomers to produce colored, polymeric compositions such as acrylate and methacrylate polymeric materials. The compounds possess good fastness (stability) to ultraviolet (UV) light, good
10 solubility in vinyl monomers, good color strength and excellent thermal stability. The present invention includes acrylic polymeric materials, i.e., polymers derived from acrylic acid esters, methacrylic acid esters and/or other copolymerizable vinyl compounds, having copolymerized therein one or more of the dye compounds of the present invention.

15

Background and Prior Art

 It is known (J.S.D.C., April 1977, pp 114-125) to produce colored polymeric materials by combining a reactive polymer such terepolymers having epoxy groups or polyacryloyl chloride with anthraquinone dyes containing
20 nucleophilic reactive groups such as amino or hydroxy groups; to graft acryloylaminoanthraquinone dyes to the backbone of vinyl or divinyl polymers; and to polymerize anthraquinone dyes containing certain olefinic groups to produce polymeric dyes/pigments. U.S. Patent 4,115,056 describes the preparation of blue, substituted 1,4-diaminoanthraquinone dyes containing one acryloyloxy group and
25 and the use of the dyes in coloring various fibers, especially polyamide fibers. U.S. Patent 4,943,617 discloses liquid crystalline copolymers containing certain blue, substituted 1,5-diamino-4,8-dihydroxyanthraquinone dyes containing an olefinic group copolymerized therein to provide liquid crystal copolymers having high dichromism. U.S. Patent 5,055,602 describes the preparation of certain substituted
30 1,4-diaminoanthraquinone dyes containing polymerizable acryloyl and

- 2 -

methacryloyl groups and their use in coloring polyacrylate contact lens materials by copolymerizing.

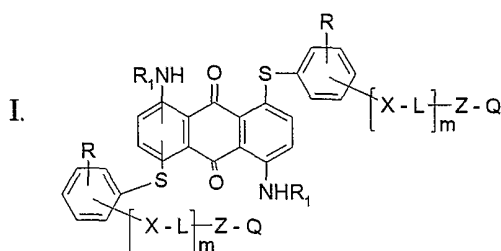
U.S. Patent 5,362,812 discloses the conversion of a variety of dye classes, including anthraquinones, into polymeric dyes by (a) polymerizing
 5 2-alkenylazlactones and reacting the polymer with dyes containing nucleophilic groups and by (b) reacting a nucleophilic dye with an alkenylazlactone and then polymerizing the free radically polymerizable dyes thus produced. The polymeric dyes are reported to be useful for photoresist systems and for colorproofing. U.S. Patent 5,367,039 discloses a process for preparing colored vinyl polymers suitable
 10 for inks, paints, toners and the like by emulsion polymerization of a vinyl monomer with reactive anthraquinone dyes prepared by functionalizing certain anthraquinone dyes with methacryloyl groups.

The preparation of a variety of dyes, including some anthraquinones, which contain photopolymerizable groups and their use for color filters suitable for use in
 15 liquid crystal television sets, color copying machines, photosensitive resist resin compositions, and the like are described in U.S. Patent 5,578,419.

Brief Summary of the Invention

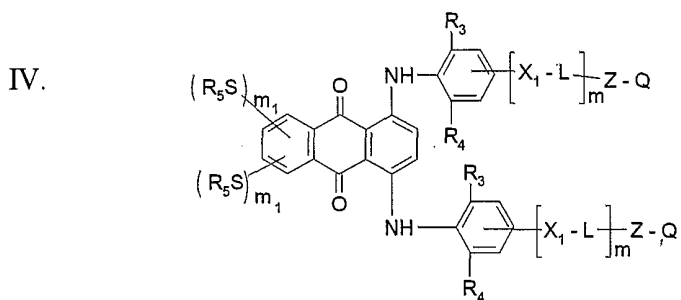
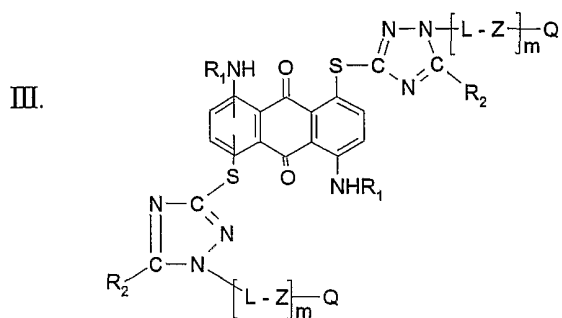
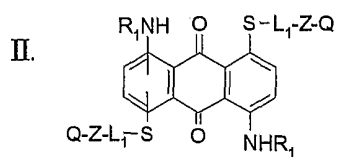
The anthraquinone dye compounds provided by the present invention are
 20 represented by general Formulae I-XXI set forth below. The dyes having Formulae I-VII are blue-cyan colorants, the dyes having Formulae VIII - XVIII are red-magenta colorants, and the dyes having Formulae XIX - XXI are yellow colorants.

Blue-Cyan Dyes

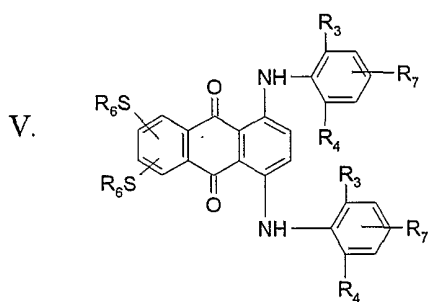


25

- 3 -

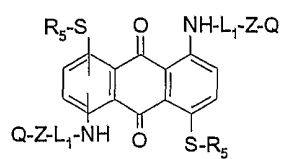


5

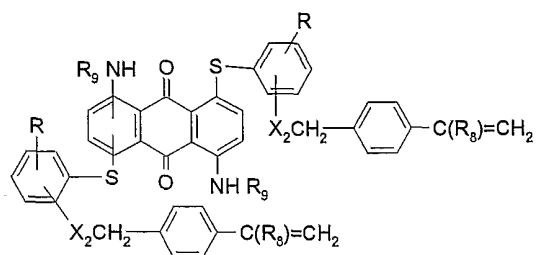


- 4 -

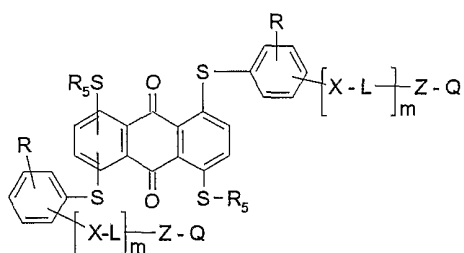
VI.



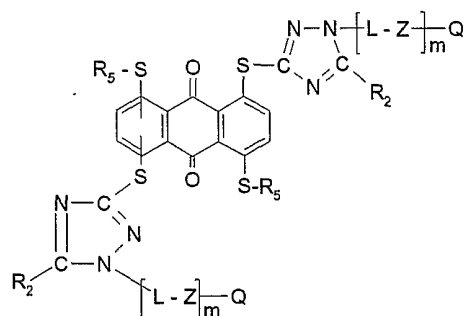
VII.

5 Red - Magenta Dyes

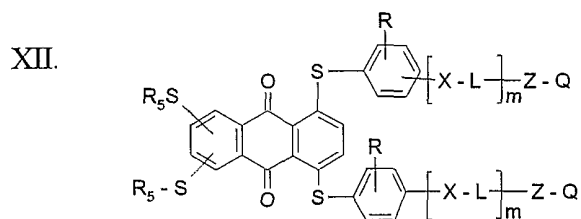
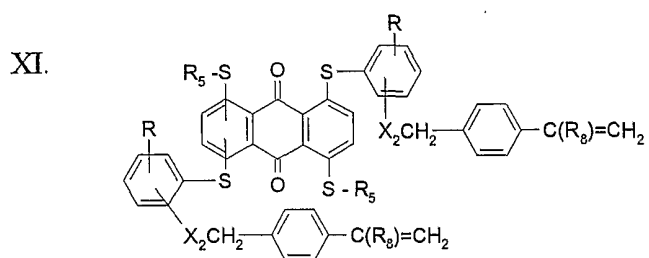
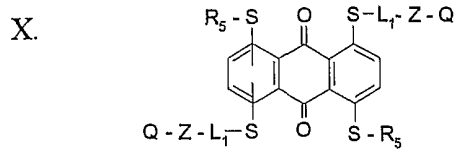
VIII.



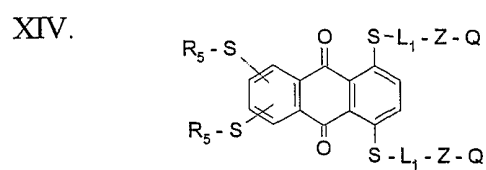
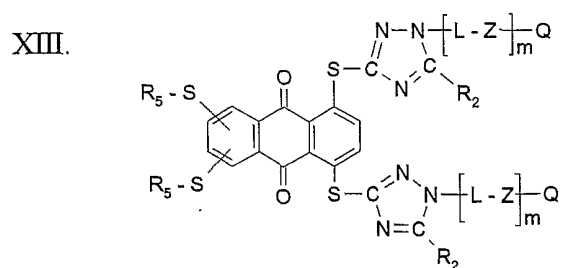
IX.



- 5 -

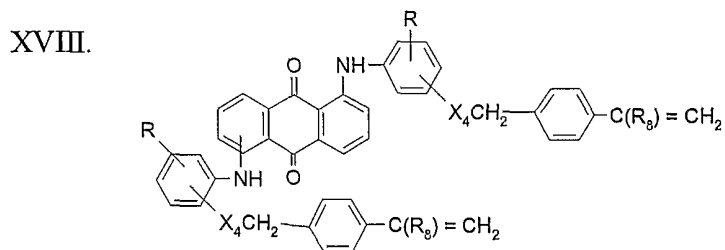
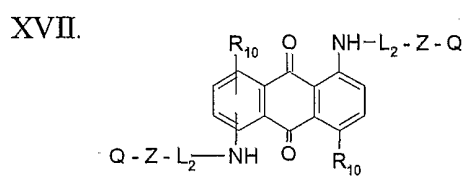
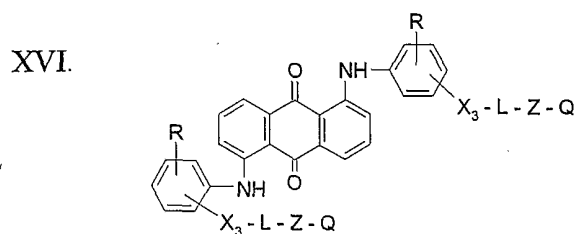
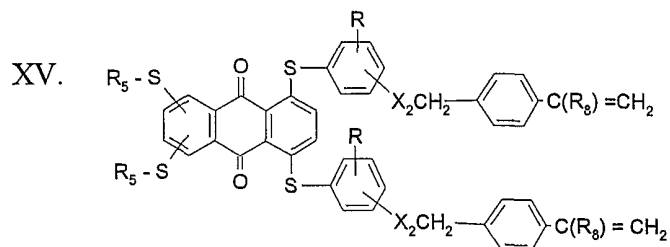


5

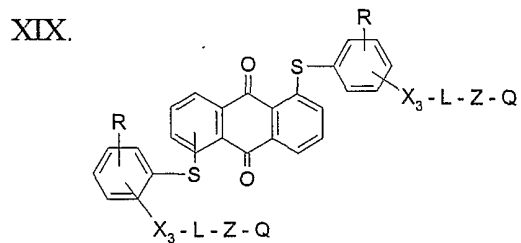


10

- 6 -

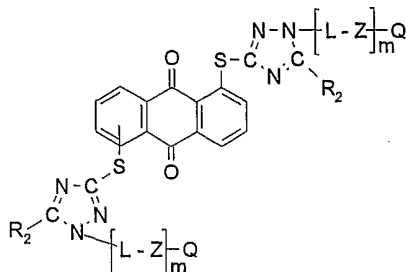


5 Yellow Dyes

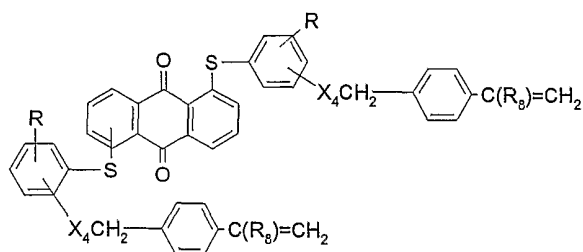


- 7 -

XX.



XXI.



