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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
31 December 2003 (31.12.2003)

PCT

(10) International Publication Number
WO 2004/000946 A1

(51) International Patent Classification[7]: C09B 7/00

(21) International Application Number:
PCT/US2003/019273

(22) International Filing Date: 19 June 2003 (19.06.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/390,049	19 June 2002 (19.06.2002)	US
10/370,288	18 February 2003 (18.02.2003)	US

(63) Related by continuation (CON) or continuation-in-part (CIP) to earlier applications:

US	60/390,049 (CON)
Filed on	19 June 2002 (19.06.2002)
US	10/370,288 (CON)
Filed on	18 February 2003 (18.02.2003)

(71) Applicant *(for all designated States except US)*: **BOARD OF REGENTS, THE UNIVERSITY OF TEXAS SYSTEM** [US/US]; 201 West Seventh Street, Austin, TX 78701 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **CHIANELLI, Russell** [US/US]; 752 Cheltenham, El Paso, TX 79912 (US).

POLETTE, Lori, A. [US/US]; 734 Mesa Hills, Apt.144, El Paso, TX 79912 (US).

(74) Agent: **HIGHLANDER, Steven, L.**; Fulbright & Jaworski L.L.P., Suite 2400, 600 Congress Avenue, Austin, TX 76701 (US).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: COLOR COMPOSITIONS

(57) Abstract: The present invention includes a paint or coating composition comprising an organic pigment or dye complexed to the surface of a layered or fibrous inorganic clay. A wide variety of paint colors can be obtained by varying the pH during the preparation as well as by varying the synthesis conditions and changing particle size of the clay. The paint has unprecedented stability.

WO 2004/000946 A1

COLOR COMPOSITIONS

BACKGROUND OF THE INVENTION

The government may own rights in the present invention pursuant to GSA Strategic Metals Grant No. 26-3000-57. This application claims benefit of priority to U.S. Provisional Application Serial No. 60/390,049, filed June 19, 2002, the entire contents of which are incorporated by reference.

I. Field of the Invention

The present invention relates to the field of paints and more specifically provides a novel long lasting, stable powder that can be incorporated into paints, plastics, and cements.

II. Description of Related Art

In the scientific literature, the term Maya blue refers to a "turquoise" brilliant shade of blue that is found on murals and archaeological artifacts, for example, throughout Mesoamerica. It is described in the literature as being composed of palygorskite clay and indigo, that when mixed and heated, produce the stable brilliant blue color similar to that found in Mesoamerica. Any proposed methods of preparation were done for the intention of trying to replicate the blue color found at the historical sites and to reproduce the techniques employed by the original Maya.

H. Van Olphen, Rutherford Gettens, Edwin Littman, Anna Shepard, and Luis Torres, were perhaps some of the most prominently involved scientists in the examination of organic/inorganic complex paint from the 1960's to the 1980's. In the early studies, only Littman and Van Olphen published information specifically on the synthesis of organic/inorganic complex (13, 14, 9, 10). While their work never definitively described the Maya technique for making the colorant, or explained the stability of the organic / inorganic complex, the results of their two decades of studies with respect to the ancient paint laid a foundation of knowledge for future investigators.

Littman has synthesized indigo-attapulgite complexes and verified that his synthetic version was indistinguishable from the original pigments found in the pre-Hispanic murals and artifacts (9, 10). The prepared samples had the same physical and chemical characteristics as the authentic Maya blue examined. Littman concluded that the remarkable stability of the attapulgite was due to the heat treatment the attapulgite received during the synthesis. Others

have also synthesized compounds similar to that of Maya blue by a number of routes (30). They employed the Gettens test to determine whether the laboratory synthesis of Maya blue was indeed authentic with the same chemical resistant properties (3). The test was necessary because initial attempts of simply mixing the palygorskite clay produced the color of Maya blue but the mixture did not possess the same chemical properties as the original organic/inorganic complex samples.

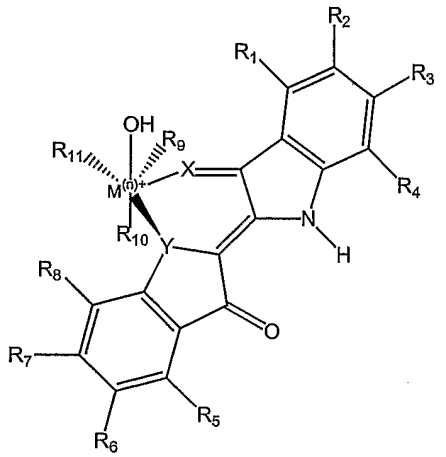
The literature for Maya paint compositions does not provide information with respect to varying the color for the paint composition based on altering the pH and particle size; nor does there appear to be mention of using alternate dye or pigment systems as described in the present invention. Formulations of paints based on the paint composition of the present invention with resins or polymeric systems have not been realized either according to the literature. The only known literature discussions of pH pertain to the alkaline pH required to reduce the indigo prior to contacting it with the clay (9, 10). Furthermore, there is a lack of understanding regarding the chemistry for producing stable and nontoxic paint systems by combining dyes and pigments with fibrous and layered clays.

Therefore, it would be advantageous to provide a novel paint composition that is stable and nontoxic.

SUMMARY OF THE INVENTION

Thus, in accordance with the present invention, there is provided a coating composition comprising (a) a molecular derivative of indigo; and (b) a fibrous or layered clay, wherein the coating composition is used for coloring surfaces. The color/hue of the composition is determined by the concentration of the dye and pH of the composition. The particle size of the coating composition may be between about 0.01 μm and 20 μm, or more particularly between about 0.1 μm and 2 μm. The fibrous clay may be selected from a palygorskite clay, a sepiolite clay, or a mixture of a palygorskite and a sepiolite clay. The layered clay may be a kaolinite, bentonite, nontronite, or mordenite clay. The molecular derivative of indigo may be dibromoindigo or thioindigo. The coating composition may be a powder or a liquid. The coating composition may be resistant to decomposition by light, acids, alkalis, and/or solvents.

In another embodiment, there is provided a composition comprising:



wherein R_1-R_8 are individually H, CH_3, CH_2CH_3, F, Cl, Br, I, CN, OH, SH, OCH_3 or OCH_2CH_3; R_9-R_{11} are individually SiO_3, SiOH or H_2O; Y is N, O, S, or Se; X is O or S; $M^{(n+)}$ is Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Pt, Pd or Zn; and n is 1,2,3,or 4.

In yet another embodiment, there is provided a formulation comprising (a) a molecular derivative of indigo; (b) a palygorskite clay, a sepiolite clay, or a mixture of a palygorskite and a sepiolite clay; (c) a polymer; and (d) an organic binding agent.

In still yet another embodiment, there is provided a formulation comprising (a) a molecular derivative of indigo; (b) a palygorskite clay, a sepiolite clay, or a mixture of a palygorskite and a sepiolite clay; and (c) a gum arabic; a linseed oil; a copal; a polycarbonate; an egg tempura; or a turpentine.

In a further embodiment, there is provided a shapeable molding material comprising (a) a molecular derivative of indigo; (b) a palygorskite clay, a sepiolite clay, or a mixture of a palygorskite and a sepiolite clay; and (c) a cement, a plastic or a polymer.

In still a further embodiment, there is provided a shapeable tile material comprising (a) a molecular derivative of indigo; (b) a palygorskite clay, a sepiolite clay, or a mixture of a palygorskite and a sepiolite clay; and (c) a cement, a plastic or a polymer.

