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(54) Title: NOVELTY COMPOSITIONS WITH COLOR CHANGING INDICATOR

(57) Abstract: Compositions and methods for producing novel paints, bubbles, markers and cosmetics are described.



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NOVELTY COMPOSITIONS WITH COLOR CHANGING INDICATOR

CROSS REFERENCE TO RELATED APPLICATIONS

[001] This application claims benefit under 35 U.S.C. § 119(e) to U.S. Serial Nos. 60/696,872, filed July 6, 2005 (Attorney docket number 186573/US), entitled "Color Changing Compositions and Articles", 60/711,183, filed August 25, 2005 (Attorney docket number 186978/US), entitled "Substituted Phenol-Based Aqueous Indicators" and 60/666,028, filed March 29, 2005 (Attorney docket number 186354/US), entitled "Color Adaptive Bubbles".

[002] The application also claims benefit under 35 U.S.C. § 119(e) to U.S. Serial Nos. 60/711,450, filed August 25, 2005 (Attorney docket number 186977/US), entitled "Mess Free Markers" and 60/727,608, filed October 18, 2005 (Attorney docket number 187054/US), entitled (Ph Sensitive Dyes for Use in Paints" and 60/734,150, filed November 7, 2005 (Attorney docket number 187220/US), entitled "Cosmetic Temporary Coloring Compositions Containing Dyes", the contents of which are incorporated herein by reference in their entirety.

FIELD OF THE INVENTION

[003] The invention relates generally to compositions that can change color from colored to colorless, one color to another color, or colorless to colored under appropriate conditions, and combinations thereof, and methods to prepare the compositions, such as bubbles, paints, cosmetics, markers and use of these compositions. Particularly, the present invention relates to compositions for general paint applications or, for finger paint applications, blowing bubbles, cosmetics and/or markers, which can be particularly useful for children. The compositions are non-toxic and, if necessary, are washable.

BACKGROUND OF THE INVENTION

[004] Paints are generally of two types. The first type is solvent borne (or oil based) paints in which a polymeric binder is dissolved or dispersed in an

organic solvent. The second type is water borne paints in which a polymeric binder is a dispersion of insoluble polymer in water. Water borne paints are often referred as 'emulsion paints' and these represent the most common type of wall and ceiling paints.

[005] Paint formulations generally comprise a film forming polymer, one or more type of non-film forming solids, such as titanium dioxide and the like, extenders, thickeners, and other additives such as leveling agents etc. The dispersed insoluble film forming polymers are usually vinyl, acrylic, epoxy, polyurethane, polyester, alkyds, glycidyl esters, glycidyl ethers etc.

[006] The non-film forming solids are generally colorants and/or titanium dioxide. The most commonly used colorants are pigments which can be either inorganic or organic pigments. Commercially available pigments are available the aggregates and agglomerates forms. Use of pigments in the paint composition often requires pigment dispersion mills for grinding the pigments. Pigments are generally ground to their primary particle size for uniformity before using them in the paints. The ground pigment formulations may flocculate back into agglomerates form which lowers the shelf life of the paints. Thus, the overall process increases the time/cost, and reduces the quality.

[007] Dyes are also used as colorants for paint formulations. Commonly used dyes are basic dyes and food dyes. The paint compositions based on either basic dyes or food dyes are not easily washable, especially, from porous and hard surfaces.

[008] Extenders are particulate non-film forming solids which are often added to paints to lower cost, to modify the rheology, or to improve pigment utilization by inhibiting pigment particle agglomeration. They differ from true pigments in having little or no effect on opacity.

[009] Thickeners are generally polymeric materials that, as name suggests, increase the viscosity of the paint. Thickeners vary widely in their chemical form, but can generally be described as water soluble or water swellable polymers having hydrophilic groups.

[010] Color change has been a fascination of individuals for a long time. Traditionally, compounds that have exhibited the ability to change from colored to colorless have been leuco dyes.