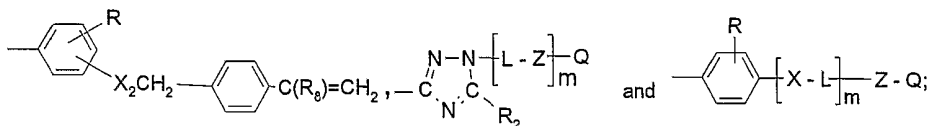
wherein:

5 R is selected from hydrogen or 1-3 groups selected from C₁ - C₆-alkyl, C₁ - C₆-alkoxy and halogen;

R₁ is selected from C₁ - C₆-alkyl, substituted C₁ - C₆-alkyl, C₃ - C₈-alkenyl, C₃ - C₈-cycloalkyl, aryl and -L₁-Z-Q; R₂ = selected from hydrogen, C₁ - C₆-alkyl, substituted C₁ - C₆-alkyl, C₃ - C₈-cycloalkyl and aryl;

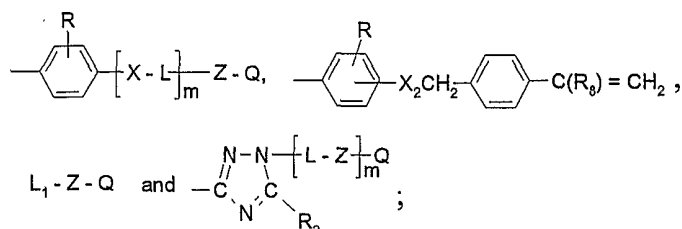
10 R₃ and R₄ are independently selected from C₁ - C₆-alkyl and bromine;

R₅ is selected from C₁ - C₆-alkyl, substituted C₁ - C₆ alkyl, C₃ - C₈-cycloalkyl, aryl, heteroaryl, -L₁-Z-Q,



R₆ is selected from

- 8 -



R_7 is selected from hydrogen, substituted or unsubstituted C_1 - C_6 -alkyl, C_1 - C_6 -alkoxy, halogen, hydroxy, substituted or unsubstituted C_1 - C_6 -alkylthio, sulfamoyl and substituted sulfamoyl;

R_8 is selected from hydrogen and C_1 - C_6 -alkyl;

5 R_9 is selected from the groups represented by R_1 and $-\text{L}-\text{Z}-\text{Q}$;

R_{10} is selected from hydrogen and halogen;

X is a covalent bond or a divalent linking group selected from $-\text{O}-$, $-\text{S}-$, $-\text{SO}_2-$, $-\text{CO}_2-$, $-\text{CON}(\text{Y})-$ and $-\text{SO}_2\text{N}(\text{Y})-$, wherein Y is selected from hydrogen, C_1 - C_6 -alkyl, substituted C_1 - C_6 -alkyl, C_3 - C_8 -cycloalkyl, C_3 - C_8 -alkenyl, aryl and

10 $-\text{L}-\text{Z}-\text{Q}$;

X_1 is selected from $-\text{O}-$, $-\text{S}-$, $-\text{SO}_2-$ and $-\text{SO}_2\text{N}(\text{Y})-$;

X_2 is selected from $-\text{CO}_2-$ and $-\text{SO}_2\text{N}(\text{Y}_1)-$, wherein Y_1 is a group selected from hydrogen, C_1 - C_6 -alkyl, substituted C_1 - C_6 -alkyl, C_3 - C_8 -alkenyl, C_3 - C_8 -cycloalkyl, aryl heteroaryl and $-\text{CH}_2\text{-p-C}_6\text{H}_4\text{-C}(\text{R}_8)=\text{CH}_2$;

15 X_3 is selected from $-\text{CO}_2-$, $-\text{SO}_2\text{N}(\text{Y})-$;

X_4 is selected from $-\text{CO}_2-$, $-\text{O}-$ and $-\text{SO}_2\text{N}(\text{Y}_1)-$;

L is a divalent linking group selected from C_1 - C_8 -alkylene, C_1 - C_6 -alkylene-arylene, arylene, C_1 - C_6 -alkylene-arylene $-\text{C}_1$ - C_6 -alkylene, C_3 - C_8 -cycloalkylene,

- 9 -

C₁-C₆-alkylene-C₃-C₈-cycloalkylene -C₁-C₆-alkylene, C₁-C₆-alkylene -Z₁-arylene-Z₁-C₁-C₆-alkylene and C₂-C₆-alkylene-[-Z₁-C₂-C₆-alkylene-]_n- wherein Z₁ is selected from -O-, -S- and -SO₂- and n is 1-3;

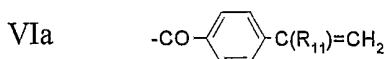
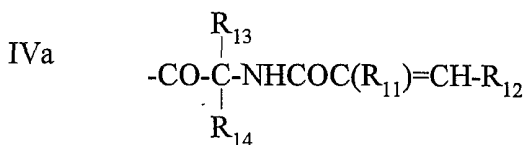
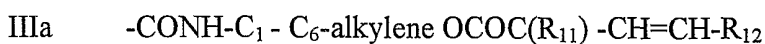
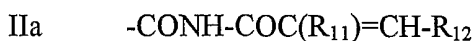
5 L₁ is a divalent linking group selected from C₂-C₆-alkylene, C₁-C₆-alkylene-C₃-C₈-cycloalkylene-C₁-C₆-alkylene, C₁-C₆-alkylene-arylene, C₃-C₈-cycloalkylene, and C₂-C₆-alkylene-[-Z₁-C₂-C₆-alkylene-]_n-;

L₂ is selected from C₂-C₆-alkylene, C₁-C₆-alkylene- arylene-C₁-C₆ alkylene and C₁-C₆-alkylene-C₃-C₈-cycloalkylene-C₁-C₆-alkylene;

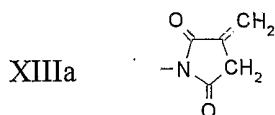
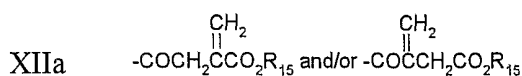
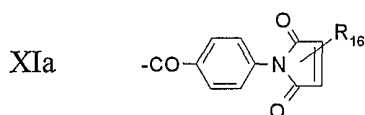
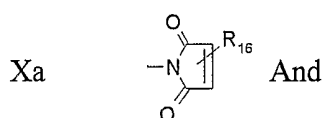
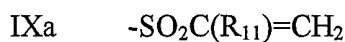
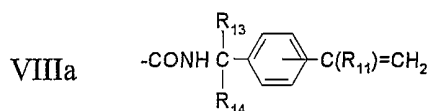
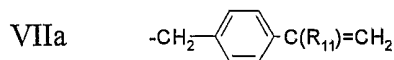
10 Z is a divalent group selected from -O-, -S-, -NH-, -N(C₁-C₆-alkyl)-, -N(C₃-C₈ alkenyl)-, -N(C₃-C₈ cycloalkyl)-, -N(aryl)-, -N(SO₂C₁-C₆-alkyl) and -N(SO₂ aryl)-, provided that when Q is a photopolymerizable optionally substituted maleimide radical, Z represents a covalent bond; Q is an ethylenically-unsaturated, photosensitive polymerizable group; and

m and m₁ each is 0 or 1.

15 The ethylenically-unsaturated, photosensitive copolymerizable groups represented by Q are selected from the following organic radicals:



- 10 -



wherein:

R_{11} is selected from hydrogen and $\text{C}_1\text{-C}_6\text{-alkyl}$;

R_{12} is selected from hydrogen; $\text{C}_1\text{-C}_6\text{-alkyl}$; phenyl and phenyl substituted
 5 with one or more groups selected from $\text{C}_1\text{-C}_6\text{-alkyl}$, $\text{C}_1\text{-C}_6\text{-alkoxy}$, $-\text{N}(\text{C}_1\text{-C}_6\text{-alkyl})$,
 nitro, cyano, $\text{C}_1\text{-C}_6\text{-alkoxycarbonyl}$, $\text{C}_1\text{-C}_6\text{-alkanoyloxy}$ and halogen; 1- and
 2-naphthyl which may be substituted with $\text{C}_1\text{-C}_6\text{-alkyl}$ or $\text{C}_1\text{-C}_6\text{-alkoxy}$; 2- and
 3-thienyl which may be substituted with $\text{C}_1\text{-C}_6\text{-alkyl}$ or halogen; 2- or 3-furyl
 which may be substituted with $\text{C}_1\text{-C}_6\text{-alkyl}$;

10 R_{13} and R_{14} are selected from hydrogen, $\text{C}_1\text{-C}_6\text{-alkyl}$, substituted $\text{C}_1\text{-C}_6\text{-alkyl}$, aryl or may be combined to represent a $-\text{[CH}_2\text{]}_{3-5}\text{-}$ radical;

R_{15} is selected from hydrogen, $\text{C}_1\text{-C}_6\text{-alkyl}$, substituted $\text{C}_1\text{-C}_6\text{-alkyl}$,

- 11 -

C₃-C₈-alkenyl, C₃-C₈-cycloalkyl and aryl;

R₁₆ is selected from hydrogen, C₁ - C₆-alkyl and aryl.

The term "C₁-C₆-alkyl" is used herein to denote a straight or branched chain, saturated aliphatic hydrocarbon radical containing one to six carbon atoms.

5 The term "substituted C₁-C₆-alkyl" is used to denote a C₁-C₆-alkyl group substituted with one or more groups, preferably one to three groups, selected from the group consisting of hydroxy, halogen, cyano, aryl, aryloxy, arylthio, C₁-C₆ alkylthio, C₃-C₈-cycloalkyl, C₁-C₆-alkanoyloxy and $[-O-R_{17}-]R_{18}$, wherein R₁₇ is selected from the group consisting of C₁-C₆ alkylene, C₁-C₆-alkylene-arylene,
10 cyclohexylene, arylene, C₁-C₆-alkylene-cyclohexylene and C₁-C₆-alkylene-cyclohexylene-C₁-C₆-alkylene;

R₁₈ is selected from the group consisting of hydrogen, hydroxy, carboxy, C₁-C₆-alkanoyloxy, C₂-C₆-alkoxycarbonyl, aryl and C₃-C₈-cycloalkyl; and p is 1, 2, or 3.

15

Detailed Description

The terms "C₁-C₆-alkylene" and "C₁-C₈-alkylene" are used to denote straight or branched chain, divalent, aliphatic hydrocarbon radicals containing one to six and one to eight carbons, respectively, and these radicals substituted with one
20 to three groups selected from C₁-C₆-alkoxy, C₁-C₆-alkoxycarbonyl, C₁-C₆-alkanoyloxy, hydroxy, aryl and halogen. Similarly, the term "C₂-C₆-alkylene" is used to denote a straight or branched chain, divalent, hydrocarbon radical which may be unsubstituted or substituted as described in this paragraph for the C₁-C₆-alkylene and C₁-C₈-alkylene radicals.

25 The terms "C₁-C₆-alkoxy", "C₁-C₆-alkoxycarbonyl", "C₁-C₆-alkanoyloxy" and "C₁-C₆-alkanoylamino" are used to denote radicals corresponding to the structures -OR₁₉, -CO₂ R₁₉, -OCOR₁₉ and NHCOR₁₉, respectively, wherein R₁₉ is C₁-C₆-alkyl or substituted C₁-C₆-alkyl. The term "C₃ - C₈-alkenyl" is used to denote an aliphatic hydrocarbon radical containing at least one double bond. The
30 term "C₃ - C₈-cycloalkyl" is used to denote a saturated, carbocyclic hydrocarbon

- 12 -

radical having three to eight carbon which may be unsubstituted or substituted with one to three C₁-C₆-alkyl group(s). The term "C₃ - C₈-cycloalkylene" is used to denote a carbocyclic, divalent hydrocarbon radical which contains three to eight carbon atoms, preferably five or six carbons.

