

United States Patent [19]

Weaver et al.

[54] THERMOPLASTIC COMPOSITIONS CONTAINING ANTHRAQUINONE POLYSULFONAMIDE COLORANTS

- [75] Inventors: Max Allen Weaver; Wayne Payton Pruett, both of Kingsport; Kay Hunt Shackelford, Johnson City; Samuel David Hilbert, Jonesborough, all of Tenn.
- [73] Assignee: Eastman Chemical Company, Kingsport, Tenn.
- [*] Notice: This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(a)(2).
- [21] Appl. No.: 08/906,647
- [22] Filed: Aug. 7, 1997

Related U.S. Application Data

- [60] Provisional application No. 60/025,367, Sep. 3, 1996.
- [51] Int. Cl.⁷ C08J 5/10; C08L 81/10

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,731,476	1/1956	Peter et al
3,299,103	1/1967	Maier .
4,116,923	9/1978	Gattner et al
4,403,092	9/1983	Davis et al
4.477.635	10/1984	Mitra .

DOCKE

Patent Number:

[45] Date of Patent: *Sep. 19, 2000

6,121,351

5,032,670	7/1991	Parham et al	
5,106,942	4/1992	Krutak et al	
5,194,463	3/1993	Krutak et al	
5,453,482	9/1995	Weaver et al	
5,650,481	7/1997	Yau et al	528/280

FOREIGN PATENT DOCUMENTS

92 07913A	5/1992	WIPO .
92/07913	5/1992	WIPO .
92/13921	8/1992	WIPO .

[11]

OTHER PUBLICATIONS

K. Vendataraman, Editor, The Chemistry of Synthetic Dyes, vol. 8, Academic Press, New York, 1978, pp. 81–131 (no month).

R. Gächter and H. Müller, Editors, Plastics Additives Handbook, Hansu Publishers, New York, 1985, pp 507–533; 729–741 (no month).

N. Ohta, Photographic Science and Engineering, vol. 15, No. 5, Sep.–Oct. 1971, pp 395–415 (no month).

Primary Examiner-Blaine Copenheaver

Assistant Examiner-John J. Guarriello

Attorney, Agent, or Firm-Karen A. Harding; Harry J. Gwinnell

[57] ABSTRACT

Thermoplastic compositions containing certain anthraquinone polysulfonamide colorants incorporated therein as toners or colorants. The anthraquinone colorant moieties which are incorporated into the polymer chain of the polysulfonamide colorants are not leachable, sublimable or extractable and do not exude from the thermoplastic compositions. The anthraquinone polysulfonamide colorants may be added to the thermoplastic polymers during production or melt blended with the polymer by conventional techniques to produce transparent thermoplastic compositions useful for a variety of end uses where nonmigrating or nonextractable colorants are needed.

20 Claims, No Drawings

Find authenticated court documents without watermarks at docketalarm.com.

45

THERMOPLASTIC COMPOSITIONS CONTAINING ANTHRAQUINONE POLYSULFONAMIDE COLORANTS

This application claims benefit of Provisional application 5 Ser. No. 60/025,367 filed Sep. 3, 1996.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to thermoplastic compositions containing certain anthraquinone polysulfonamide colorants incorporated therein as toners or colorants. Since the anthraquinone colorant moieties are incorporated into the polymer chain of the polysulfonamide colorants, they are not leachable, sublimable or extractable and do not exude 15 from the thermoplastic compositions. The anthraquinone polysulfonamide colorants may be added to the thermoplastic polymers during production or melt blended with the polymer by conventional techniques to produce transparent thermoplastic compositions useful for a variety of end uses 20 where nonmigrating or nonextractable colorants are needed.

Thermoplastics are typically colored by organic pigments when superior brilliance and tinctorial strength are important. Opacity, however, is introduced into the polymer composition as a result of the insoluble pigment. Also, toxicity considerations have presented chronic problems relative to the use of organic pigments, since some have been shown to be potential carcinogens and to cause contact dermatitis.