In still yet a further embodiment, there is provided a method of producing a coating composition comprising (a) providing a molecular derivative of indigo; (b) combining the molecular derivative of indigo with a fibrous or layered clay to form a coating composition; (c) heating the coating composition; and (d) adjusting the pH of the dye or pigment composition. The method may further comprise: (a) treating the coating composition with acid to remove

impurities from the clay; (b) applying the coating composition to a surface; (c) blending the coating composition with a polymer or organic binder; or homogenizing the dye composition by blending, grinding, milling or stirring.

The heating may comprise heating at a temperature of between 100°C and 300°C, or more particularly between 115°C and 150°C. The heating may last up to four days. The coating composition may contain water, may have a pH between about 3 and about 7.5, may contain a dye in the range of 0.01% to 20% by weight, may contain a molecular derivative of indigo in the range of about 0.1% to 7% by weight, or more particularly by about 6% by weight at neutral or acidic pH. The fibrous clay may be a palygorskite clay, a sepiolite clay, or a mixture of a palygorskite and a sepiolite clay. The layered clay may be a kaolinite, bentonite, nontronite, or mordenite clay. The particle size of the coating composition is between about 0.01 μm and 20 μm, or more particularly between about 0.1 μm and 2 μm. The molecular derivative of indigo may be thioindigo or dibromoindigo. The method may further comprise adding a binding agent to the coating composition.

BRIEF DESCRIPTION OF THE DRAWINGS

The following drawings form part of the present specification and are included to further demonstrate certain aspects of the present invention. The invention may be better understood by reference to one or more of these drawings in combination with the detailed description of specific embodiments presented herein.

FIG. 1 – Color variations of synthetic organic/inorganic complexes prepared using various concentrations of indigo derivatives. Vertically shown are the effects of pH on a synthetic sample made with 4% wt. Indigo derivatives.

FIG. 2 – Color changes as a function of temperature and heating time of synthetic organic/inorganic complexes.

FIG. 3 – Synchrotron X-ray Diffraction of Attagel (palygorskite) and organic/inorganic complex at 25°C and 140°C. Simulated diffraction of Indigo derivatives are also shown.

FIG. 4 – IR Analysis of crystal violet mixed with palygorskite clay. Temperatures are room temperature (25°C) and after heating and reaction at 140°C. The cationic exchange

reaction with the clay does not produce a color change, and thus it does not chemically alter the IR spectra.

FIG. 5 – IR Analysis of maya blue (indigo pigment mixed with palygorskite clay). One is at room temperature (25°C), where there is no chemical reaction or color change when the indigo is merely mixed with the clay. After 140°C heating and reaction of the mixture, the IR spectra clearly changes. The changes in the peaks are indicative of a new chemical interaction between the indigo and clay.

DETAILED DESCRIPTION OF THE INVENTION

The present invention includes a color composition of matter comprising organic pigments and dyes complexed to the surface of inorganic clays. These organic/inorganic hybrid materials are useful as paints and coatings for artisan and industrial purposes, as well as color compositions to be used with cements, plastics, papers and polymers. Upon grinding and heating the organic and inorganic component as solid mixtures or in aqueous solutions, the resulting color composition has unprecedented stability relative to the original starting material alone. The inorganic component is either a layered clay or a fibrous clay. The fibrous clay can be either palygorskite or sepiolite clay. The layered clay may be, for example, a kaolinite, bentonite, nontronite, or mordenite clay. The organic component is an organic dye or pigment of which some examples are found in the book Color Chemistry, 2nd ed. (33). Using the clay with various dyes or pigments results in achieving a color composition possessing a wide variety of colors.

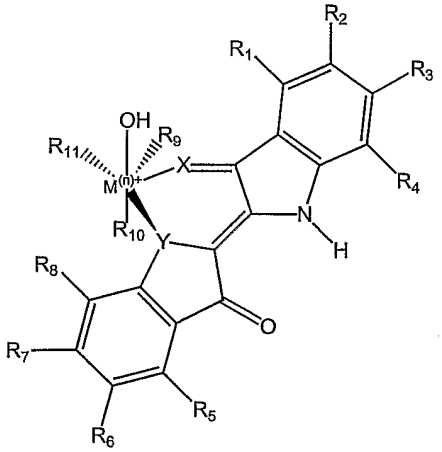
By changing the pH during the preparation of such color compositions control of the final composition color can be attained within any given set of clay/pigment materials. Additionally, by selecting a particular particle size of the clay starting material, a wide range of colors and hues can also be created. The color composition can be suspended in an organic binder, resins or polymers, depending on the final application. The paint powder can also be formulated with a gum arabic; a linseed oil; a copal; a polycarbonate; an egg tempura; or a turpentine, depending on the final application.

The coating composition may be applied to a surface by any of the means known in the art for paint application such as by brushing or spraying. Also, multiple shapeable materials can be formed by incorporating the color composition of the present invention in liquid, powder, or solid form, or as an emulsion with cements, plastics or polymers, to produce molding materials,

tiles, concrete and other forms produced using layered or fibrous clays. The color composition can also be incorporated into portland cement concrete materials to be used as color markers on road surfaces or bridges. Some examples of portland cement concrete materials are covered in the *U.S. Department of Transportation Manual* (31) and other concrete materials are covered in *Concrete* (12). Methods of incorporating the color compositions into cement or concrete can be found in *Cement Science, In concrete Admixtures Handbook: Properties, Science, and Technology* (26).

I. Dyes

The color for the color composition comes from an organic dye or pigment. This chromophore may be a molecular derivative of indigo such as dibromoindigo or thioindigo. Other derivatives of indigo may also be used to vary the color or other physical properties of the color composition. These chromophores are shown in Scheme 1. The chromophore may also be a different derivative, such as one containing an additional conjugated ring or ligand.



Scheme 1. Possible derivatives of Indigo:

wherein R_1-R_8 are individually H, CH_3, CH_2CH_3, F, Cl, Br, I, CN, OH, SH, OCH_3 or OCH_2CH_3; R_9-R_{11} are individually SiO_3, SiOH or H_2O; Y is N, O, S, or Se; X is O or S; $M^{(n+)}$ is Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Pt, Pd or Zn; and n is 1,2,3,or 4.

II. Clays

As used herein, the term "clay" refers to layered clays as well as fibrous clay. The fibrous clay is preferentially a palygorskite clay, a sepiolite clay, or a mixture of palygorskite and sepiolite clays. The mixture may be in any ratio. For example, it may be 50% palygorskite and 50% sepiolite or it may be 10%/90%, 20%/80%, 30%/70%, 40%/60%, 60%/40%, 70%/30%, 80%/20%, or 90%/10% (palygorskite/sepiolite). As used herein the term palygorskite and attapulgity are used interchangeably to refer to the same type of clay. The layered clay may be, for example, a kaolinite, bentonite, nontronite, or mordenite clay.

Previous work has shown that synthesis of comparable organic/inorganic complex paint using clays with plate-like structures, including kaolinite, bentonite, nontronite, and mordenite all produce a blue colored pigment, but without the stability of the indigo derivative/palygorskite complex (13, 14). This indicates that the possible stability of the Maya blue pigment is due to the fiber-like structure of the clays used since the use of plate-like clays had not been shown to yield a stable pigment (13, 14, 9, 10).

The particle size of the clay may be varied. It is preferentially between 0.01 μm and 20 μm, 0.05 μm and 10 μm or more preferably between 0.1 μm and 2 μm. As the color changes with the size of the particles, varying the particle size allows for greater control of color. Smaller particles will tend to be more blue in hue where the larger particles tend towards green in hue.