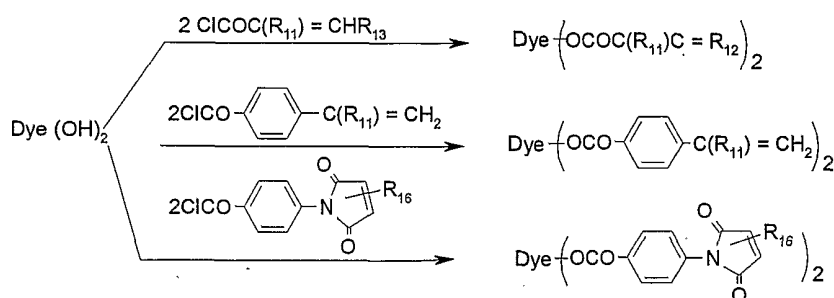
5 The term "aryl" as used herein denotes phenyl and phenyl substituted with one to three substituents selected from C₁-C₆-alkyl, substituted C₁-C₆-alkyl, C₁-C₆-alkoxy, halogen, carboxy, cyano, C₁-C₆-alkanoyloxy, C₁-C₆-alkylthio, C₁-C₆-alkylsulfonyl, trifluoromethyl, hydroxy, C₁-C₆-alkoxycarbonyl, C₁-C₆-alkanoylamino and -O-R₂₀, S-R₂₀, -SO₂-R₂₀, -NHSO₂R₂₀ and -NHCO₂R₂₀,
10 wherein R₂₀ is phenyl or phenyl substituted with one to three groups selected from C₁-C₆-alkyl, C₁-C₆-alkoxy and halogen. The term "arylene" as used herein denotes includes 1,2-, 1,3- and 1,4-phenylene and such divalent radicals substituted with one to three groups selected from C₁-C₆-alkyl, C₁-C₆-alkoxy and halogen. The term "heteroaryl" as used herein denotes a 5- or 6- membered aromatic ring
15 containing one to three hetero atom selected from oxygen, sulfur and nitrogen. Examples of such heteroaryl groups are thienyl, furyl, pyrrolyl, imidazolyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, triazolyl, thiadiazolyl, oxadiazolyl, tetrazolyl, pyridyl, pyrimidyl, benzoxazolyl, benothiazolyl, benzimidazolyl, indolyl and the like. The heteroaryl radicals may be substituted
20 with one to three groups selected from C₁-C₆-alkyl, C₁-C₆-alkoxy, substituted C₁-C₆-alkyl, halogen, C₁-C₆-alkylthio, aryl, arylthio, aryloxy, C₁-C₆-alkoxycarbonyl and C₁ - C₆-alkanoylamino.

 The term "halogen" is used to include fluorine, chlorine, bromine, and iodine. The terms "sulfamoyl and substituted sulfamoyl" denote radicals having
25 the structure -SO₂N(R₂₁)R₂₂, wherein R₂₁ and R₂₂ are independently selected from hydrogen, C₁-C₆-alkyl, substituted C₁-C₆-alkyl, C₃-C₈-alkenyl, C₃-C₈-cycloalkyl, aryl and heteroaryl.

 The preferred dye compounds of Formulae I, II, III, IV, V, VI, VIII, IX, X, XII, XIII, XIV, XVI, XVII, XIX, and XX are those where Z is -O-. These dyes are
30 prepared by reacting the corresponding dihydroxy dye [Dye (OH)₂] with a reagent

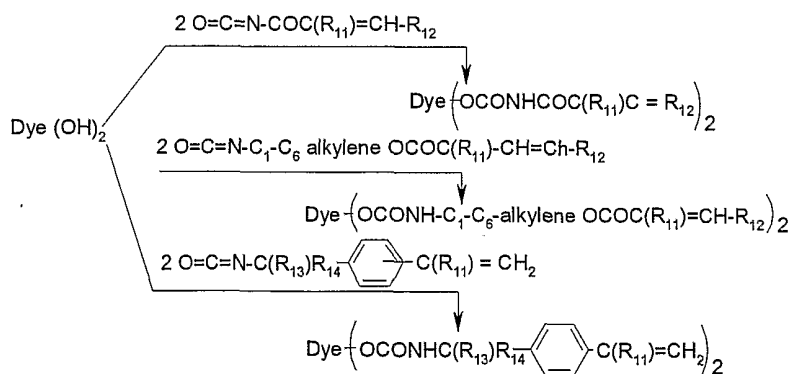
- 13 -

to introduce the reactive vinyl functionality. For example, the dyes wherein Q corresponds to structure Ia, VIa, XIa, respectively, are prepared by reacting the dihydroxy dyes with the corresponding acid chlorides and/or anhydrides as follows:



5

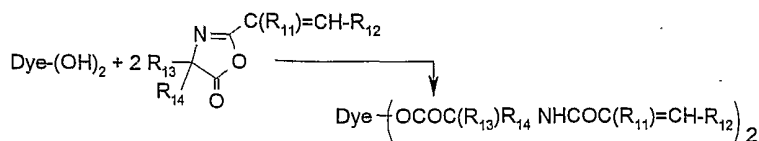
The dyes wherein Z is -O- and Q corresponds to structures IIa, IIIa, and VIIa are prepared by reacting the dihydroxy dyes with the corresponding isocyanates:



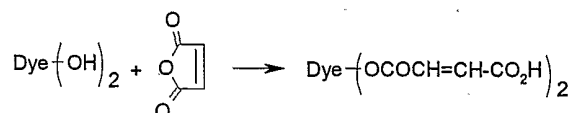
10

The dyes where Z is -O- and where Q corresponds to structure IVa are prepared by reacting the dihydroxy dyes with 2-alkenylazlactones as generally described in Encyclopedia of Polymer Science and Eng., Second Ed., Vol. 11, John Wiley & Sons, pp. 558 - 571:

15



The dyes wherein Z is -O- and Q corresponds to structure Va are generally prepared by reacting the dihydroxy dyes with maleic anhydride to give the mono maleate esters:



5 The remaining acid groups may be esterified by the usual type esterification reactions such as heating in alcohols in the presence of acid catalysts and reacting the alkali metal salts of the acids with alkylating agents such as alkyl halides, alkyl sulfates and alkyl sulfonates, such as methyl 4-toluene sulfonate, to prepare the methyl ester. Fumaric acid and its derivatives also may be used to prepare the dyes
10 where Q is radical Va. Itaconic anhydride (methylenesuccinic anhydride) may be used to react with the dihydroxy dyes to prepare the functionalized dyes wherein Z is -O- and Q corresponds to structure XIIa ($R_{15}=\text{H}$). These acidic compounds may be esterified as described above for preparing the dyes where Q corresponds to structure Va.

15 Anthraquinone dyes containing aliphatic hydroxy groups useful for reacting as described above to produce dyes containing reactive Q groups are disclosed in U.S. Patents 4,267,306, 4,359,570, 4,403,092, 4,804,719, 4,999,418, 5,032,670, 5,194,463, 5,372,864, 5,955,564 and 5,962,557. Anthraquinone dyes containing 1(H)-1,2,4-triazol-3ylthio groups which are useful in preparing dyes of Formulae
20 III, IX, XIII and XX are disclosed in U.S. Patents 3,689,501, 4,267,306, 5,962,557 and WO 98/23690 (4 June 1998). Anthraquinone dyes containing carboxy groups and which are useful in the practice of the invention are disclosed in U.S. Patents 4,359,570, 4,403,092, 4,999,418, 5,372,864, 5,955,564, 5,962,557 and WO 98/23690. Hydroxy-alkyl groups may be introduced into these compounds by
25 alkylation of the acids with hydroxyalkyl halides or alkylene carbonates to give the hydroxyalkyl derivatives useful for reacting further as shown herein to introduce reactive Q groups.

To prepare the dyes wherein Z is -S-, -NH-, -N(C₁-C₆ alkyl)-, -N(C₃-C₈ alkenyl)-, -N(C₃-C₈ cycloalkyl)-, -N(aryl)-, -N(SO₂ C₁-C₆ alkyl)- and -N(SO₂ aryl)-,

- 15 -

the corresponding anthraquinone dyes containing two of the following nucleophilic ZH groups, respectively, are reacted with the reagents mentioned above for preparing the dyes where Z = -O-, -SH, -NH(C₁-C₆ alkyl), -NH(C₃-C₈ alkenyl), -NH(C₃-C₈ cycloalkyl), -NH(aryl)-, NH(SO₂ C₁-C₆ alkyl) and -NH(SO₂ aryl). All of the dyes mentioned above containing two ZH groups may be reacted with vinylsulfonyl halides to prepare dyes where Q = -SO₂C(R₁₁)=CH₂ (Structure IXa). When Q corresponds to Structure IXa, the preferred Z group is -NH-. Dyes wherein Q corresponds to structure Xa and XIIIa and Z is a covalent bond are prepared by reacting dyes containing two primary amine groups with, for example, maleic anhydride and itaconic anhydride, respectively.

The functionalized dyes of Formulae VII, XI, XV, XVIII and XXI wherein X₂ and X₄ are -CO₂- are prepared by alkylating the intermediate dye containing two carboxy groups with an alkylating agent having the structure ClCH₂-p-C₆H₄-C(R₈)=CH₂, with 4-vinylbenzyl chloride (R₈ = H) being particularly preferred. The reaction is easily accomplished in the presence of alkali metal carbonates and trialkyl amines as bases. The functionalized dyes corresponding to Formulae III, IX, XIII and XX wherein m is O are prepared by reacting the intermediate dyes containing two 1(H)-1,2,4-triazol-3ylthio groups with an alkylating agent having the structure ClCH₂-p-C₆H₄-C(R₈)=CH₂, with 4-vinylbenzyl chloride (R₈ = H) being preferred, in the presence of a base such as alkali metal carbonates or trialkylamines.

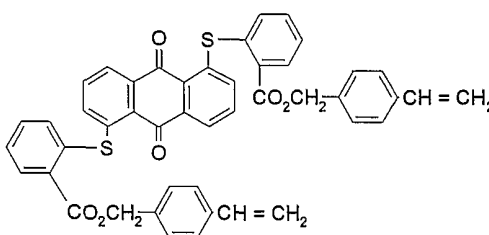
The yellow, red-magenta, blue-cyan dyes of this invention are particularly useful for making combination shades as subtractive colors. They have particular value for copolymerizing into acrylic polymeric materials by free radical polymerization, having one or more advantages over the prior art dyes such as thermal stability, solubility in the acrylate or methacrylate ester comonomer(s) to be used, fastness to UV light, color strength, ease of manufacture and the like. The dyes of this invention are particularly useful for providing acrylic polymer color coatings for glass optical fibers where good thermal stability of dyes is required.

Examples

The copolymerizable dye compounds provided by the present invention and the preparation thereof are further illustrated by the following examples.

5 EXAMPLE 1

A mixture of 1,5-bis-(2-carboxyphenylthio) anthraquinone (U.S. Patent 4,359,570, Example 1) (5.13g, 0.01 mol), potassium carbonate (2.84g, 0.02 mol) and N, N-dimethylformamide (DMF, 100 mL) was stirred and heated to about 100°C. To the stirred mixture, was added 4-vinylbenzyl chloride (Aldrich, 3.76g, 0.022m). Thin-layer chromatography (TLC) using a 50/50 mixture of tetrahydrofuran(THF)/cyclohexane after heating the reaction mixture at about 105°C for 30 min. showed only one spot with no starting material or mono- reacted product being observed. The reaction mixture was heated for an additional 20 minutes and the yellow dye precipitated by the addition of a mixture of methanol and water. The solid dye was collected by filtration, washed with water and then with a little methanol. The yield of air-dried product was 6.85g (92% of the theoretical yield). Field desorption mass spectrometry (FDMS) supported the following structure:

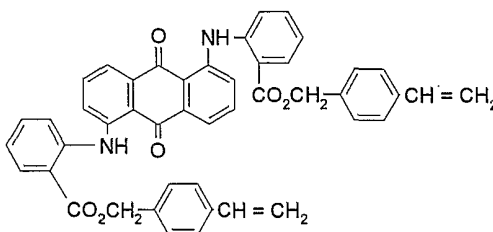


20 An absorption maximum at 447nm was observed in the UV-visible absorption spectrum in DMF.

EXAMPLE 2

25 A mixture of 1,5-bis-(2-carboxyanilino) anthraquinone (U.S. Patent 4,359,570, Example 2) (4.78g, 0.01 mol), potassium carbonate (2.76g, 0.02 mol) and DMF (100 mL) was stirred and heated to about 90°C and 4-vinylbenzyl

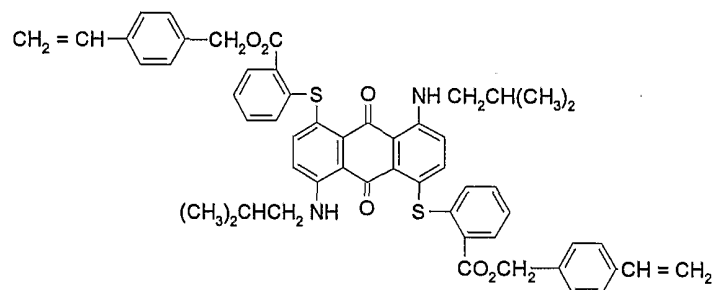
chloride (Aldrich, 3.76g, 0.022 mol) was added and heating and stirring continued at about 100°C for 60 min. TLC (50/50 THF/cyclohexane) showed complete reaction. Methanol (120 mL) was added gradually with stirring to precipitate the red product, which was collected by filtration, washed with water and then dried in
5 air (yield - 6.18g, 87% of the theoretical yield). FDMS supports the following structure:



10 EXAMPLE 3

A mixture of 1,5-bis-(isobutylamino)-4,8-bis-(2-carboxyphenylthio) anthraquinone (WO 98/23690, Example 2) (6.54g, 0.01 mol), potassium carbonate (2.76g, 0.02m) and DMF (150 mL) was stirred and heated to about 100°C. To the stirred reaction mixture was added 4-vinylbenzyl chloride (3.76g, 0.02 mol). The reaction mixture was heated at 95-100°C for about 60 minutes. The reaction mixture was cooled and the gummy product was drowned out by the addition of methanol/water. The liquid was decanted off and the product triturated with methanol. The resulting dark blue solid was collected by filtration, washed with methanol and dried in air (yield - 6.95g, 78% of the theoretical yield). FDMS supported the following structure:

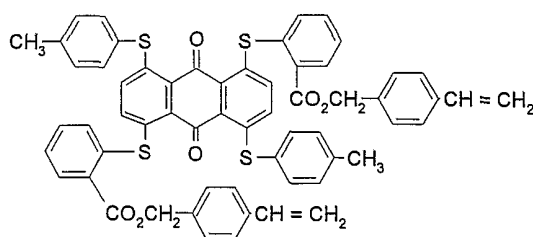
- 18 -



Absorption maxima at 600nm and 645nm were observed in the UV-visible absorption spectra in DMF.