Plastics are also colored by using color concentrates consisting of physical admixtures of polymers and colorants (usually solvent dyes). However, the use of such physical admixtures to color polymeric materials such as polyester, e.g., poly(ethylene terephthalate) and blends thereof, present a number of problems:

- 1. Colorant migration during drying of the colored polyester pellets.
- Colorant migration during extrusion and colorant accumulation on dies or plateout on rollers which can cause shutdowns for clean-up. Such colorant migration and accumulation result in time consuming and difficult 40 clean-up, particularly when a polymer of another color is subsequently processed on the same equipment.
- 3. Colorants may not mix well, for example, when using two or more color concentrates to obtain a particular shade.
- Colorants may diffuse or exude during storage and use of the colored polymeric material.

The use of polysulfonamide colorants eliminate or minimize the aforementioned problems associated with the use of conventional dyes and pigments. 50

2. Description of the Prior Art

It is well-known in the art to color thermoplastic resins by adding pigments or solvent dyes (e.g. see Thomas G. Weber, Editor, Coloring of Plastics, John Wiley and Sons, New York, 1979). The use of pigments, however, is accompanied 55 by undesirable properties such as opacity, dullness of color, low tinctorial strength, etc. Also, difficulties in blending the insoluble pigments uniformly with the thermoplastic resin are encountered. Also, useful for coloring thermoplastic resins are solvent dyes (K. Vendataraman, Editor, The 60 Chemistry of Synthetic Dyes, Vol. 8, Academic Press, New York, 1978, pp 81-131), which give compositions having improved clarity, brightness in hue and high tinctorial strength, but which may lead to dye migration, extraction, etc. from the colored thermoplastic resin. These problems are of particular concern when solvent dyes are used to color 65 flexible resins such as polyvinyl chloride, polyethylene and polypropylene which have low glass transition temperatures.

It is known, also, to prepare solvent soluble nonextractable polymeric aminotriarylmethane dyes having polyester, polycarbonate, polyurethane, or polyethyleneimine backbones and to incorporate them into resins such as polyvinyl chloride, polyvinylidene chloride and acrylic resins such as poly(methyl methacrylate) etc. by solvent blending techniques [S. Mitra (to 3M Corp.), U.S. Pat. No. 4,477,635 (1984)]. Difficulties are encountered in preparing these polymeric colored compounds because a non-colored intermediate aromatic amine containing polymer must be prepared and then the aromatic amine moiety in the polymer structure must be converted into the aminotriarylmethane moiety by further reaction with a diaryl ketone in the presence of condensation catalyst such as phosphorous oxychloride in an inert organic solvent. These previously disclosed polymeric aminotriarylmethane compositions also do not have the requisite thermal stability for use in coloring thermoplastic resins via the more favorable method of melt blending when high temperatures are encountered.

It is further known from U.S. Pat. No. 4,116,923 (1978) to color plastics, in particular polyolefins, with low melting, cross-linked colored polyester compositions containing residues of terephthalic acid, isophthalic acid, or both, a lowmolecular weight trimethylol alkane, i.e. 1,1,1-triethylol propane and a copolymerizable colorant, said colorant being present at a level of 0.1-25% by weight. Difficulties are encountered, however, in preparing these highly crosslinked colored polymers as extreme care as regards to the temperature, amount of vacuum, the level of colorant present and the reaction time is necessary to attempt to reproduce the same quality of cross-linked colored polyester composition. Furthermore, these colored polyester compositions are brittle and low melting and may cause deterioration in physical properties of thermoplastic resins when added in quantities sufficient to produce a high level of coloration. Critical in the preparation of these previously disclosed polymers is the achievement of a low degree of polymerization to give a low melting polymer which has adequate solubility characteristics in the resin to be colored; however, to accomplish this the colorant may not be copolymerized, particularly when added at high levels, thus leading to undesirable extractable colorant.

Additionally, it is known to produce polyester color concentrates having colorants copolymerized therein and to use these for coloring thermoplastics (See U.S. Pat. No. 5,032,670; U.S. Pat. No. 5,106,942; WO 92/07913; WO 92113921). The polycondensation reactions required to prepare these polymeric colorants require high temperature conditions (>250° C.) and continuous large scale processing to be cost effective, in contrast to the polysulfonamide colorants of this invention which can be prepared at relatively low temperatures (e.g. usually 100° C., or less) in batch processing equipment.