III. Polymers, Binding Agents and Modifiers

One or more binding agent or modifiers may be added to the paint composition to increase stability, uniformity, spreadability, adhesion, coating thickness etc. Binding agents and modifiers are well known in the art of paint formulation and may be included in the current coating composition. Binding agents such as solvent-containing binding agents (acryl, cyclized rubber, butyl rubber, hydrocarbon resin, α-methylstyrene-acrylonitrile copolymers, polyester imide, acryl acid butyl esters, polyacrylic acid esters, polyurethanes, aliphatic polyurethanes and chloro sulphonated polyethylene), and thermoplastic materials (polyolefins, α-ethylstyrene-acrylonitrile copolymers, polyester imide and polyamide) may be added to the paint composition. Similarly, polymers such as acrylate, styrene acrylate, acrylonitrile copolymer, polyethylene, polyethylene oxidate, chlorosulfonated polyethylene, ethylene-acrylic acid copolymer, methacrylate, vinylpyrrolidone-vinyl acetate copolymer, vinylidene chloride copolymer, polyvinylpyrrolidone, polyisopropyl acrylate, polyurethane, cyclized rubber, butyl rubber,

hydrocarbon resin, α-methylstyrene-acrylonitrile copolymer, polyester imide, acryl acid butyl esters, or polyacrylic acid esters may be added.

The paint composition can be blended with a variety of other medium including gum arabic, linseed oil, copal, polycarbonate, egg tempura, and turpentine to create blended systems. The blended paint color can be altered depending on the medium in which it is blended. Grinding the initial powder to various particle sizes prior to or during blending with a medium can result in color control.

IV. Color Optimization

A series of experiments were developed to optimize the properties and hues of the synthetic versions of organic/inorganic complex. The synthetic versions of organic/inorganic complex were tested for stability using the Gettens test; however, the inventors have found that the Gettens test is limited and alternative methods such as IR have also been employed in these studies. Specifically, by examining the effects of dye or pigment, such as dibromoindigo, concentration, pH, and particle size, a paint possessing a color remarkably similar and stable to that of a known organic/inorganic complex was developed. The stability of the complex can be seen by its resistance to decomposition when exposed to light. Since the complex is formed with both organic and inorganic components, the stability is much higher than if only organic components were used. Based on these studies, a wide range of blues and green hues were developed as well. The present invention has established a synthetic route that can be reproduced based on the instrumental analysis that have established the chemical interactions necessary for a stable reproducible paint. This invention has led to a fundamental understanding of the complex chemical interaction between indigo derivatives and palygorskite or other types of clays.

If one wishes to reproduce a "color" that resembles another color, there are many limitations on how the two could be compared. The concept of color is only accurate if one considers that color does not exist independently of normal color vision. Spectroscopic analyses such as UV/Visible are unavailing considering that certain indigo derivatives are practically insoluble in aqueous acids and aqueous alkaline solutions. Indigo derivatives are soluble in some non-polar solvents but only in the concentration range of 10^{-5} -10^{-6} mol/L. Heating a mixture of an indigo derivative and palygorskite may indeed produce a color that 'looks' like the organic/inorganic complex seen at so many archaeological sites. But in the absence of knowing

the precise quantity, conditions, and binding agents that the Maya used, the reproductions described in the literature could only be analyzed by an aesthetic visual comparison and represent different chemical techniques for producing a Maya Blue "type" organic/inorganic paint powder. The various shades of organic/inorganic complex that the inventors produced as a function of altering the concentration of indigo derivatives and the pH of the solution are shown in FIG. 1.

Early attempts at recreating Maya blue were made by first reducing indigo with sodium hydrosulfite, as shown in FIG. 1, then contacting it with clay and exposing the mixture to air (14). It was also found that heating the paint pigments at moderate temperatures caused the treated pigments to become stable to hot concentrated mineral acids, stable to acetone extraction, and stable to color change when exposed to heat (250°C) (13, 14).

Heat is introduced to the sample to dramatically increase the stability and can be used to alter the color. Both the temperature and the duration of heating affect the stability and color of the final paint composition. Heating may be done in an oven, or by other means of raising the temperature to the desired setting. The temperature should be between 100°C and 300°C as the paint composition starts to decompose above this point. More preferentially, the heating temperature should be between 100°C and 200°C or between 115°C and 150°C. The duration the sample is heated can also be varied, depending upon the requirements for the particular application. The heat may be applied for up to several hours, 1 day, 2 days, 3 days or up to 4 days.

The paint composition produced in this manner is resistant to decomposition by light. This means that, when exposed to strong sunlight or other light sources as is common for painted surfaces, the composition will not noticeably change in color and the intensity, as measured by IR spectroscopy or x-ray diffraction, and will not decrease more than 10% over a 1 year period. The composition is also resistant to decomposition by acids, alkalis, and solvents. When exposed to acidic or basic solutions, the composition will not noticeably change in color and the intensity, as measured by IR spectroscopy or x-ray diffraction, will not decrease more than 10% over a 1 year period.

V. General Method for Producing Color Composition

The general method for producing a color composition comprises of (a) providing a molecular derivative of indigo or any cationic organic dye or cationic pigment. The derivative of indigo can be selected from any indigo derivative shown in Scheme 1. The amount of dye or pigment used can be in the range of 0.01%, 0.02%, 0.03%, 0.04%, 0.05%, 0.06%, 0.07%, 0.08%, 0.09%, 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1.0%, 2.0%, 3.0%, 4.0%, 5.0%, 6.0%, 7.0%, 8.0%, 9.0%, 10.0%, 11.0%, 12.0%, 13.0%, 14.0%, 15.0%, 16.0%, 17.0%, 18.0%, 19.0%, or 20.0% by weight or more preferably 0.1% to 7% by weight or ideally at about 6% by weight.

The next step (b) can consist of combining the molecular derivative of indigo with an appropriate weight of fibrous clay, such as a palygorskite clay, a sepiolite clay, or a mixture of a palygorskite and a sepiolite clay, or a layered clay, such as a kaolinite, bentonite, nontronite, or mordenite clay to form a color composition. Step (b) further comprises the grinding of the dye or pigment with the layered or fibrous clay which can be carried out in, but not limited to, a blender, industrial blender, industrial mixer, shear blender, or a precise solid state blender. The clay and the dye may be ground separately and then ground together or they may be combined and ground to both mix the two components in order to obtain the preferred particle size. If the clay is already at the preferred size, the clay and indigo may be mixed together without grinding. Techniques for grinding and blending the dye and clay compositions are found in *Mixing of Solids* (32), *Powder and Bulk Solids Handling Processes* (6), or *Bulk Solids Mixing* (5). De-ionized water may be added during blending to attain a homogenized mixture. The clay or clay mixture should be ground to obtain particles of between about 0.005 μm and 50 μm, 0.01 μm and 20 μm, 0.05 μm and 10 μm, or more particularly between about 0.1 μm and 2 μm. A range of particles sizes is expected, but over 60% or over 80% or over 90% or over 95% or over 99% of the particles should be the desired size. For example, when the particles are ground to about 2.0 μm, 80% of the particles should be between 1.7 μm and 2.3 μm.

The next step comprises (c) heating the color composition. The heating may comprise heating at a temperature of 100°C, 110°C, 115°C, 120°C, 125°C, 130°C, 135°C, 140°C, 145°C, 150°C, 155°C, 160°C, 165°C, 170°C, 175°C, 180°C, 185°C, 190°C, 195°C, 200°C, 205°C, 210°C, 215°C, 220°C, 225°C, 230°C, 235°C, 240°C, 245°C, 250°C, 255°C, 260°C, 265°C, 270°C, 275°C, 280°C, 285°C, 290°C, 295°C or 300°C, or more particularly between 115°C and

150°C. The heating may be for several hours, 1 day, 2 days, 3 days, or may last up to four days. The heating can be carried out in, but not limited to, a batch oven, a drying oven, an infrared oven, or a powder coating oven.