5 EXAMPLE 4

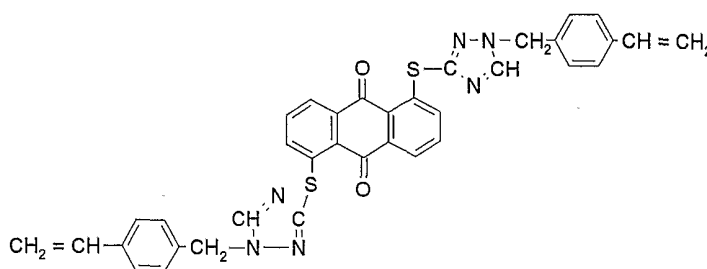
A mixture of 1,5-bis-(2-carboxyphenylthio)-4,8-bis-(4-tolylthio)-anthraquinone (WO 98/23690) (7.56g, 0.01 mol), potassium carbonate (K_2CO_3) and DMF (300 mL) was stirred and heated to about 100°C and then 4-vinylbenzyl chloride (3.84g, 0.025 mol) was added. The reaction mixture was heated and stirred at about 100°C for 60 minutes. TLC (50/50 THF/cyclohexanol) showed complete reaction. After cooling, the sticky product was obtained by drowning the reaction mixture with methanol/water. The red product solidified upon standing in contact with methanol and was collected by filtration and dried in air (yield - 7.67g, 78% of the theoretical yield). FDMS supported the following structure:



An absorption maximum was observed at 520nm in the UV-visible absorption in DMF.

EXAMPLE 5

A mixture of 1,5-bis-[(1H)-1,2,4-triazol-3-ylthio]] anthraquinone (U.S. Patent 3,689,501) (4.06g, 0.01 mol), potassium carbonate (2.76g, 0.02 mol) and DMF (100 mL) was stirred and heated to about 100°C and 4-vinylbenzyl chloride (3.76g, 0.022 mol) was added. TLC (50/50 THF/cyclohexane) still showed some mono-substituted product after heating the reaction mixture for 2 hrs. Additional quantities of 4-vinylbenzyl chloride (4.14g) and potassium chloride (1.38g) were added and heating continued for another hour to complete the reaction. A gummy yellow solid was produced by drowning the cooled reaction mixture with water. The product was washed by decantation with water and then dissolved in DMF. The DMF solution was drowned gradually into cold water with good stirring and the yellow solid was collected by filtration and dried in air (3.46g, 54% of the theoretical yield). FDMS supported the following structure:



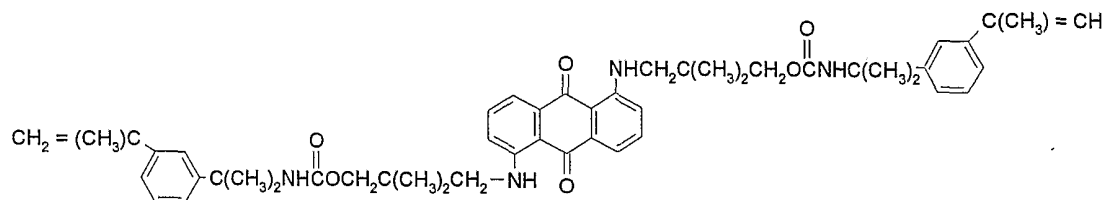
An absorption maximum at 420nm was observed in the UV-visible absorption spectrum in DMF.

EXAMPLE 6

A mixture of 1,5-bis-(2,2-dimethyl-3-hydroxypropylamino) anthraquinone (U.S. Patent 4,999,418, Example 1) (4.10g, 0.01 mol), DMF (25 mL) and 3-isopropenyl- α,α -dimethylbenzyl isocyanate (Aldrich; 5 mL, 0.025 mol) was heated and stirred at about 75°C for 48 hrs. TLC (50/50-THF/cyclohexane) showed all of the starting material to be reacted and a mixture of the desired product plus the mono-reaction product. After addition of an additional quantity (1 mL) of 3-isopropenyl- α,α -dimethylbenzyl isocyanate, the reaction mixture was heated and

- 20 -

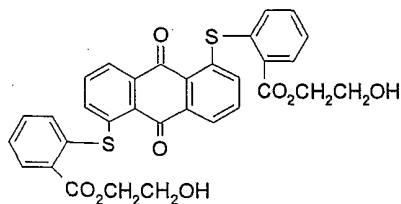
stirred at about 90°C for 12 hrs. Triethylamine (0.5 mL) was added and the reaction mixture was stirred at about 100°C for another 24 hrs. The cooled reaction mixture was drowned into water (200 mL) to produce a sticky solid which hardened upon standing. The water was decanted off and the solid redissolved in DMF (200 mL) by heating on a steam bath. Water (50 mL) was added gradually to the hot DMF with stirring. After allowing to stand overnight a red solid had formed. Additional water (150 mL) was added and the product was collected by filtration, washed with water and dried in air. Essentially a quantitative yield of the following product was obtained:



which was soluble in methanol, methylene chloride and somewhat soluble in hexane.

EXAMPLE 7a

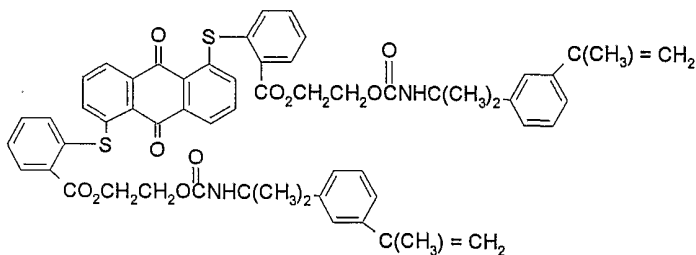
A mixture of 1,5-bis-(2-carboxyphenylthio) anthraquinone (U.S. Patent 4,359,570, Example 1) (30.6g, 0.06 mol), ethylene carbonate (88.0g, 1.0 mol), ethylene glycol (50 mL) and pulverized potassium iodide (5.2g) was heated and stirred at about 125°C for about 2.0 hours and then allowed to cool. The reaction mixture was drowned into cold water (150 mL) with stirring. The yellow solid was collected by filtration, washed with warm water and dried in air (yield-35.2g, 97.8% of the theoretical yield). FDMS supported the following structure:



- 21 -

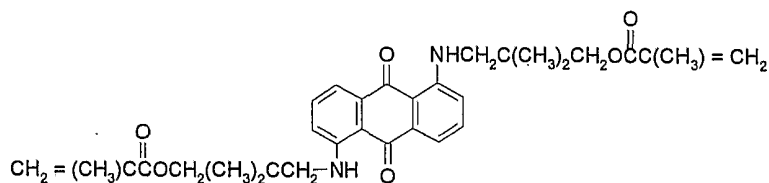
EXAMPLE 7b

A mixture of the product of Example 7a (6.0g, 0.01 mol), DMF (25 mL) and 3-isopropenyl- α,α -dimethylbenzyl isocyanate (6 mL, 0.03 mol) was heated and stirred, under nitrogen at about 95-100°C for about 48 hours. Triethylamine (0.5 mL) was added and heating continued for an additional 48 hours. Water (60 mL) was added portionwise to the hot reaction mixture with stirring. After allowing to cool to room temperature, the yellow product was collected to filtration, washed with water and dried in air. Essentially a quantitative yield of the following product was obtained:

EXAMPLE 8

A mixture of 1,5-bis-(2,2-dimethyl-3-hydroxypropylamino) anthraquinone (U.S. Patent 4,999,418, Example 1) (1.0g, 2.44 mmol) and toluene (50 mL) was prepared and then most of the toluene was evaporated under reduced pressure to remove any water present. DMF (50 mL), hydroquinone (50mg), 4-(dimethylamino)pyridine (DMAP; 59.6mg), triethylamine (1.0 mL) and methacrylic anhydride (1.33g, 7.32 mmol) were added and the reaction mixture was stirred at room temperature for about 20 hours. TLC (50/50 hexane/ethyl acetate) indicated complete reaction. The reaction mixture was poured into water (300 mL) and the red product was collected by filtration, washed with water and dried in vacuo (yield-1.30g, 98% of the theoretical yield). FDMS supported the following structure:

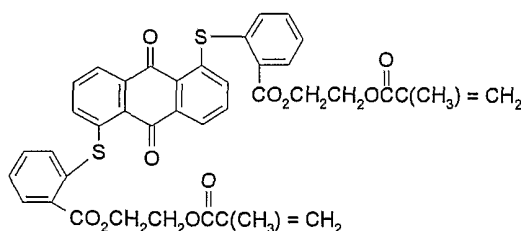
- 22 -



The functionalized red dye had an absorption maximum at 526nm in DMF solution in the UV-visible absorption spectrum.

5 EXAMPLE 9

The dye of Example 7a above (2.0g, 3.33 mmol) and toluene (20 mL) were mixed and stirred while most of the toluene was removed under reduced pressure. DMF (50 mL), DMAP (82mg), triethylamine (1.4 mL), hydroquinone (50mg) and methacrylic anhydride (1.53g, 9.99 mmol) were added and the reaction mixture stirred at room temperature for 15 hours. The yellow functionalized dye which was precipitated by drowning into water (200 mL) and allowing to stand for several days was collected by filtration, washed with water and 1:1 methanol: water and dried in vacuo. The yield was 2.23g (91% of the theoretical yield). FDMS supported the following structure:



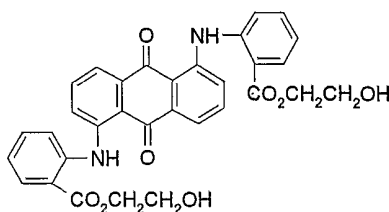
An absorption maximum at 444nm was observed in the UV-visible absorption spectrum in DMF.

EXAMPLE 10a

A mixture of 1,5-bis-(carboxyanilino) anthraquinone (U.S. Patent 4,359,570, Example 2) (59.75g, 0.125 mol), ethylene carbonate (165g, 1.875 mol), ethylene glycol (550 mL) and pulverized potassium iodide (11.3g) was heated at

- 23 -

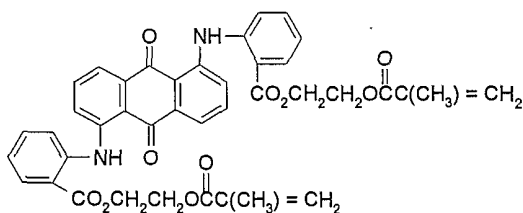
120-125°C for 6.5 hours and the mixture allowed to cool. Methanol (400 mL) was added to the stirred reaction mixture. The red solid was collected by filtration, washed with water and dried in air (yield - 69.5g, 98.2% of the theoretical yield). FDMS supported the following structure:



5

EXAMPLE 10b

A portion (2.0g, 3.53 mmol) of the dye of Example 10a above was mixed with toluene (10 mL) and most of the toluene removed under vacuum. DMF (50 mL), DMAP (86mg), triethylamine (1.5 mL), hydroquinone (20mg) and methacrylic anhydride (1.63g, 10.6 mmol) were added and the resulting solution was stirred for 15 hours at room temperature. The reaction mixture was drowned into water (200) and allowed to stand at room temperature for several days. The functionalized red dye was collected by filtration, washed with water and dried in vacuo (yield - 2.10g, 85% of the theoretical yield). FDMS supported the following structure:

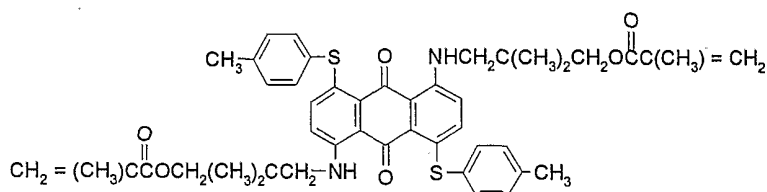
10
15

An absorption maximum at 525nm was observed in DMF solution in the UV-visible absorption spectrum.