Finally, it is known (U.S. Pat. No. 5,194,463) to color thermoplastics using polyurethane color concentrates; however, these colorants have the inherent disadvantage of being derived from diisocyanate compounds as one of the reactants, which are known to be toxic and difficult to handle safely on a large scale.

This invention provides thermoplastic compositions comprising one or more thermoplastic materials and one or more anthraquinone polysulfonamide colorants. The colorant may be added during the preparation of the thermoplastic or afterwards via melt blending techniques.

SUMMARY OF THE INVENTION

The invention provides a colored thermoplastic composition which comprises at least one thermoplastic polymer having combined therewith at least one colorant having the formula I:

Find authenticated court documents without watermarks at docketalarm.com.

5

45

T

 $- [N(R)O_2S - Ar - x - AQ - X' - Ar' - SO_2N(R') - R]_{n}$

wherein:

- AQ is a divalent anthraquinone radical which may be substituted with from 1 to 6 substituents which may be the same or different and are selected from C_1-C_8 alkyl, C_1-C_8 alkoxy, C_1-C_8 alkanolyamino, aroylamino, C_1-C_8 alkylthio, halogen, amino, nitro, C_1-C_8 alkylamino, C_3-C_8 cycloalkylamino, C_1-C_8 alkanoyl, C_1-C_8 alkoxy-carbonyl, trifluoromethyl, cyano, C_3-C_8 cycloalkoxy, C_3-C_8 cycloalkylthio, heteroarylthio, C_1-C_8 alkylsulfonyl, arylsulfonyl, aroyl, carbamoyl, sulfamoyl, C_1-C_8 alkanoylamino, aroylamino, C_1-C_8 alkylsulfonamido, arylsulfonamido, arylthio, aryloxy, arylamino, and hydroxy groups;
- X and X' are independently Y, -Y—alkylene, ²⁰ -Y—alkylene—Y'—)_m, -Y— alkylene—C₃–C₈cycloalkylene, Y—C₃–C₈-cycloalkylene—Y', or Y—alkylene—C₃–C₈-cycloalkylene—alkylene—Y', wherein m is 1–3, and Y and Y' are independently -O—, -S—, -N(R)CO—, $-N(R)SO_2$ —, or—N ²⁵ (R₂)—;
- Ar and Ar' are independently a divalent benzene or naphthalene radical which may be substituted with from 1 to 4 substituents which may be the same or different and are selected from C_1-C_8 alkyl, C_1-C_8 30 alkoxy, C_1-C_8 alkanolyamino, aroylamino, C_1-C_8 alkylthio and halogen groups;
- R and R' are independently hydrogen, C_{1-C8} alkyl, C₃-C₈ cycloalkyl, heteroaryl or aryl;
- R_1 is a divalent organic radical, with the proviso that when ³⁵ R_1 is ethylene, R and R' may be combined to represent an ethylene radical;
- R_2 is hydrogen, C_1-C_8 alkyl, C_3-C_8 cycloalkyl, C_1-C_8 alkanoyl, aroyl, C_1-C_8 alkylsulfonyl, arylsulfonyl, carbamoyl, or sulfamoyl; and n is an integer of from ⁴⁰ about 3 to about 30.

The invention also provides a method of forming a thermoplastic composition which comprises melting a thermoplastic polymer and blending therewith a colorant having the above formula I.

The invention further provides a colored thermoplastic composition which comprises, at least one thermoplastic polymer having combined therewith at least one colorant having a unit of the above formula I.

The toned and colored thermoplastic compositions into 50 which the colorants of the present invention are incorporated have a high enough molecular weight so that the resultant colored polymer will not be leachable, extractable, sublimable, migratable, etc. from the thermoplastic composition thus minimizing toxicity concerns with human exposure. The colored compositions are nonhazardous, have good brilliance, clarity, fastness to light, high heat stability, excellent homogeneity of colorant, and which normally maintain the desirable physical properties of the uncolored thermoplastic materials.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In accordance with the present invention thermoplastic compositions are produced by adding, during the preparation of the thermoplastics or by melt blending the ⁶⁵ thermoplastic, anthraquinone polysulfonamide colorants of the Formula I

wherein:

N(R)O₂S

Ar and Ar' each independently represent a divalent radical of the benzene or naphthalene series; X and X' are independently selected from Y, -Y-alkylene, -Y-alkylene $-Y'_m$, -Y-alkylene $-C_3-C_8$ -cycloalkylene, $Y-C_3-C_8$ -cycloalkylene-Y', Y—alkylene— C_3 - C_8 -cycloalkylene—alkylene—Y', wherein m is 1-3, Y and Y' are independently selected from —O—, —S—, —N(R)CO—, —N(R)SO₂—, and $-N(R_2)$ -, AQ is a divalent anthraquinone radical; R and R' are independently selected from hydrogen, C₁-C₈ alkyl, C₃-C₈ cycloalkyl, heteroaryl and aryl; R₁ is a divalent organic radical, with the proviso that when R_1 is ethylene, R and R' may be combined to represent an ethylene radical; and R_2 is selected from hydrogen, C₁-C₈ alkyl, C₃-C₈ cycloalkyl, C₁-C₈ alkanoyl, aroyl, $\rm C_1-\rm C_8$ alkyl
sulfonyl, arylsulfonyl, carbamoyl, and sulfamoyl; n is an integer of from about 3 to about 30, preferably an integer from about 5 to about 20.

4

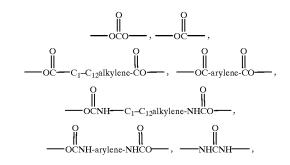
T

 $-SO_2N(R')$ -

Each divalent radical represented by Ar and Ar' may be further substituted with 1–4 groups which may be the same or different and are selected from C_1-C_8 alkyl, C_1-C_8 alkoxy, C_1-C_8 alkanolyamino, aroylamino, C_1-C_8 alkylthio and halogen.

The divalent anthraquinone radical (AQ) may be further substituted with 1–6 groups which may be the same or different and are selected from C_1-C_8 alkyl, C_1-C_8 alkoxy, C_1-C_8 alkanolyamino, aroylamino, C_1-C_8 alkylthio, halogen, amino, nitro, C_1-C_8 alkylamino, C_3-C_8 cycloalkylamino, C_1-C_8 alkanoyl, C_1-C_8 alkoxycarbonyl, trifluoromethyl, cyano, C_3-C_8 cycloalkoxy, C_3-C_8 cycloalkylthio, heteroarylthio, C_1-C_8 alkylsulfonyl, arylsulfonyl, aroyl, carbamoyl, sulfamoyl, C_1-C_8 alkanoylamino, aroylamino, C_1-C_8 alkylsulfonamido, arylsulfonamido, arylthio, aryloxy, arylamino, and hydroxy.

The organic radical R_1 can be selected from a wide variety of divalent linking groups including, C_2-C_{12} alkylene, C_3-C_8 cycloalkylene, $-CH_2-C_3-C_8$ cycloalkylene-CH₂-, carbocyclic and heterocyclic arylene and these in combination. The alkylene linking groups may contain within or attached to their main chain one or more hetero atoms, e.g., oxygen, sulfur, nitrogen, substituted nitrogen, and/or cyclic groups such as C_3-C_8 cycloalkylene, carbocyclic arylene, divalent aromatic heterocyclic groups or ester/amide groups such as



5

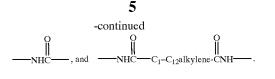
10

15

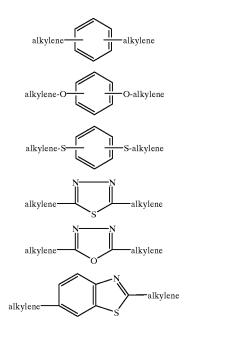
20

55

60

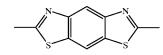


Examples of C_2 - C_{12} alkylene radicals containing cyclic moieties in the alkylene chain include