Next the pH of the color composition may be adjusted to an acidic or neutral pH, depending on the final color desired. Exemplary examples of the acid used to adjust the pH comprise: any protonic acid, H_2SO_4, $HClO_4$, $HClO_3$, H_3PO_4, HNO_3, HCN, HF, HBr, HI, H_3O^+, or CH_3COOH, or more preferably HCl. Exemplary examples of the base used to adjust the pH comprise: LiOH, NaOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$ or more preferably NaOH. The pH of the color composition can be 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12. The pH of the system can be monitored with a pH meter that is calibrated with buffers of pH 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12.

Additional steps in making the color composition may comprise: treating the color composition with acid such as but not limited to any protonic acid, H_2SO_4, $HClO_4$, $HClO_3$, H_3PO_4, HNO_3, HCN, HF, HBr, HI, H_3O^+, or CH_3COOH, or more preferably HCl, to remove impurities from the clay; applying the color composition to a surface; blending the color composition with a polymer, plastic or organic binder as discussed in *Encyclopedia of Polymer Science and Engineering, 2nd ed.* (11) and *Paint and Surface Coatings: Theory and Practice, 2nd ed.* (8).

The following patents are included as examples to demonstrate certain embodiments of the invention. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention. Patent 3,950,180 covers the method of manufacturing color compositions that include zeolite and montmorillonite. Patent 5,061,290 covers the method of using indigo derivatives as a dyeing agent. Patent 4,246,036 covers the method of manufacturing color compositions that are comprised of asbestos-cement. Patent 4,640,862 covers color compositions that are used for coating an expanded polystyrene "drop-out" ceiling tile. Patent 4,868,018 covers color compositions that are used with a mixture of epoxy resin, epoxy resin hardener, and portland cement to form a coating which can be applied to a surface to form simulated marble products. Patent 4,874,433 covers a method for encapsulating color compositions in and/or to a zeolite. Patent 5,574,081 covers a method of manufacturing waterborne clay-containing emulsion paints

with improved application performance using color compositions. Patent 5,972,049 covers the method of manufacturing and using color compositions to form dye carriers used in the dyeing process for hydrophobic textiles. Patent 5,993,920 covers the method of manufacturing and using color compositions with stone powder and/or cement powder, fine sawdust and/or the heart of a kaoliang stalk and other materials to form an incombustible artificial marble. Patent 6,339,084 covers the method of manufacturing thiazine-indigo pigments. Patent 6,402,826 covers the method and manufacturing of color compositions for paper coating.

As used herein, the term "organic/inorganic complex" refers to a complexation of one or more organic molecules with one or more inorganic molecules. As used herein the term "color composition" refers to a pigment or dye complexed to a fibrous or a layered clay. As used herein, the term "coating composition" is synonymous with "color composition" and "paint powder". As used herein, the term "cement" refers to Portland cement types I, II, III, IV, IA, IIA, IIIA or as covered in *The Chemistry of Portland Cement, 2nd ed.* (2); or any cement type discussed in the Dictionary of Cement Manufacture & Technology Zement Woerterbuch (1). The chemistry of cements use in the present invention is covered in *The Chemistry of Cements*, 2nd volume (29). As used herein, the term clay refers to a fibrous clay, such as, but not limited to, a palygorskite or a sepiolite clay or a layered clay, such as, but not limited to, kaolinite, bentonite, nontronite, or mordenite clay.

As used herein, the term "about" means within 25% of the stated value, or more preferentially within 15% of the value. As used herein the specification, "a" or "an" may mean one or more. As used herein in the claim(s), when used in conjunction with the word "comprising", the words "a" or "an" may mean one or more than one. As used herein "another" may mean at least a second or more.

VI. Examples

The following examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventor to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate

that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

PROPHETIC EXAMPLE 1

Indigo Derivatives Concentration Experiments

A 0.05 g sample of indigo derivatives (from BASF) was suspended in ~50 ml of water. Sodium hydrosulfite, 0.03 g, and 15 drops of 1 M NaOH were added to the solution to reduce the indigo derivative. The solution was heated to 90°C while stirring with a magnetic stirrer. The solution remained blue, at which point an additional 0.1 g of sodium hydrosulfite was added. The solution turned clear indicating that the indigo derivative had been reduced and was now soluble. The leucoindigo derivative was then poured over 5 g of palygorskite clay, and was stirred. Immediately upon contact with the clay and being exposed to air, the solution turned dark blue. The solution was placed in the oven at 125°C for four days, at which point it resembled the color of organic/inorganic complex. The hue was slightly lighter and less intense than that of original organic/inorganic complex; hence, a series of clay pigments were prepared with various concentrations to examine color differences as a function of the concentration of indigo derivative. Additionally, it was determined, as has been cited in the literature, that it was not necessary to reduce the indigo derivatives prior to blending it with the clay. Thus, the rest of the synthetic organic/inorganic complex samples were prepared without reducing the indigo derivatives first.

Preparing a series of organic/inorganic complex samples with varying concentrations was accomplished by grinding a 0.01 g, 0.02 g, 0.03 g, 0.04 g, and 0.05 g of indigo derivatives with 5.00 g of palygorskite clay, respectively. Each concentration series was then placed in a blender with 100 ml of de-ionized water and blended for several minutes to ensure that a homogenous mixture was obtained. The corresponding solutions were placed in a 250 ml beaker in the oven at 125°C for four days. It was confirmed by I.R. that a blue color could also be produced simply by grinding the indigo derivative and clay without water, provided the two were subsequently heated. For later studies, the simplest method of grinding was employed.

EXAMPLE 2

pH Experiments of Synthetic Organic/Inorganic Complex

Synthetic samples were prepared using either sodium hydroxide or sodium hydrochloride to prepare the samples in acidic or basic solution. For the pH studies, 0.1 g of indigo was ground with 5.0 g of clay four times to obtain four samples. To each ground mixture was added 100 ml DI water, and dropwise either 1 M NaOH, or 1 M HCl to obtain solutions with pH's of 4, 7, 9, and 11. The pH of the system was monitored with a pH meter that had been calibrated with buffers of pH 4, 7, and 11.

As shown in FIG. 1, the colors arranged horizontally, prepared with increasing concentrations of indigo, visually range from a pale bluish-green to a darker grayish blue-green. The variations of color seen in the vertical direction range from grayish blue-green under basic conditions to brighter, vibrant blues at neutral to acidic pH. Visually, the organic/inorganic complex prepared with the highest percentage (2%) of indigo derivatives under neutral pH conditions was closest in resembling the 'authentic' organic/inorganic complex.

EXAMPLE 3

Mixing of Organic/Inorganic Complex

Synthesis of organic/inorganic complex requires grinding or milling. It is known that under mechanical milling the fiber bundles can disaggregate and the ends become splayed. At the frayed ends, the bond strength of the tetrahedral layers is reduced such that the guest indigo molecule can enter the channel and pry apart the weaker layers to create a superlattice structure. Furthermore, as organic molecules interact with the clay surface there is a reorientation of the OH - groups which initiates the elastic deformation of the interlayer spacing, thus allowing penetration of the guest molecule. The inventors have solid state NMR and IR evidence of how the OH - groups on the palygorskite surface reorient during this process. This reorientation, or change in Si-O-Si bond angle is directly related to the adsorption of indigo derivative to the external surface.