20

EXAMPLE 11

A mixture of 1,5-bis-(2,2-dimethyl-3-hydroxypropylamino)-4,8-bis-(tolylthio)anthraquinone (U.S. Patent 5,955,564) (2.0g, 3.06 mmol) and toluene (10 mL) was stirred and most of the toluene removed under vacuum. DMF (50 mL), triethylamine (1.3 mL), DMAP (75mg), hydroquinone (20mg) and methacrylic anhydride (1.41g, 9.18 mmol) were added and the reaction mixture was stirred at room temperature for 15 hours. After drowning into water (200 mL) and allowing the mixture to stand for several days the functionalized blue dye was collected by filtration, washed with water and dried in vacuo. Essentially a quantitative yield was obtained. FDMS supported the following structure:

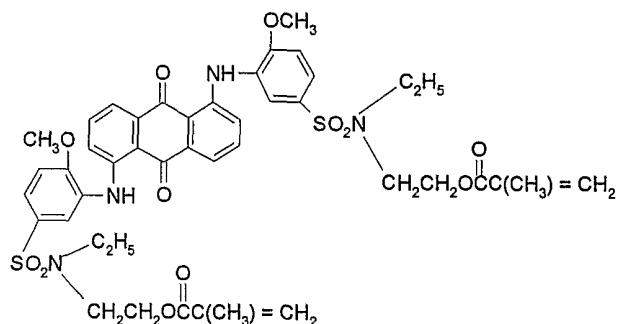


An absorption maximum at 650nm was observed in DMF solution in the UV-visible light absorption spectrum.

15 EXAMPLE 12

A mixture of 1,5-bis-[5-(N-ethyl-N-(2-hydroxyethyl)sulfamoyl)-2-methoxyanilino]anthraquinone (U.S. Patent 5,372,864, Example 21) (2.0g, 2.66 mmol) and toluene (10 mL) was stirred and most of the toluene was removed under reduced pressure. DMF (50 mL), DMAP (65mg), triethylamine (1.1 mL), hydroquinone (20mg) and methacrylic anhydride (1.22g, 7.98 mmol) were added and the reaction mixture was stirred overnight at room temperature for about 15 hours. The functionalized blue dye was precipitated by drowning into water (200 mL) and allowing the mixture to stand for several days at room temperature and was collected by filtration washed with water and dried in vacuo. Essentially a quantitative yield was obtained. FDMS supported the following structure:

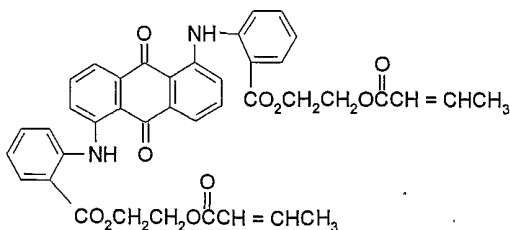
- 25 -



An absorption maximum at 527nm in DMF solution was observed in the UV-visible absorption spectrum.

5 EXAMPLE 13

A portion (2.0g, 3.53 mmol) of the dye from Example 10a above was mixed with toluene and stirred while most of the toluene was removed under reduced pressure. DMF (50 mL), DMAP (86mg), triethylamine (1.5 mL), hydroquinone (20mg) and crotonic anhydride (1.63g, 10.6 mmol) were added and the reaction mixture was stirred for 24 hours. The functionalized red dye was isolated by drowning into water (200 mL), allowing the mixture to stand for a little while and then collecting by filtration. After washing with water the dye was dried in vacuo (yield - 2.11g, 85% of the theoretical yield). FDMS supported the following structure:



An absorption maximum at 522nm in DMF solution was observed in the UV-visible light absorption spectrum.

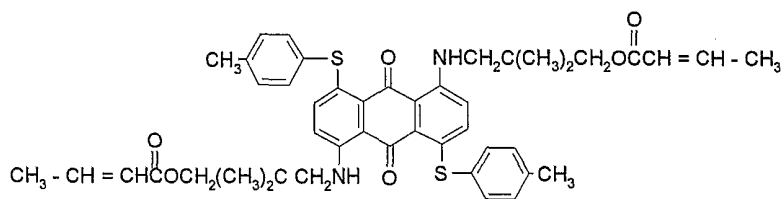
- 26 -

EXAMPLE 14

A mixture of 1,5-bis-(2,2-dimethyl-3-hydroxypropylamino)-4,8-bis-(4-tolylthio) anthraquinone (U.S. Patent 5,955,564) (2.0g, 3.06 mmol) and toluene (10 mL) was stirred and most of the toluene removed under reduced pressure.

5 DMF (50 mL), DMAP (75mg), triethylamine (1.3 mL), hydroquinone (20mg) and crotonic anhydride (1.41g, 9.18 mmol) were added. The reaction mixture was stirred at room temperature for 24 hours and then drowned into water (200 mL). After allowing the mixture to stand for awhile, the functionalized blue dye was collected by filtration, washed with water and dried in vacuo. The yield was

10 essentially quantitative. FDMS supported the following structure:



An absorption maximum at 650nm was observed in DMF in the UV-visible absorption spectrum.

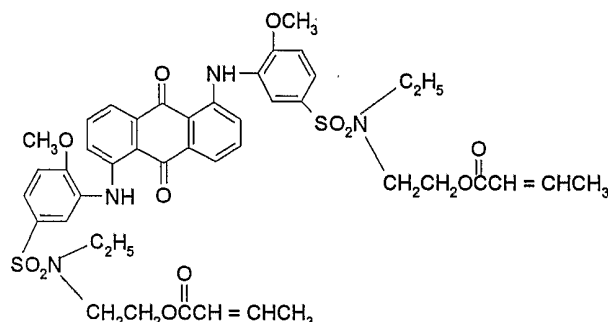
15 EXAMPLE 15

A mixture of 1,5-bis-[5-(N-ethyl-N-(2-hydroxyethyl) sulfamoyl)-2-methoxyanilino]-anthraquinone (U.S. Patent 5,372,864, Example 21) (2.0g, 2.66 mmol) and toluene (10 mL) were stirred and most of the toluene removed under reduced pressure. DMF (50 mL), DMAP (65mg), triethylamine (1.1 mL),

20 hydroquinone (20mg) and crotonic anhydride (1.23g, 7.98 mmol) were added. After being stirred at room temperature for 24 hours the reaction mixture was drowned into water (200 mL) and the mixture allowed to stand for awhile. The functionalized red dye was collected by filtration, washed with water and dried in vacuo. The yield was 1.96g of product (83% of the theoretical yield). FDMS

25 supported the following structure:

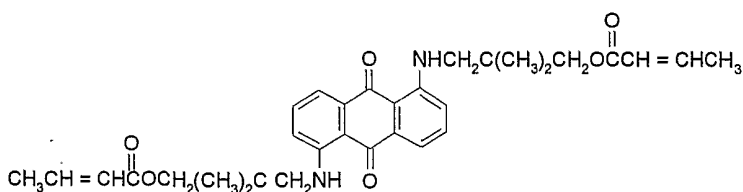
- 27 -



An absorption maximum at 529nm was observed in the UV-visible light absorption spectrum.

5 EXAMPLE 16

A mixture of 1,5-bis-(2,2-dimethyl-3-hydroxypropylamino) anthraquinone (U.S. Patent 4,999,418, Example 1) (2.0g, 4.88 mmol) and toluene (10 mL) was stirred and most of the toluene was removed under reduced pressure. DMF (50 mL), DMAP (120mg), triethyl amine (2.0 mL) and crotonic anhydride (2.25g, 14.6 mmol) were added. The reaction mixture was stirred at room temperature for 24 hours and then drowned into water (200 mL) and the mixture allowed to stand awhile. The functionalized red dye was collected by filtration, washed with water and dried in vacuo. The yield was 2.24g (98% of the theoretical yield). FDMS supported the following structure:



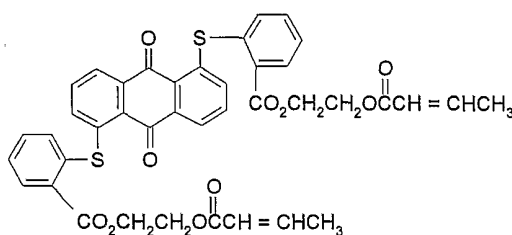
An absorption maximum at 527nm was observed in the UV-visible light spectrum in DMF as the solvent.

EXAMPLE 17

20 A mixture of a portion (2.0g, 3.33 mmol) of the dye of Example 7a above and toluene (10 mL) was stirred and most of the toluene removed under vacuum.

- 28 -

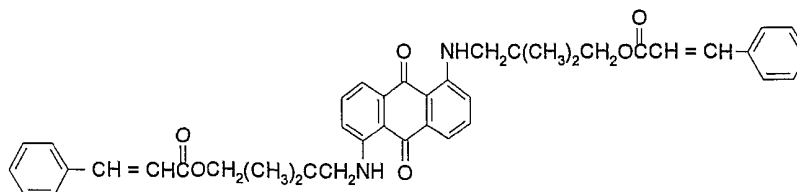
DMF (50 mL), DMAP (86mg) triethylamine (1.4 mL), hydroquinone (20mg) and crotonic anhydride (7.54g, 9.99 mmol) were added. The reaction mixture was stirred at room temperature for 24 hours and drowned into water (200 mL) with stirring. The mixture was allowed to stand awhile and the functionalized yellow dye was collected by filtration, washed with water and dried in vacuo (yield 2.01g, 82% of the theoretical yield). FDMS supported the following structure:



An absorption maximum at 446nm was observed in DMF in the UV-visible light absorption spectrum.

EXAMPLE 18

A mixture of 1,5-bis-(2,2-dimethyl-3-hydroxypropylamino) anthraquinone (U.S. Patent 4,999,418, Example 1) (1.0 g, 2.44 mmol) and toluene (50 mL) was stirred and most of the toluene removed under reduced pressure. DMF (50 mL), DMAP (60mg), triethylamine (1.0 mL), hydroquinone (50mg) and cinnamoyl chloride (Aldrich; 1.22g, 7.35 mmol) were added. The reaction mixture was stirred at about 50°C temperature for about 12 hours and then drowned into water (100 mL). The functionalized red dye was collected by filtration, washed with water and dried in vacuo (yield - 1.61g, 99% of the theoretical yield). FDMS supports the following structure:



- 29 -

An absorption maximum at 527nm was observed in DMF in the UV-visible absorption spectrum.

The functionalized dyes which contain vinyl or substituted vinyl groups are polymerizable or copolymerizable, preferably by free radical mechanisms, said free radicals being generated by exposure to UV light by methods known in the art of preparing UV-cured resins. Polymerization can be facilitated by the addition of photoinitiators. The colored acrylic polymeric materials normally are prepared by dissolving the functionalized dyes containing copolymerizable groups in a polymerizable monomer with or without another solvent and then preparing the resin by typical polymerization methods.

Typical copolymerizable monomers useful in the present invention include (meth)acrylic acid and their anhydrides, crotonic acid, itaconic acid and its anhydride, cyanoacrylic acid and its esters; esters of (meth)acrylic acid such as allyl, methyl, ethyl, n-propyl, isopropyl, butyl, tetrahydrofurfuryl, cyclohexyl, isobornyl, n-hexyl, n-octyl, isooctyl, 2-ethylhexyl, lauryl, stearyl, benzyl, and di(meth)acrylate esters of ethylene and propylene glycols, 1,3-butylene glycol, 1,4-butanediol, diethylene and dipropylene glycols, triethylene and tripropylene glycols, 1,6-hexanediol, neopentyl glycol, polyethylene glycol, and polypropylene glycol, ethoxylated bisphenol A, propoxylated neopentyl glycol; tri(meth)acrylate esters of tris-(2-hydroxyethyl)isocyanurate, trimethylolpropane, pentaerythritol, glycerol, ethoxylated and propoxylated glycerol; tetra(meth)acrylate esters of pentaerythritol; acrylonitrile; vinyl acetate; vinyl toluene; styrene; N-vinyl pyrrolidinone; alphas-methylstyrene; maleate/fumarate esters; maleic/fumaric acid; crotonate esters, and crotonic acid.