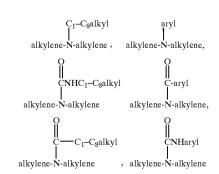
The cycloalkylene groups in the definition of R_1 are typically groups such as 1,2-; 1,3-; and 1,4-cyclohexylene. ³⁵ The carbocyclic arylene groups in the definition of R_1 include typically 1,2-; 1,3-; and 1,4-phenylene and 1,4-; 1,5-; 1,8-; 2,6-; and 2,7-naphthalenediyl and these substituted with one or more groups selected from C_1-C_{12} alkyl, C_1-C_{12} alkoxy and halogen. 40

Examples of the divalent heterocyclic arylene groups include unsubstituted and substituted triazines such as 1,3, 5-triazin-2,4-diyl-, 6-methoxy-1,3,5-triazin-2,4-diyl; diazines such as 2,4-pyrimidindiyl, 6-methyl-2,4-pyrimidindiyl, 6-phenyl-2,4-pyrimidindiyl, 3,6-pyridazindiyl and 2-methyl-3-oxo-4,5-pyrazindiyl; dicyano pyridines such as 3,5-dicyano-2,6-pyridindiyl; quinolines and isoquinolines such as 2,4-quinolindiyl and 2,8-isoquinolinediyl; quinoxalines such as 2,3-quinoxalindiyl; azoles such as 2,5thiazoldiyl, 5-methylene-2-thiazolyl, 3,5-isothiazoldiyl, 5-methylene-3-isothiazolyl, 1,3,4-thiadiazol-2,5-diyl, 1,2,4thiadiazol-3,5-diyl, 2,6- benzothiazoldiyl, 6-methylene-2benoxazoldiyl, and the group having the formula:



and maleimides such as 1-methyl-3,4-maleimidyl and 1-phenyl-3,4-maleimidediyl.

In addition to the possible substitution described above, the nitrogen atom of the nitrogen containing alkylene groups may be substituted, for example, with C_1 - C_8 alkyl, aryl, ⁶⁵ C_1 - C_8 alkanoyl, aroyl, C_1 - C_8 alkylsulfonyl or carbamoyl, e.g.



The term "alkylene" is used herein to represent straight or branched chain divalent hydrocarbon moieties having 1–8 carbons which may be further substituted by C_1-C_8 alkoxy, C_1-C_8 alkanoyloxy, aroyloxy, or halogen. The term " C_3-C_8 cycloalkyl" is used to describe

The term " C_3-C_8 cycloalkyl" is used to describe cycloaliphtic hydrocarbon radicals containing three to eight carbon atoms and these optionally substituted with C_1-C_8 alkyl, halogen, hydroxymethyl or C_1-C_8 alkanoyloxym-

ethyl. The term " C_3-C_8 cycloalkylene" is used to represent divalent cycloalkylene radicals containing from 3-8, pref-25 erably 5 or 6, ring carbons and which may be further substituted by C_3-C_6 alkyl or halogen.

substituted by C_1-C_8 alkyl or halogen. The term " C_1-C_8 alkyl" is used to describe a monovalent straight or branched chain hydrocarbon radical which may be further substituted by one or more groups selected from C_1-C_8 alkoxy, C_1-C_8 alkanoyloxy, aroyloxy, C_3-C_8 cycloalkyl, cyano, aryl, heteroaryl, and halogen.

The term "halogen" is used to include fluorine, chlorine, bromine, and iodine.

The terms "aryl" and "aroyl" are used herein to describe a group wherein the aromatic portion is a phenyl or naphthyl radical, optionally substituted with one to four groups which may be the same or different and are selected from C_1-C_8 alkyl, C_1-C_8 alkoxy, C_1-C_8 alkylthio, C_3-C_8 cycloalkyl, halogen, carboxy, C_1-C_8 -alkoxy carbonyl, C_1-C_8 alkanoylamino, benzoylamino, C_1-C_8 alkylsulfonamido, and benzenesulfonamido. The benzoyl and benzene radicals of benzoylamino and benzenesulfonamide may be further substituted by one or more groups selected from C_1-C_8 alkyl, C_1-C_8 alkoy, and halogen, respectively. The term "heteroaryl is used herein to represent mono or

The term "heteroaryl is used herein to represent mono or bicyclic hetero aromatic radicals containing at least one "hetero" atom selected from oxygen, sulfur, and nitrogen, or a combination of these atoms in combination with carbon to complete the aromatic ring. Examples of suitable heteroaryl groups include: thiazolyl, quinolinyl, benzothiazolyl, pyrazolyl, pyrrolyl, thienyl, furyl, thiadiazolyl, oxadiazolyl, benzoxazolyl, benzimidazolyl, pyridyl, pyrimidinyl, and triazolyl and such groups substituted 1–3 times with a group selected from halogen, C_1 – C_8 alkyl, C_1 – C_8 alkanoylamino, aroylamino, C_1 – C_8 alkylsulfonamido, or arylsulfonamido.