EXAMPLE 4

Temperature Study of Indigo/Palygorskite

One interesting observation is that one can visually see the gradual color changes of the clay/indigo mixture while it is heated in the oven. To monitor these color changes and consequently, monitor the chemical interaction, a synthetic organic/inorganic complex was made as previously described. During the process the reaction was stopped at various temperatures. Initially, 0.3 g of indigo derivative was blended with 4.7 g of palygorskite. One gram of this mixture was placed in a vial. The remaining sample mixture was heated for 24 hours at 100°C at which point another gram was taken from the mixture and placed in a vial. The remaining mixture was heated an additional 24 hours at 140°C and then placed in a vial for later analyses. The clay samples, at 25°C, 100°C, and 140°C were analyzed using synchrotron x-ray diffraction, x-ray diffraction simulations and IR spectroscopy. A representation of the colors and hues of the starting materials and changes in the color and hue upon heating are shown in FIG. 3.

EXAMPLE 5

Synchrotron X-ray Diffraction of Synthetic Organic/Inorganic Complex

The palygorskite clay (Attagel) and organic/inorganic complex prepared at 25°C and 140°C were run at SSRL on beam line 2-1. The diffraction of indigo was simulated using Cerius 2. The resulting data were compared and are shown in FIG. 3. The diffraction pattern of the unheated mixture of clay and indigo (25°C) still has peaks due to the crystalline phase of indigo. Once the clay and indigo are heated together to make the 140°C sample, the indigo phase no longer gives diffraction peaks. Clearly, the crystal structure of indigo has been disrupted as a consequence of its binding to the clay surface.

EXAMPLE 6

Particle Size Experiment Example

Two indigo derivative samples (0.05 g each) were separately ground in a blender with 4.7 g of palygorskite clay. One of the clay samples was 0.1 μm in size and the other was 2 μm in particle size. Each mixture was heated to 125°C for three days. The sample prepared with the 2 μm particle size clay had a darker green hue. The sample prepared with the 0.1 μm size clay had a darker blue hue.

EXAMPLE 7

Other Dye/Pigment Systems

0.05 g of thioindigo was ground with palygorskite and heated in the oven for three days at 125°C. A remarkable color change (from magenta red to royal blue) was observed during the heating process. Other dyes also may be used in this manner.

EXAMPLE 8

Cationic Organic/Inorganic Complexes

Several cationic dyes were reacted with the palygorskite clay. Each dye (0.1g each) was separately ground in a blender with 4.9 g of palygorskite clay and 100mL of water. The mixtures were then placed in the oven at 125oC until the water evaporated. The samples were ground in a mortar and pestle and then any excess dye that was not bound to the clay was extracted with water or an appropriate solvent. For the cationic complexes, no changes in color were observed because the binding mechanism does not involve electron charge transfer, as is the case with neutral molecules. Infrared analysis following excess dye extraction was used to analyze the final clay/cationic dye complex (FIGS. 4 and 5). The list of successfully employed cationic dyes includes crystal violet, aniline blue, methylene blue, victoria blue R, malachite green oxalate, methylene green, neutral red, quinoldine red, alpahazurine A, janus green B, ethyl violet. The compounds have the general structure:

Clay Surface—$O^-H^+ + R^+X^-$ reacts to give: Clay surface—$O^-R^+ + H^+X^-$

* * * * * * * * * * * * * * * *

All of the methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the invention. More specifically, it will be apparent that certain agents which are both chemically and physiologically related may be substituted for the agents described herein while the same or similar results would be achieved. All such similar substitutes and modifications

apparent to those skilled in the art are deemed to be within the spirit, scope and concept of the invention as defined by the appended claims.

REFERENCES

The following references, to the extent that they provide exemplary procedural or other details supplementary to those set forth herein, are specifically incorporated herein by reference:

1. Amerongen, C.V. *Dictionary of Cement Manufacture & Technology Zement Woerterbuch* French & European Pubns., October 1, 1986.
2. Bogue, R. H. *The Chemistry of Portland Cement, 2d ed.* New York: Reinhold Publishing Corp, 1955.
3. Gettens, R. J. *Amer. Antiquity* 27, 557-564, 1962.
4. Gettens, R. J., Stout, G. L. *Painting Materials: A Short Encyclopedia* D. van Nostrand, New York, N.Y., 1946.
5. Gyenis, J., Gyenis. J. *Bulk Solids Mixing* Imperial College Press, 1999.
6. Iinoya, K., Masuda, H., Watanabe, K. *Powder and Bulk Solids Handling Processes* Marcel Dekker, July 1, 1988.
7. Josè-Yacamán, M., Rendón L., Arenas, J., Carmen, J., Puche, M. C. S. "Maya Blue Organic / inorganic Complex Paint: An Ancient Nanostructured Material" *Science* Vol. 273, 223-225, 1996.
8. Lambourne, R., Strivens, T.A. *Paint and Surface Coatings: Theory and Practice*, 2nd ed. William Andrew, 1999.
9. Littman, E. R. *Amer. Antiquity* 45, 87-101, 1980.
10. Littman, E. R., *Amer. Antiquity* 47, 404-408, 1982.
11. Herman, M.F., *Encyclopedia of Polymer Science and Engineering*, 2nd ed. John Wiley & Sons, 1990.
12. Mindess, S., and Young, J. F. *Concrete* Englewood Cliffs, N.J.: Prentice-Hall, Inc., 1981.

13. Olphen, Van H. *Science* 154, 645-646, 1966a.

14. Olphen, Van H. *American Antiquity* 645-646, 1966b.

15. U.S. Patent 3,950,180

16. U.S. Patent 5,061,290

17. U.S. Patent 4,246,036

18. U.S. Patent 4,640,862

19. U.S. Patent 4,868,018

20. U.S. Patent 4,874,433

21. U.S. Patent 5,574,081

22. U.S. Patent 5,972,049

23. U.S. Patent 5,993,920

24. U.S. Patent 6,339,084

25. U.S. Patent 6,402,826

26. Ramachandran, V. S., and Feldman, R. F. *Cement Science, In Concrete Admixtures Handbook: Properties, science, and technology* Park Ridge, N.J.: Noyes Publications, 1-54, 1984.

27. *Scientific American Discovering Archaeology*, p.4, August 2000.

28. Shepard, A. O. *Amer. Antiquity* 27, 565-566, 1962.

29. Taylor, *The Chemistry of Cements,* 2 volumes, London: Academic Press W. F. W., ed. 1964.

30. Torres, L. *Maya Blue: How the Mayas Could Have Made the Pigment, Materials Research Society Symposium* Materials Research Society, 1988.

31. U.S. Department of Transportation, Federal Highway Administration, *Portland Cement Concrete Materials Manual* Report no. FHWA-Ed-89-006, Washington: FHWA, August, 1990.

32. Weinekotter, R., Gericke, H. *Mixing Of Solids* (Powder Technology Series, Number 12), Kluwer Academic Publishers, 2000.

33. Zollinger, H. *Color Chemistry*, 2nd ed., John Wiley & Son, 1991.

WHAT IS CLAIMED:

1. A coating composition comprising:

   a) a molecular derivative of indigo; and

   b) a fibrous or layered clay;

   wherein said coating composition is used for coloring surfaces.

2. The coating composition of claim 1, wherein the color/hue of said composition is determined by the concentration of said dye and pH of said composition.

3. The coating composition of claim 1, wherein the particle size of said coating composition is between 0.01 μm and 20 μm.