The copolymerizable compositions of the present invention optionally may contain organic solvents if desired to facilitate application and coating of the compositions onto the surface of substrates. Typical examples of suitable solvents include, but are not limited to ketones, alcohols, esters, chlorinated hydrocarbons, glycol ethers, glycol esters, and mixtures thereof. Specific examples include, but

- 30 -

are not limited to acetone, 2-butanone, 2-pentanone, ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, ethylene glycol diacetate, ethyl 3-ethoxypropionate, methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, ethylene glycol, propylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl glycol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, propylene glycol monomethyl ether, diethylene glycol monobutyl ether acetate, diethylene glycol monoethyl ether acetate, ethylene glycol monobutyl ether acetate, propylene glycol monomethyl ether acetate, methylene chloride, chloroform, and mixtures thereof. Certain monomers may serve as both reactant and solvent. These contain at least one unsaturated group capable of undergoing polymerization upon exposure to UV radiation in the presence of a photoinitiator. Specific examples include, but are not limited to: methacrylic acid, acrylic acid, ethyl(meth)acrylate, methyl(meth)acrylate, hydroxyethyl(meth)acrylate, diethylene glycol diacrylate, trimethylolpropane triacrylate, 1,6 hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, N-vinyl pyrrolidone, and mixtures thereof. In addition, the compositions of the present invention may be dispersed in water rather than dissolved in a solvent to facilitate application and coating of the substrate surface.

In the water-dispersed compositions of the present invention a co-solvent is optionally used. Typical examples of suitable cosolvents include but are not limited to acetone, 2-butanone, methanol, ethanol, isopropyl alcohol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, and ethylene glycol monobutyl ether, ethylene glycol, and propylene glycol. Typical examples of water-soluble ethylenically unsaturated solvents include but are not limited to: methacrylic acid, acrylic acid, N-vinyl pyrrolidone, 2-ethoxyethyl (meth)acrylate, polyethylene glycol dimethacrylate polypropylene glycol mono(meth)acrylate, and mixtures thereof. The amount of suitable aqueous organic solvent (i.e., organic solvent and water) in the dispersed

- 31 -

coating compositions of the present invention is 10 to 90 weight percent, preferably 75 to 90 weight percent of the total coating composition.

The coating compositions of the present invention optionally contain a photoinitiator. The amount of photoinitiator is typically 2 to 7 wt.% based on the weight of the non-volatile, ethylenically unsubstituted content of the coating composition; preferably 3 to 5 wt. %. Typical photoinitiators include benzoin and benzoin ethers such as marketed under the tradenames ESACURE BO, EB1, EB3, and EB4 from Fratelli Lamberti; VICURE 10 and 30 from Stauffer; benzil ketals such as IRGACURE 651 from Ciba Geigy, Uvatone 8302 by Upjohn; alpha, alpha-dialkoxyacetophenone derivatives such as DEAP and UVATONE 8301 from Upjohn; alpha-hydroxyalkylphenones such as IRGACURE 184 from Ciba Geigy; DAROCUR 116, 1173, and 2959 by Merck; mixtures of benzophenone and tertiary amines. Further details regarding such photoinitiators and curing procedures may be found in the published literature such as U.S. Patent 5,109,097, incorporated herein by reference. Depending upon the thickness of the coating (film), product formulation, photoinitiator type, radiation flux, and source of radiation, exposure times to ultraviolet radiation of 0.5 second to 30 minutes are typically required for curing. Curing can also occur even in the sunshine.

Another embodiment of the present invention comprises a curable composition as described above, further comprising one or more leveling, rheology, and flow control agents such as silicones, fluorocarbons or cellulose; flattening agents; pigment wetting and dispersing agents; surfactants; ultraviolet (UV) absorbers; UV light stabilizers; tinting pigments; defoaming and antifoaming agents; anti-settling, anti-sag and bodying agents; anti-skinning agents; anti-flooding and anti-floating agents; fungicides and mildewcides; corrosion inhibitors; thickening agents; or coalescing agents. The compositions of the present invention also may contain non-reactive modifying resins. Typical non-reactive modifying resins include homopolymers and copolymers of (meth)acrylic acid; alkyl esters of (meth)acrylic acid such as methyl, ethyl, n-propyl, isopropyl, butyl, tetrahydrofurfuryl, cyclohexyl, isobornyl, n-hexyl, n-octyl, isooctyl, 2-ethylhexyl, lauryl,

- 32 -

stearyl, benzyl; (meth)acrylated urethane, epoxy, and polyester resins, silicone acrylates, cellulose esters such as cellulose acetate butyrates, cellulose acetate, propionates, nitrocellulose, cellulose ethers such as methyl cellulose, ethyl cellulose, hydroxypropyl cellulose, and hydroxypropyl methyl cellulose.

5 Typical plasticizers include alkyl esters of phthalic acid such as dimethyl phthalate, diethyl phthalate, dipropyl phthalate, dibutyl phthalate, and dioctyl phthalate; citrate esters such as triethyl citrate and tributyl citrate; triacetin and tripropionin; and glycerol monoesters such as Eastman 18-04, 18-07, 18-92 and 18-99 from Eastman Chemical Company. Specific examples of additional additives
10 can be found in *Raw Materials Index*, published by the National Paint & Coatings Association, 1500 Rhode Island Avenue, N.W., Washington, D.C. 20005.

 The coatings of the compositions of the present invention typically have a solvent resistance of at least 100 double rubs using ASTM Procedure D-3732; preferably a solvent resistance of at least 200 double rubs. Such coatings also
15 typically have a pencil hardness of greater than or equal to F using ASTM Procedure D-3363; preferably a pencil hardness of greater than or equal to H. The coating compositions can be applied to substrates with conventional coating equipment. The coated substrates are then exposed to radiation such as ultraviolet light in air or in nitrogen which gives a cured finish. Mercury vapor or Xenon
20 lamps are applicable for the curing process. The coatings of the present invention can also be cured by electron beam.

 The radiation-curable compositions of this invention are suitable as adhesives and coatings for such substrates as metals, plastics, glass, wood, and leather. Various additional pigments, plasticizers, and stabilizers may be
25 incorporated to obtain certain desired characteristics in the finished products. These are included in the scope of the invention.

- 33 -

Coating, Curing, and Testing Procedures:

Samples of formulations were used to coat glass plates using a knife blade. The wet film thickness was about 10 mil. The solvent was evaporated to give a clear, somewhat tacky film with a thickness of approximately 1 mil. Prior to exposure to UV radiation, each film was readily soluble in organic solvents.

The dried film on the glass plate was exposed to UV radiation from a 200 watt per inch medium pressure mercury vapor lamp housed in an American Ultraviolet Company instrument using a belt speed of 25 ft. per minute. One to five passes under the lamp resulted in a crosslinked coating with maximum hardness and solvent resistance.

Each cured coating (film) may be evaluated for pencil hardness (ASTM D3363), solvent resistance by the methyl ethyl ketone double-rub test, and solubility in acetone before and after exposure to UV radiation. The pencil hardness scale is in order of increasing hardness: 5B 4B 3B 2B B HB F H 2H 3H 4H 5H. The methyl ethyl ketone (MEK) double rub test is carried out by saturating a piece of cheesecloth with methyl ethyl ketone, and with moderate pressure, rubbing the coating back and forth. The number of double rubs is counted until the coating is removed. This test is in accordance with ASTM Procedure D-3732. The acetone solubility test is carried out by immersing a dry, pre-weighed sample of the cured film in acetone for 48 hours at 25°C. The film is removed, dried for 16 hours at 60°C in a forced-air oven, and reweighed. The weight percent of the insoluble film remaining is calculated from the data.

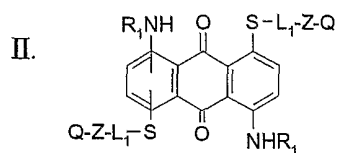
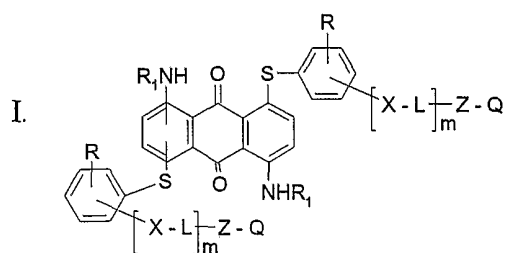
The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

- 34 -

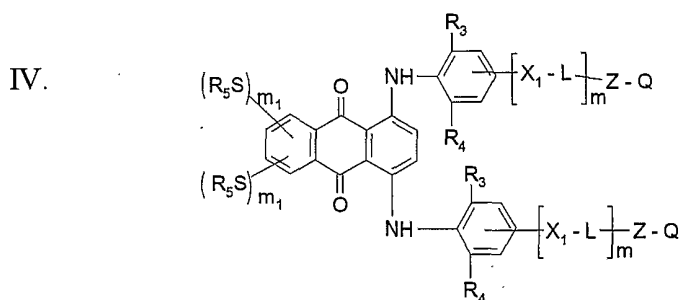
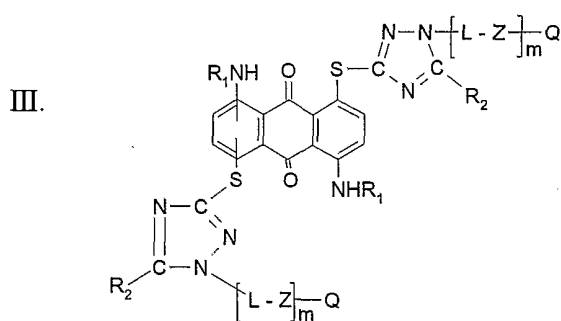
CLAIMS

We claim:

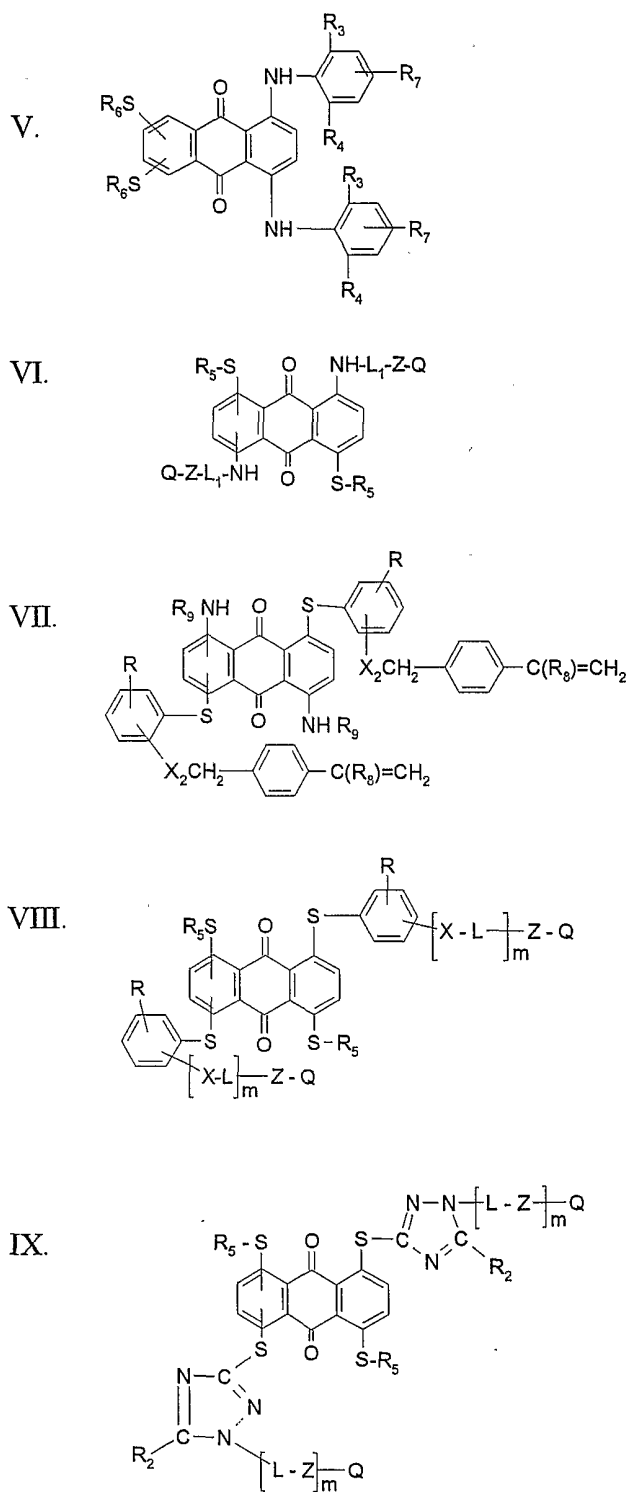
1. Anthraquinone dye compounds having the formulae:



5

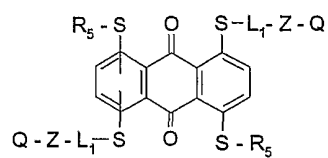


- 35 -

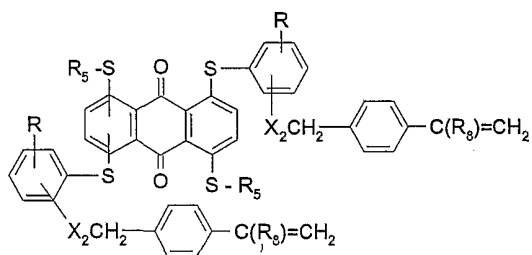


- 36 -

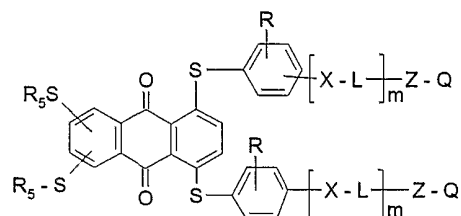
X.