[011] Leuco dyes are of limited use to produce materials that begin as colored and end as colorless since three components are generally required to effect the transition. Generally, a color former (the leuco dye), a developer (such as a phenolic compound) and a reversible matrix, such as a long chain alcohol, are combined. An often noted drawback with leuco dye systems is their water insolubility.

[012] Traditional painting materials, provide specific color to the substrate. A drawback with traditional painting materials is that they do not change color when required, tend to be messy and leave unwanted marks. Thus parents often limit the use of painting materials, especially finger painting materials because of the possibility of household objects, such as carpet, furniture, skin and clothing, being stained by the finger painting materials. The unwanted marks are usually extremely difficult or impossible to remove.

[013] Accordingly, many manufactures and inventors have spent great time and resources trying to create products and methods to reduce or eliminate staining. They have also spent a great deal of effort to produce products that simulate marking. However, such products have not offered the creative freedom and flexibility of traditional finger painting materials. Most of the commercial finger painting materials labeled "washable" have been found to be difficult or impossible, for example, to remove from fingers, hands or cloths. The traditional paints or finger paints generally do not change color, nor are they completely washable, often leaving residue or stain.

[014] Bubbles have long fascinated children, adults, and scientists alike. The formation of bubbles for recreation and entertainment is a well-recognized and widely practiced past-time. In its simplest form, bubble blowing involves dipping a shaped article having an opening into a liquid soap solution followed by blowing into the opening to form one or more bubbles. A bubble is generally defined as a small volume of gas contained within a thin liquid spherical envelop.

A wand, for example, is generally immersed into a bubble solution and air is blown through spherical opening to generate bubbles. Surface tension causes the bubble solution to form a film across the opening. Upon application of a sufficient force or pressure upon one side of the film, a bubble is formed and expelled from the opening.

[015] A variety of bubble solutions have been marketed over the years, many of them claiming to have special features like longer lasting bubbles, solutions that produce greater numbers of bubbles, or solution that provide bubbles having a colorful in appearance. Some manufacturers adorn their bubble packaging with illustrations of colored bubbles, or add colorants to tint their bubble solution, in an effort to provoke the illusion of a colored bubble. Some manufactures have added modifying agents like glycerin to produce a transparent bubble with a transparent iridescent rainbow effect. One manufacturer added color directly to the bubble and/or the bubble solution in an effort to create designs on a piece of paper with what they labeled a colored bubble. This composition of liquid solution does not produce a visually colored bubble, but rather a bubble that is used as a vehicle to transport the color to the marking surface. The bubble wall is transparent and does not produce a uniformly colored bubble. Rather the color runs to the bottom of the bubble wall. Others manufacturers claim to produce bubble that is illuminated when viewed in the dark with infrared radiation or black light, but transparent in regular light.

[016] Additionally, the aqueous solutions that are currently provided by manufacturers afford bubbles that do not withstand environmental stresses, such as wind, airborne particulate, or contact with a surface, among many other physically detrimental impediments. Contact with a surface generally causes the bubble to burst, decreasing the enjoyment one obtains from experiencing the bubble.

[017] Traditional marking materials, such as paints, markers, pens, spray-paint, chalk, lipstick, and doll cosmetics, are given to children for drawing, painting, decorating, styling and coloring purposes. A drawback with traditional marking materials is that they tend to be messy and leave unwanted marks. Thus

parents often limit the use of marking materials because of the possibility of household objects, such as carpet, furniture, skin and clothing, being stained by the marking materials. The unwanted marks are usually extremely difficult or impossible to remove. Accordingly, many manufactures and inventors have spent great time and money trying to create products and methods to reduce or eliminate staining. They have also spent an equal amount of effort to produce products that simulate marking but do not offer the creative freedom and flexibility of traditional marking materials. Most of the commercial marking materials labeled "washable" have been found to be difficult or impossible, for example, to remove from simple cotton t-shirts.