4. The coating composition of claim 3, wherein the particle size of said coating composition is between 0.1 μm and 2 μm.

5. The coating composition of claim 1, wherein said fibrous clay is a palygorskite clay, a sepiolite clay, or a mixture of a palygorskite and a sepiolite clay.

6. The coating composition of claim 1, wherein said layered clay is a kaolinite, bentonite, nontronite, or mordenite clay.

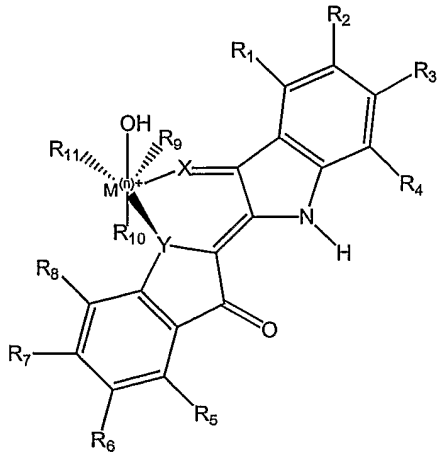
7. The coating composition of claim 1, wherein said molecular derivative of indigo is dibromoindigo or thioindigo.

8. The coating composition of claim 1, wherein the coating composition is a powder or a liquid.

9. The coating composition of claim 1, wherein said coating composition is resistant to decomposition by light.

10. The coating composition of claim 1, wherein said coating composition is resistant to decomposition by acids, alkalis, and solvents.

11. A composition comprising:



wherein:

R_1-R_8 are individually H, CH_3, CH_2CH_3, F, Cl, Br, I, CN, OH, SH, OCH_3 or OCH_2CH_3;

R_9-R_{11} are individually SiO_3, SiOH or H_2O;

Y is N, O, S, or Se;

X is O or S;

$M^{(n+)}$ is Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Pt, Pd or Zn; and n is 1, 2, 3 or 4.

12. A formulation comprising:

a) a molecular derivative of indigo;

b) a palygorskite clay, a sepiolite clay, or a mixture of a palygorskite and a sepiolite clay;

c) a polymer; and

d) an organic binding agent.

13. A formulation comprising:

a) a molecular derivative of indigo;

b) a palygorskite clay, a sepiolite clay, or a mixture of a palygorskite and a sepiolite clay; and

c) a gum arabic; a linseed oil; a copal; a polycarbonate; an egg

tempura; or a turpentine.

14. A shapeable molding material comprising:

a) a molecular derivative of indigo;
b) a palygorskite clay, a sepiolite clay, or a mixture of a palygorskite and a sepiolite clay; and
c) a cement, a plastics or a polymer.

15. A shapeable tile material comprising:

a) a molecular derivative of indigo;
b) a palygorskite clay, a sepiolite clay, or a mixture of a palygorskite and a sepiolite clay; and
c) a cement, a plastic or a polymer.

16. A method of producing a coating composition comprising:

a) obtaining a molecular derivative of indigo;
b) combining said molecular derivative of indigo with a fibrous or layered clay to form a coating composition;
c) heating said coating composition; and
d) adjusting the pH of the dye or pigment composition.

17. The method of claim 16, further comprising treatment of said coating composition with acid to remove impurities from the clay.

18. The method of claim 16, further comprising applying said coating composition to a surface.

19. The method of claim 16, further comprising blending said coating composition with a polymer or organic binder.

20. The method of claim 16, further comprising homogenizing said dye composition by blending, grinding, milling or stirring.

21. The method of claim 16, wherein said heating comprises heating at a temperature of between 100°C and 300°C.

22. The method of claim 21, wherein the temperature is between 115°C and 150°C.

23. The method of claim 16, wherein said heating lasts a maximum of four days.

24. The method of claim 16, wherein said coating composition contains water.

25. The method of claim 16, wherein said coating composition has a pH between 3 and 7.5.

26. The method of claim 16, wherein said coating composition contains a dye in the range of 0.01% to 20% by weight.

27. The method of claim 16, wherein said coating composition contains a molecular derivative of indigo in the range of 0.1% to 7% by weight.

28. The method of claim 16, wherein said coating composition contains a molecular derivative of indigo at about 6% by weight at neutral or acidic pH.

29. The method of claim 16, wherein said fibrous clay is a palygorskite clay, a sepiolite clay, or a mixture of a palygorskite and a sepiolite clay.