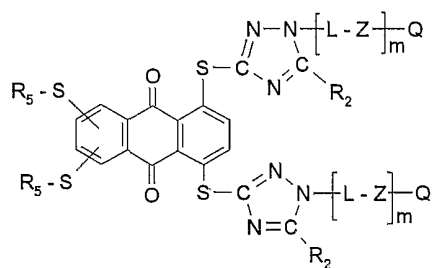
XI.



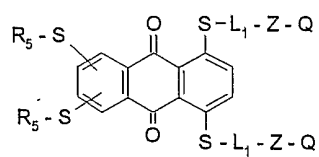
XII.



XIII.

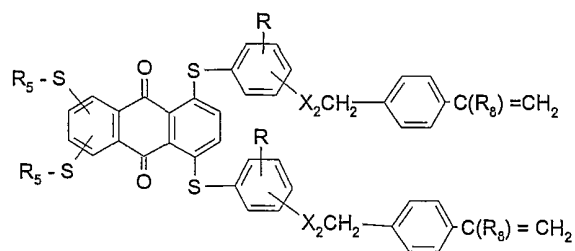


XIV.



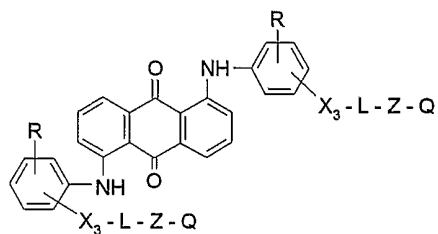
5

XV.

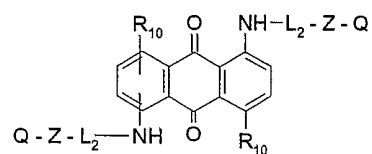


- 37 -

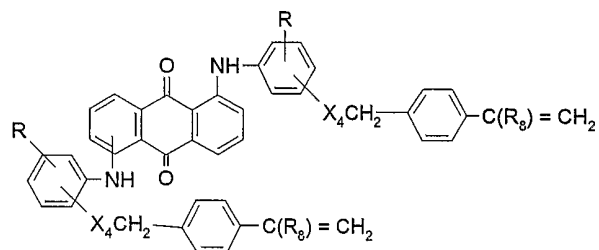
XVI.



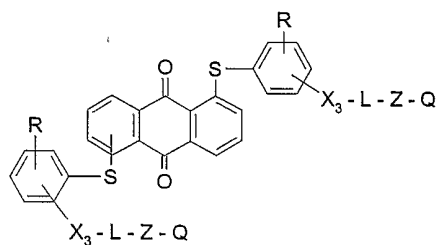
XVII.



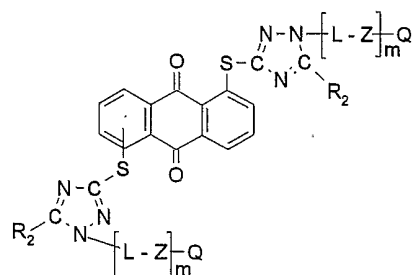
XVIII.



XIX.

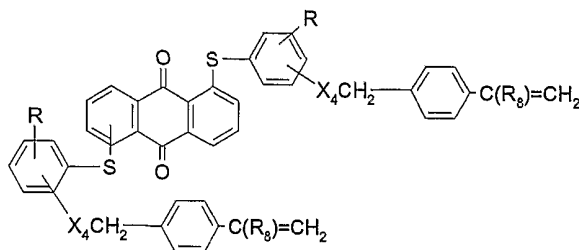


XX.



- 38 -

XXI.



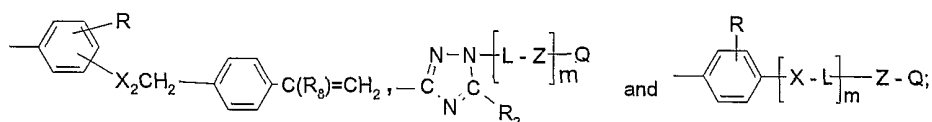
wherein:

R is selected from hydrogen or 1-3 groups selected from C₁ - C₆-alkyl, C₁ - C₆-alkoxy and halogen;

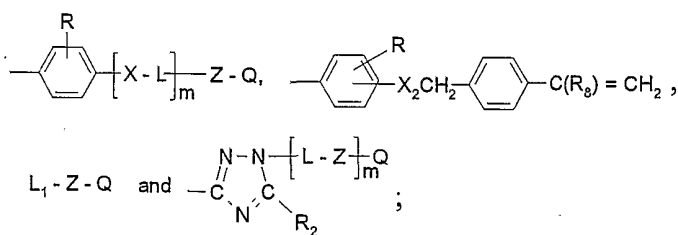
5 R₁ is selected from C₁ - C₆-alkyl, substituted C₁ - C₆-alkyl, C₃ - C₈-alkenyl, C₃ - C₈-cycloalkyl, aryl and -L₁-Z-Q; R₂ = selected from hydrogen, C₁ - C₆-alkyl, substituted C₁ - C₆-alkyl, C₃ - C₈-cycloalkyl and aryl;

R₃ and R₄ are independently selected from C₁ - C₆-alkyl and bromine;

10 R₅ is selected from C₁ - C₆-alkyl, substituted C₁ - C₆ alkyl, C₃ - C₈-cycloalkyl, aryl, heteroaryl, -L₁-Z-Q,



R₆ is selected from



15 R₇ is selected from hydrogen, substituted or unsubstituted C₁ - C₆-alkyl, C₁ - C₆-alkoxy, halogen, hydroxy, substituted or unsubstituted C₁ - C₆-alkylthio, sulfamoyl and substituted sulfamoyl;

R₈ is selected from hydrogen and C₁ - C₆-alkyl;

R₉ is selected from the groups represented by R₁ and -L - Z - Q;

- 39 -

R₁₀ is selected from hydrogen and halogen;

X is a covalent bond or a divalent linking group selected from -O-, -S-,
-SO₂-, -CO₂-, -CON(Y)- and -SO₂N(Y)-, wherein Y is selected from hydrogen,
C₁-C₆-alkyl, substituted C₁-C₆-alkyl, C₃-C₈-cycloalkyl, C₃-C₈-alkenyl, aryl and
5 -L-Z-Q;

X₁ is selected from -O-, -S-, -SO₂- and -SO₂N(Y)-;

X₂ is selected from -CO₂- and -SO₂N(Y₁), wherein Y₁ is a group selected
from hydrogen, C₁-C₆-alkyl, substituted C₁-C₆-alkyl, C₃-C₈-alkenyl,
C₃-C₈-cycloalkyl, aryl, heteroaryl and -CH₂-p-C₆H₄-C(R₈)=CH₂;

10 X₃ is selected from -CO₂-, -SO₂N(Y)-;

X₄ is selected from -CO₂-, -O- and -SO₂N(Y₁)-;

L is a divalent linking group selected from C₁-C₈-alkylene, C₁-C₆-alkylene-
arylene, arylene, C₁-C₆-alkylene-arylene -C₁-C₆-alkylene, C₃-C₈-cycloalkylene,
C₁-C₆-alkylene -C₃-C₈-cycloalkylene -C₁-C₆-alkylene, C₁-C₆-alkylene - Z₁-arylene
15 -Z₁-C₁-C₆-alkylene and C₂-C₆-alkylene-[-Z₁-C₂-C₆-alkylene-]_n- wherein Z₁ is
selected from -O-, -S- and -SO₂- and n is 1-3;

L₁ is a divalent linking group selected from C₂-C₆-alkylene, C₁-C₆-
alkylene-C₃-C₈-cycloalkylene-C₁-C₆-alkylene, C₁-C₆-alkylene-arylene,
C₃-C₈-cycloalkylene, and C₂-C₆-alkylene-[-Z₁-C₂-C₆-alkylene-]_n;

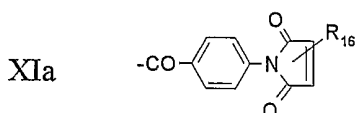
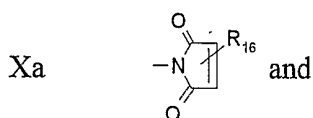
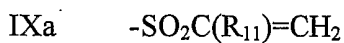
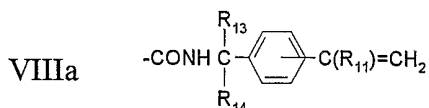
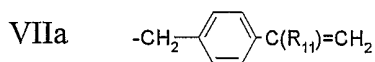
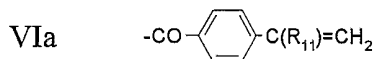
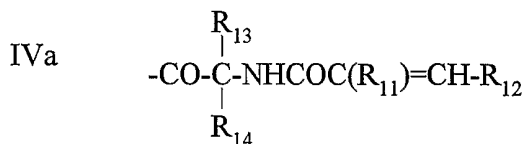
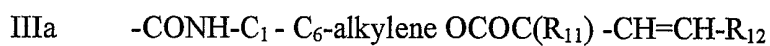
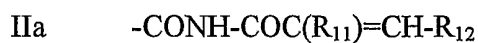
20 L₂ is selected from C₂-C₆-alkylene, C₁-C₆-alkylene- arylene-C₁-C₆ alkylene and
C₁-C₆-alkylene-C₃-C₈-cycloalkylene-C₁-C₆-alkylene;

Z is a divalent group selected from -O-, -S-, -NH-, -N(C₁-C₆-alkyl)-,
-N(C₃-C₈ alkenyl)-, -N(C₃-C₈ cycloalkyl)-, -N(aryl)-, -N(SO₂C₁-C₆-alkyl) and
-N(SO₂ aryl)-, provided that when Q is a photopolymerizable optionally substituted
25 maleimide radical, Z represents a covalent bond; Q is an ethylenically-unsaturated,
photosensitive polymerizable group; and

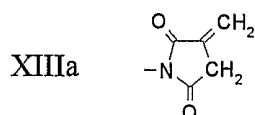
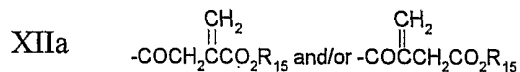
m and m₁ each is 0 or 1.

- 40 -

2. Anthraquinone compounds according to Claim 1 wherein the ethylenically-unsaturated, photosensitive copolymerizable groups represented by Q are selected from the following organic radicals:



- 41 -



wherein:

R_{11} is selected from hydrogen and $\text{C}_1\text{-C}_6\text{-alkyl}$;

R_{12} is selected from hydrogen; $\text{C}_1\text{-C}_6\text{-alkyl}$; phenyl and phenyl substituted
 5 with one or more groups selected from $\text{C}_1\text{-C}_6\text{-alkyl}$, $\text{C}_1\text{-C}_6\text{-alkoxy}$, $-\text{N}(\text{C}_1\text{-C}_6\text{-alkyl})$,
 nitro, cyano, $\text{C}_1\text{-C}_6\text{-alkoxycarbonyl}$, $\text{C}_1\text{-C}_6\text{-alkanoyloxy}$ and halogen; 1- and
 2-naphthyl which may be substituted with $\text{C}_1\text{-C}_6\text{-alkyl}$ or $\text{C}_1\text{-C}_6\text{-alkoxy}$; 2- and
 3-thienyl which may be substituted with $\text{C}_1\text{-C}_6\text{-alkyl}$ or halogen; 2- or 3-furyl
 which may be substituted with $\text{C}_1\text{-C}_6\text{-alkyl}$;

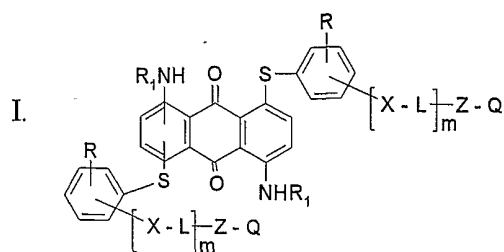
10 R_{13} and R_{14} are selected from hydrogen, $\text{C}_1\text{-C}_6\text{-alkyl}$, substituted $\text{C}_1\text{-C}_6\text{-alkyl}$, aryl or may be combined to represent a $-\text{[CH}_2\text{]}_{3-5}-$ radical;

R_{15} is selected from hydrogen, $\text{C}_1\text{-C}_6\text{-alkyl}$, substituted $\text{C}_1\text{-C}_6\text{-alkyl}$,
 $\text{C}_3\text{-C}_8\text{-alkenyl}$, $\text{C}_3\text{-C}_8\text{-cycloalkyl}$ and aryl;

R_{16} is selected from hydrogen, $\text{C}_1\text{-C}_6\text{-alkyl}$ and aryl.