The term "arylene" as used herein preferably denotes divalent benzene and naphthalene radicals and these optionally substituted by one or more groups selected from C_1-C_8 alkyl, C_1-C_8 alkoxy, C_1-C_8 alkylthio, halogen, and C_1-C_8 alkoxycarbonyl. The preferred arylene groups are 1,2-; 1,3-; and 1,4-phenylene.

In the terms "C₁-C₈ alkoxycarbonyl"; "C₁-C₈ alkanoyl", "C₁-C₈ alkanoyloxy", "C₁-C₈ alkanoylamino", "C₁-C₈ alkoxy", "C₁-C₈ alkysulfonyl", "C₁-C₈ alkylsulfonamido", "C₁-C₈ alkylthio" the alkyl portion of the groups have 1-8 carbons and are straight or branched chain hydrocarbon radicals, optionally substituted with one or more groups listed above as possible substitutents for the C₁-C₈ alkyl radicals.

Find authenticated court documents without watermarks at <u>docketalarm.com</u>.

The terms "carbamoyl" and "sulfamoyl" refer to groups of formulae — $CON(R_3)R_4$ and — $SO_2N(R_3)R_4$, respectively, wherein R_3 and R_4 are independently selected from hydrogen, C_1 – C_8 alkyl, C_3 – C_8 cycloalkyl, heteroaryl, and aryl.

A wide range of thermoplastic polymers useful for blending with the anthraquinone polysulfonamide colorants in the practice of the present invention are known in the art and includes homopolymers and copolymers of polyesters e.g., poly(ethylene terephthalate); polyolefins, e.g., polypropylene, polyethylene, linear low density 10 polyethylene, polybutylene and copolymers made from ethylene, propylene and/or butylene; copolymers from styrene and acrylonitrile; polyamides, e.g., Nylon 6 and Nylon 66; polyvinyl chloride; polyurethanes; polyvinylidene chloride; polycarbonates; cellulose esters, e.g., cellulose acetate, propionate, butyrate or mixed esters; polyacrylates, e.g., poly(methyl methacrylate); polyimides; polyester-amides; polystyrene; etc.

The preferred thermoplastic polymers are polyesters, particularly poly(ethylene terephthalate), modified poly ²⁰ (ethylene terephthalate), polycarbonate, cellulose esters and polyamides, particularly Nylon 6 and Nylon 66.

According to the invention the anthraquinone polysulfonamide colorants are incorporated into the thermoplastic polymers using conventional techniques e.g., solution or ²⁵ melt-blending, such as those employed to incorporate other additives in such resins (see R. Gächter and H. Müller, Editors, Plastics Additives Handbook, Hansu Publishers, New York, 1985, pp 507–533; 729–741). For example, the colored polyester compositions may be dry blended in form ³⁰ of powders of pellets with the thermoplastic resin in the form of pellets or ground powders with or without an adhesion promoter or a dispersing agent. This premix can be subsequently processed on extruders or injection molding machines. ³⁵

It is also within the scope of this invention to prepare a first thermoplastic composition containing one or more polysulfonamide colorants and then to prepare another second thermoplastic composition by melting and blending with an uncolored thermoplastic.

The actual amount of the anthraquinone polysulfonamide ⁴⁰ colorant used to color the thermoplastic polymer will depend upon the inherent tinctorial strength of the anthraquinone chromophore and the desired depth of shade. Typically, the amount of anthraquinone polysulfonamide colorant added to the thermoplastic polymer is such that the total amount by ⁴⁵ weight in the final thermoplastic polymer is such that the total amount by weight in the final thermoplastic polymer blend composition is from about 0.001% to about 20%, preferably from about 0.01% to about 10.