30. The method of claim 16, wherein said layered clay is a kaolinite, bentonite, nontronite, or mordenite clay.

31. The method of claim 16, wherein the particle size of said coating composition is between 0.01 μm and 20 μm.

32. The method of claim 31, wherein the particle size of said coating composition is between 0.1 μm and 2 μm.

33. The method of claim 16, wherein said molecular derivative of indigo is thioindigo or dibromoindigo.

34. The method of claim 16, further comprising adding a binding agent to said coating composition.

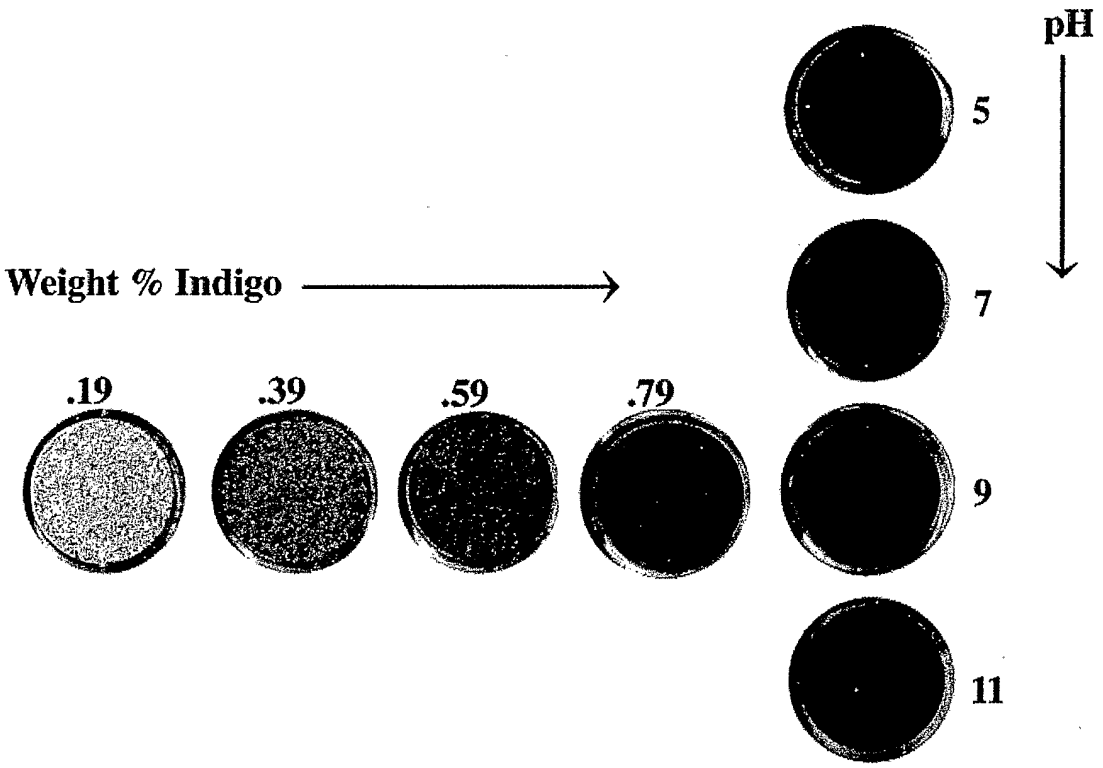


FIG. 1

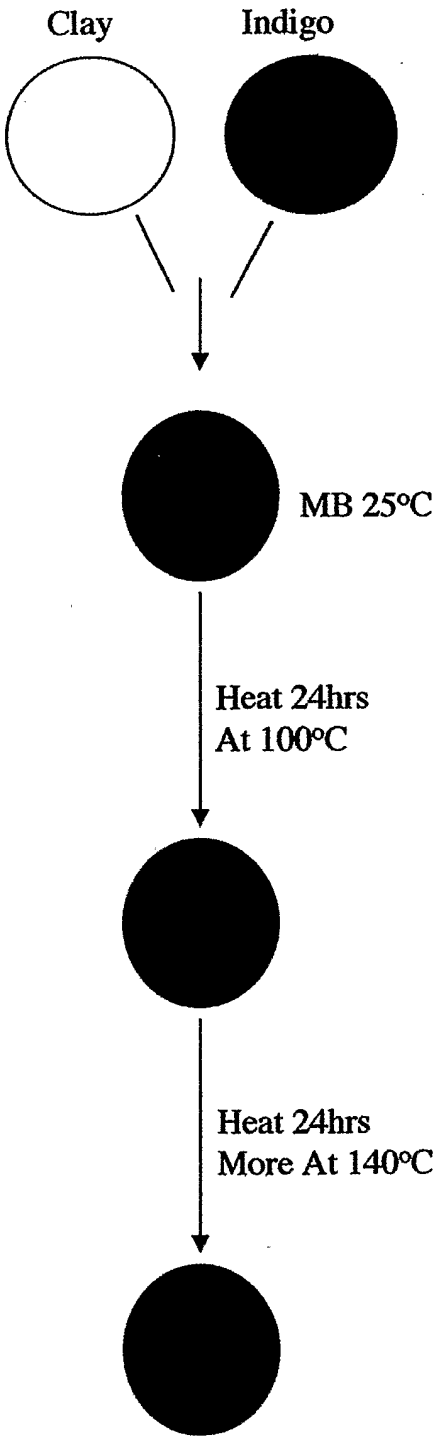


FIG. 2

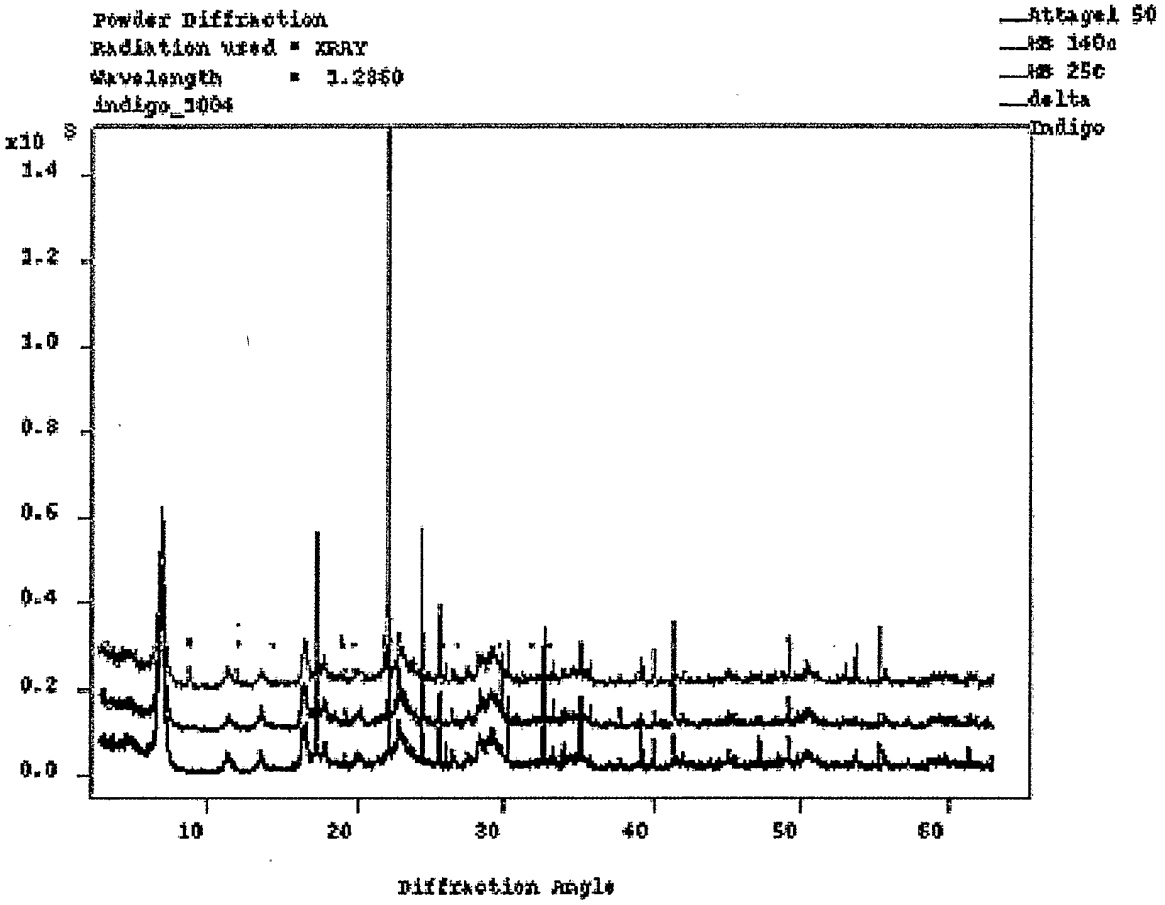

Powder Diffraction
Radiation Used = XRAY
Wavelength = 1.2350
Indigo_1004
Attagel 50
HB 140c
HB 25c
delta
Indigo
x10
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
10
20
30
40
50
60
Diffraction Angle