15

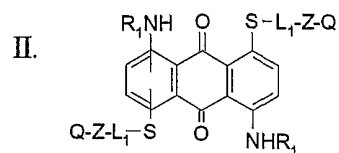
3. Anthraquinone compounds according to Claim 2 having the formula:



wherein Z is $-\text{O}-$.

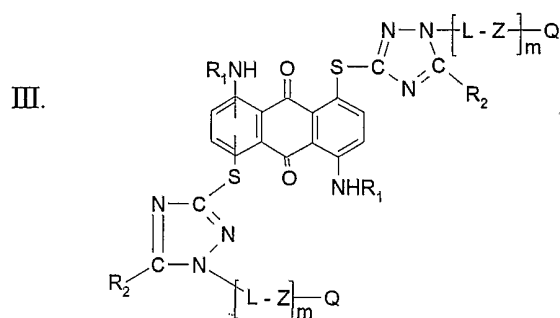
- 42 -

4. Anthraquinone compounds according to Claim 2 having the formula:



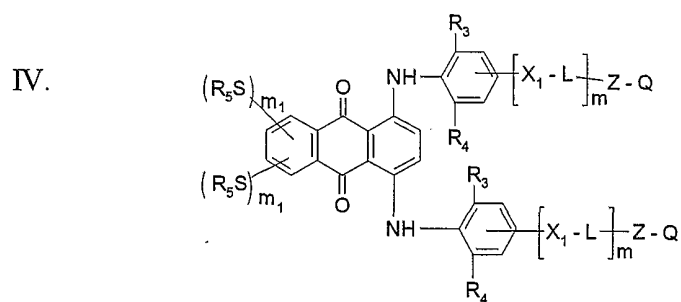
wherein Z is -O-.

5. Anthraquinone compounds according to Claim 2 having the formula:



wherein Z is -O-.

6. Anthraquinone compounds according to Claim 2 having the formula:

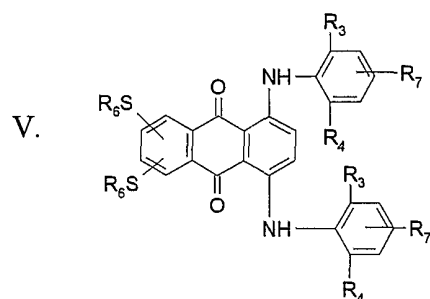


10

wherein Z is -O-.

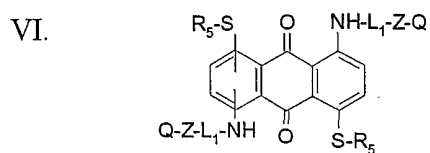
- 43 -

7. Anthraquinone compounds according to Claim 2 having the formula:



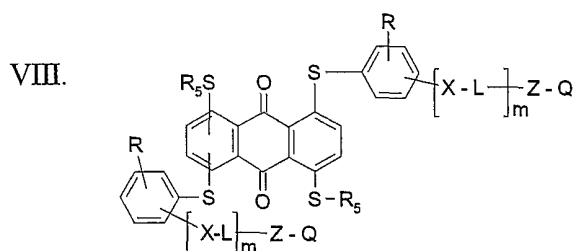
wherein Z is -O-.

- 5 8. Anthraquinone compounds according to Claim 2 having the formula:



wherein Z is -O-.

9. Anthraquinone compounds according to Claim 2 having the formula:

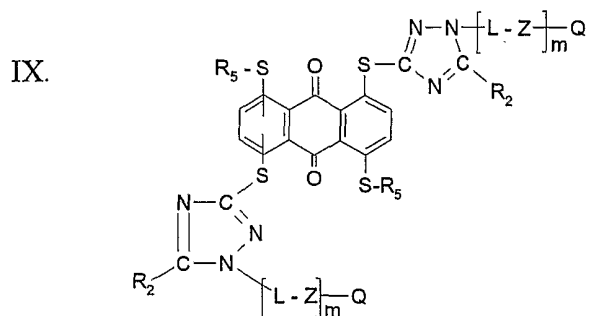


10

wherein Z is -O-.

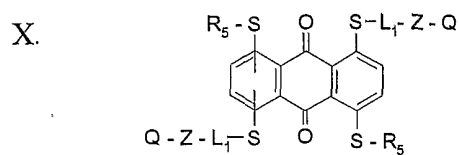
- 44 -

10. Anthraquinone compounds according to Claim 2 having the formula:



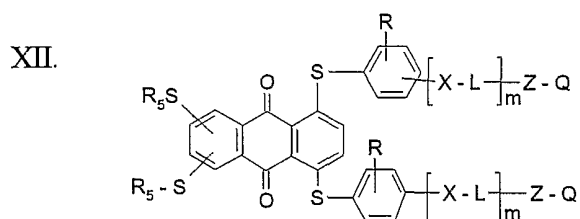
wherein Z is -O-.

- 5 11. Anthraquinone compounds according to Claim 2 having the formula:



wherein Z is -O-.

12. Anthraquinone compounds according to Claim 2 having the formula:

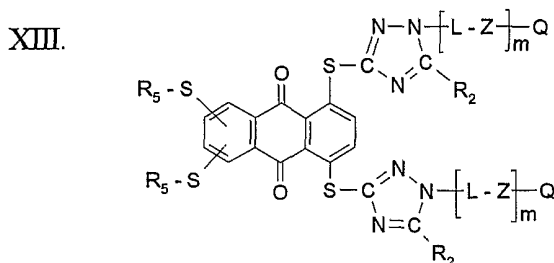


10

wherein Z is -O-.

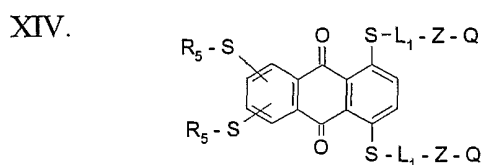
- 45 -

13. Anthraquinone compounds according to Claim 2 having the formula:



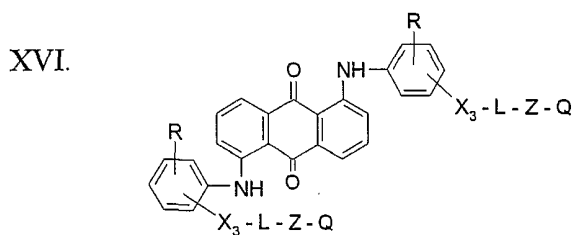
wherein Z is -O-.

- 5 14. Anthraquinone compounds according to Claim 2 having the formula:



wherein Z is -O-.

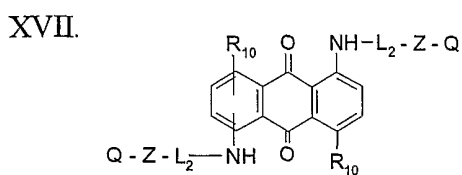
15. Anthraquinone compounds according to Claim 2 having the formula:



10

wherein Z is -O-.

16. Anthraquinone compounds according to Claim 2 having the formula:



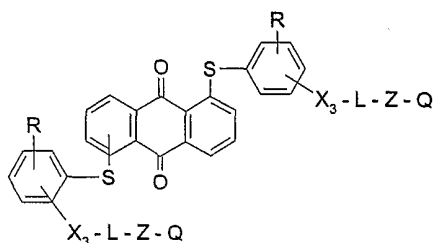
15

wherein Z is -O-.

- 46 -

17. Anthraquinone compounds according to Claim 2 having the formula:

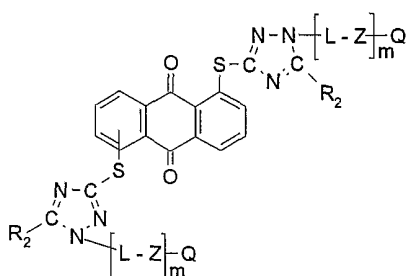
XIX.



wherein Z is $-O-$.

5 18. Anthraquinone compounds according to Claim 2 having the formula:

XX.



wherein Z is $-O-$.

10 19. Anthraquinone compounds according to Claim 2 wherein Q is organic radical Ia.

20. Anthraquinone compounds according to Claim 2 wherein Q is organic radical Ia wherein R_{11} is hydrogen or methyl and R_{12} is hydrogen.

15 21. Anthraquinone compounds according to Claim 2 wherein Q is organic radical VIIa.

22. Anthraquinone compounds according to Claim 2 wherein Q is organic radical VIIa wherein R_{11} is hydrogen.

- 47 -

23. Anthraquinone compounds according to Claim 2 wherein Q is organic radical VIIIa.
24. Anthraquinone compounds according to Claim 2 wherein Q is organic radical VIIIa wherein R_{11} is hydrogen or methyl and R_{13} and R_{14} are methyl.
25. Anthraquinone compounds according to Claim 3 wherein X is $-\text{CO}_2-$, L is $-\text{CH}_2\text{CH}_2-$, and m is 1.
26. Anthraquinone compounds according to Claim 5 wherein L is $-\text{CH}_2\text{CH}_2-$, m is 1, and R_2 is hydrogen.
27. Anthraquinone compounds according to Claim 8 wherein L_1 is $-\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2-$ and R_5 is aryl.
28. Anthraquinone compounds according to Claim 9 wherein X is $-\text{CO}_2-$, L is $-\text{CH}_2\text{CH}_2-$, and m is 1.
29. Anthraquinone compounds according to Claim 10 wherein L is $-\text{CH}_2\text{CH}_2-$, R_2 is hydrogen and m is 1.
30. Anthraquinone compounds according to Claim 12 wherein X is $-\text{CO}_2-$, L is $-\text{CH}_2\text{CH}_2-$, and m is 1.
31. Anthraquinone compounds according to Claim 13 wherein L is $-\text{CH}_2\text{CH}_2-$, R_2 is hydrogen and m is 1.
32. Anthraquinone compounds according to Claim 15 wherein X_3 is $-\text{CO}_2-$, L is $-\text{CH}_2\text{CH}_2-$, and R is hydrogen or bromine.

- 48 -

33. Anthraquinone compounds according to Claim 16 wherein L_2 is $-\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2-$, and R_{10} is hydrogen.
34. Anthraquinone compounds according to Claim 17 wherein X_3 is $-\text{CO}_2-$, L is $-\text{CH}_2\text{CH}_2-$, and R is hydrogen.
35. Anthraquinone compounds according to Claim 18 wherein L is $-\text{CH}_2\text{CH}_2-$, R_2 is hydrogen, and m is 1.
36. Anthraquinone compounds according to Claim 6 wherein X is $-\text{SO}_2\text{N}(\text{Y})-$, L is $\text{C}_2\text{-C}_6$ alkylene, R_3 and R_4 are methyl or ethyl, Y is hydrogen, m is 1 and m_1 is 0.
37. Anthraquinone compounds according to Claim 6 wherein X is $-\text{SO}_2\text{N}(\text{Y})-$, L is $\text{C}_2\text{-C}_6$ alkylene, R_3 and R_4 are methyl or ethyl, Y is hydrogen, m is 1 and m_1 is 1.
38. Anthraquinone compounds according to Claim 1 having formula VII wherein X_2 is $-\text{CO}_2-$ and R and R_8 are hydrogen.
39. Anthraquinone compounds according to Claim 1 having formula XI wherein X_2 is $-\text{CO}_2-$ and R_1 and R_8 are hydrogen.
40. Anthraquinone compounds according to Claim 1 having formula XVII wherein X_4 is $-\text{CO}_2-$ and R and R_8 are hydrogen.
41. Anthraquinone compounds according to Claim 1 having formula XXI wherein X_4 is $-\text{CO}_2-$ and R and R_8 are hydrogen.

- 49 -

42. Anthraquinone compounds according to Claim 1 having formula IV wherein X_1 is -O-, Z is -O-, L is -CH₂CH₂-, R₃ and R₄ are methyl or ethyl, m is 1 and m₁ is 0.

- 5 43. An acrylic polymeric composition comprising a polymer of acrylic acid esters, methacrylic acid esters and/or other copolymerizable vinyl compounds, having copolymerized therein one or more of the dye compounds defined in Claim 1.