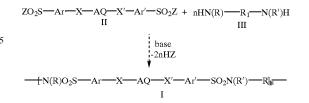
The colored thermoplastic polymer composition provided 50 by the present invention are useful as thick and thin plastic films, extruded coatings and lamination layers, plastic sheeting, molded plastic articles and fibers.

When added as toners, e.g. to neutralize the yellow color produced in the manufacture of some condensation polymers such as poly(ethylene terephthalate) the anthraquinone polysulfonamide colorants are used at low levels such as from about 1 to about 10 parts per million (ppm), preferably from about 3 to about 8 ppm.

The particular chromophore groups present will, of course, determine the color (hue+value+chroma) of the ⁶⁰ anthraquinone polysulfonamide colorant and finally the color (hue+value+chroma) of the thermoplastic or polymer blends of the invention. A large gamut of colors may be obtained by blending two or more anthraquinone polysulfonamide colorants with the thermoplastic polymers to be ⁶⁵ colored, followed by molding or extruding or by first blending two or more anthraquinone polysulfonamide colorants

together and then blending these premixed materials with the thermoplastic polymer or polymers to be colored. Alternatively, a concentrate of the anthraquinone polysulfonamide colorants in an appropriate vehicle may be prepared. The concentrate may be in the form of liquids, pastes, slurries, or solids, e.g., powders, compacted powders, pellets, etc., and may be incorporated by known methods into the thermoplastic polymer(s).

The anthraquinone polysulfonamide colorants of Formula I are prepared by the following general route:



wherein Ar, Ar', X, X', AQ, R, R', R₁, and n are as previously defined and Z is fluoro, chloro, or bromo, preferably chloro. The dihalosulfonyl colorant compounds II, containing the anthraquinone chromophore, are reacted with diamines m in a solvent in the presence of an acid acceptor to yield the polysulfonamides of Formula I. Normally, the amide producing reactions are carried out at from about 25° C. up to 150° C., but usually at about 50° C. up to about 130° C. Suitable solvents are those in which II and III have sufficient solubility at the desired reaction temperature to facilitate reaction and which will not react with II or III, with aprotic solvents such as N,N-dimethyl formamide, N,Ndimethylacetamide, N-methylpyrrolidinone, hexamethylphosphoramide, dimethylsulfoxide and pyridine being particularly useful. Bases such as trialkylamines, e.g. triethylamine and tri-n-butylamine, N-alkylmorpholines, e.g. 4-methylmorpholine, N,N-dialkylpiperazines, e.g. 1,4dimethylpiperazine, bicyclic nitrogen containing bases having non-hindered electron pairs, such as 1,8-biazabicyclo [5,4,0] undec-7-ene (DBU) and 1,4-diazadicyclo [2,2,2] octane (DABCO®), and alkali metal carbonates and bicarbonates, e.g. potassium carbonate are useful as acid acceptors to facilitate the polycondensation reaction.

Polysulfonamide colorants I may vary considerably in weight average molecular weight and still be useful; however, it is usually desirable that a weight average molecular weight of at least 1,500–2,000 be achieved to avoid problems related to extraction, migration, sublimation, etc. in the use of the colorants at high temperatures. If extremely high weight molecular weights are encountered, the polysulfonamides may not dissolve when used to color thermoplastics, thus functioning as pigments instead of dyes. Normally, a weight average molecular weights and which will still allow the polysulfonamide colorants to be largely soluble in the thermoplastic substrate.

Typical dihalosulfonylanthraquinone intermediates II which are useful in the practice of the invention are presented in Table I and typical diamines are given in Table II. Any reactant in Table I may be reacted with any diamine of Table II to produce a polysulfonamide colorant.

Find authenticated court documents without watermarks at docketalarm.com.

DOCKET A L A R M



Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

Real-Time Litigation Alerts



Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

Advanced Docket Research



With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

Analytics At Your Fingertips



Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

LAW FIRMS

Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

FINANCIAL INSTITUTIONS

Litigation and bankruptcy checks for companies and debtors.

E-DISCOVERY AND LEGAL VENDORS

Sync your system to PACER to automate legal marketing.