FIG. 3

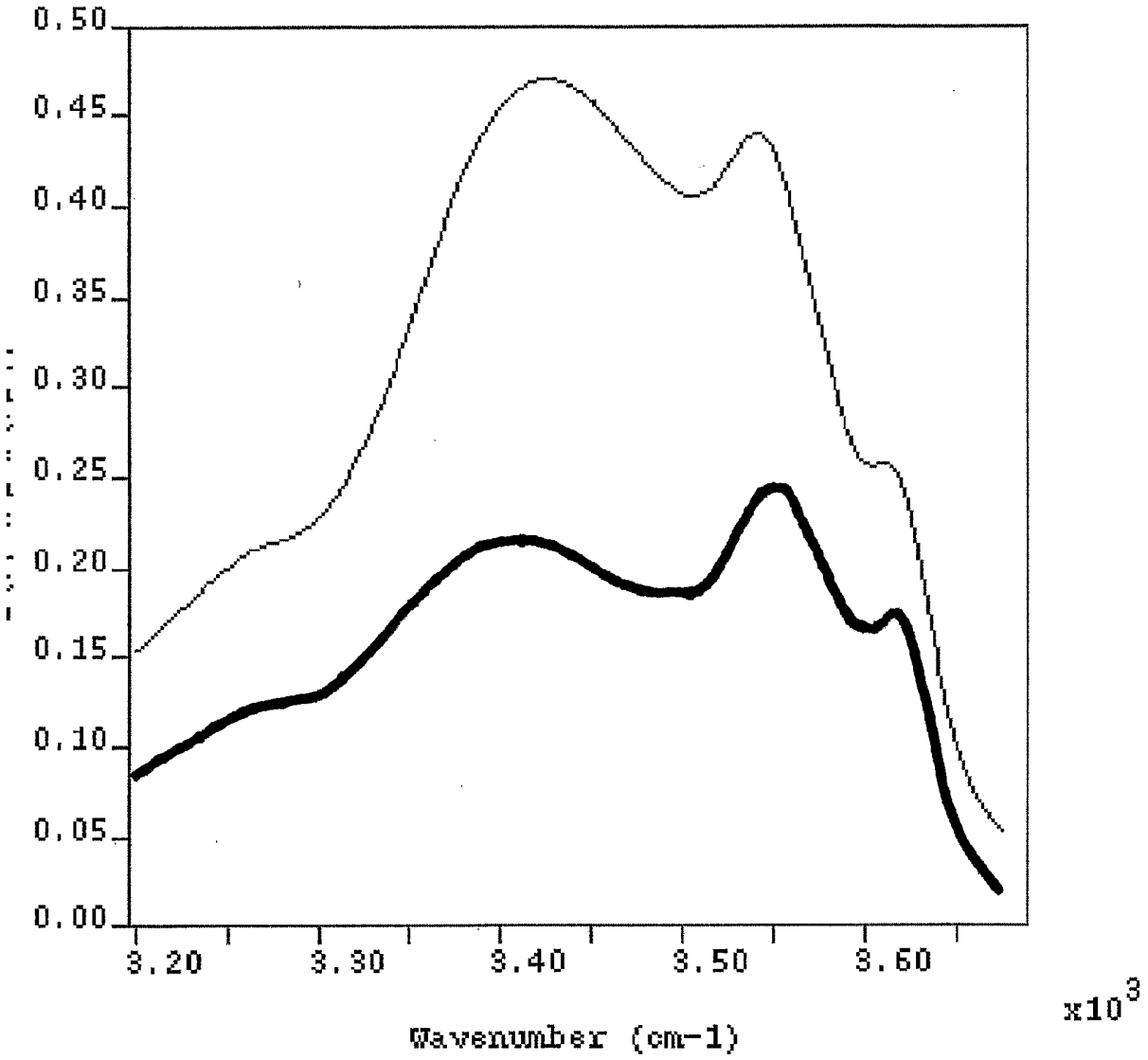

0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3.20
3.30
3.40
3.50
3.60
x10^3
Wavenumber (cm-1)

FIG. 4

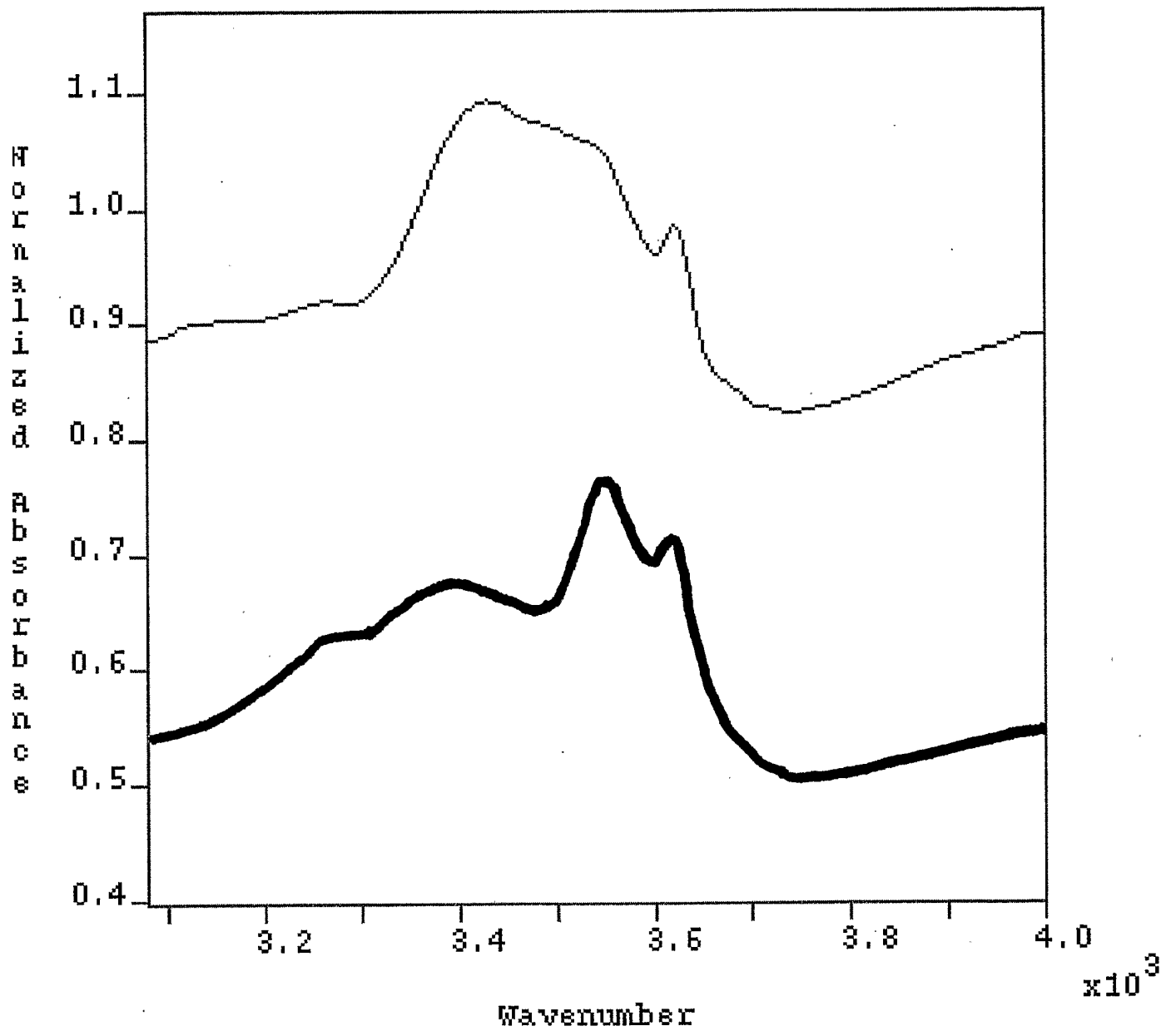

Normalized Absorbance
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
3.2
3.4
3.6
3.8
4.0
x10^3
Wavenumber

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US03/19273

A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) : C09B 7/00
US CL : 106/401, 487
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 106/401, 487

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 1,058,021 A (SCHMIDT) 01 April 1913.	1-10 & 12-34
A	US 2,940,928 A (DUPZYK et al.) 14 June 1960.	1-10 & 12-34
A	US 3,950,180 A (KATO) 13 April 1976.	1-10 & 12-34
A	US 5,972,049 A (WICKER, JR. et al.) 26 October 1999.	1-10 & 12-34
A	US 6,402,826 B1 (YUAN et al.) 11 June 2002.	1-10 & 12-34

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
20 October 2003 (20.10.2003)

Date of mailing of the international search report
12 NOV 2003

Name and mailing address of the ISA/US
Mail Stop PCT, Attn: ISA/US
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
Facsimile No. (703)305-3230

Authorized officer
Anthony J. Green
Telephone No. 703-308-0661

Jean Proctor
Paralegal Specialist

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

PCT/US03/19273

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claims 1-10 and 12-34, drawn to various coating compositions and a method for preparing the coating composition comprising a molecular derivative of indigo and a clay .

Group II, claim 11, drawn to a compound.

The inventions listed as Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Group II is drawn to a composition that does not require the particulars of Group I namely the addition of a clay material.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US03/19273

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
Please See Continuation Sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 1-10 and 12-34

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.