[018] Cosmetics are generally applied to an area to affect a change in color, tone, appearance, suppleness, or other visible attributes. Generally, the application lasts for many hours, a day, or in the case of hair color, weeks or months. For children, it would be fun to have cosmetics that provide the desired change but do not last for a lengthy period of time.

[019] Therefore, a need exists for new compositions that can provide one or more of: a change in color (or to colorless), water washable, do not leave a stain or residue, provide a wide range of color across the color spectrum, are water soluble, can be easily prepared in high yields with a simple procedure, and are non-toxic.

BRIEF SUMMARY OF THE INVENTION

[020] The present invention provides unique phthalein acid-base compositions as detailed throughout the specification that are useful in paints, bubbles, markers and cosmetics. These phthalein acid-base compositions are previously unknown and can be used in any of the above-identified applications (and those listed throughout the specification). The phthalein compositions provide novel colors, previously not achievable by known synthetic procedures. Additionally, the colored phthalein compositions of the invention can be made to change to colorless, a first color to a second color, or colorless to a color under appropriate conditions.

[021] In one embodiment, the present invention provides an aqueous composition that includes a surfactant and an acid-base indicator. The compositions provide a composition, such as a bubble, that is a uniformly colored composition. Alternatively, the uniformly colored composition can change to colorless under appropriate conditions. The compositions are non-toxic and/or washable.

[022] Prior to the present invention, it was generally considered extremely difficult if not impossible to make a broad spectrum of colored phthalein compositions which provide the entire spectrum of colors from yellow, orange, red, pink, magenta, purple, violet, blue, green and black. Additionally, preparation of phthaleins, up until the present invention did not generally provide high yield, high purity phthaleins by a simple process.

[023] Up until the present invention, there also existed a need to develop color changing systems which were non-toxic and washable. Food dyes are non-toxic but do not change color and leave stains and are thus not washable. Most known dyes/pigments generate stains and leave residue or spots on the substrates. Therefore, the present invention provides phthaleins and compositions thereof that develop a color and which can be easily washable from skin, fabric, leather, hard/porous surfaces such as stones, brick, concrete, and wood (finished/unfinished).

[024] The present invention overcomes some of the disadvantages of known dyes and pigments by providing color compositions which can change color and can provide the spectrum of colors from yellow, orange, red, pink, magenta, purple, violet, blue, green and black.

[025] The present invention therefore provides paint systems, compositions, and methods to use the compositions for the permanent or temporary painting (color change) of intended surfaces with the ability to remove color from unintended surfaces, which can be particularly useful for children.

[026] The present invention provides paint systems which include acid-base indicator dyes compositions that can change color from colored to colorless, one color to another color, or colorless to a colored under appropriate conditions,

and can further include a substrate which includes a treated surface. For example, application of paint to a treated surface produces color that will not fade with exposure to air. Conversely, application of the composition to non-treated substrates produce a painted mark whose color will fade with pressure, water, or extended exposure to air. Little or no colored paint composition will remain after pressure, water, or extended exposure to air on untreated substrates such as skin, clothing, carpeting, walls, finished or unfinished wood, stones, bricks or other household surfaces.

[027] Paint systems of the present inventions can be applied with the use of various devices known in the art such as, brushes, felt-type writing instruments, wick-type writing instruments, by means of spatulas, and also with the fingers (finger paints). Paint compositions of the present invention are usually present either in a low viscosity state, a high viscosity state or in a pasty state.

[028] In particular, the present invention provides a painting system for general paint application and finger paint application.

[029] In one aspect, the present invention provides a painting system that can be easily washable and is also non-toxic.

[030] One or more additives, such as, for example, surface-active agents, antioxidants, buffers, basics, or glycerin, humectants, rheology-controlling agents, defoaming agents, ultraviolet absorbers, photostabilizers, curing agents, preservatives can be included in the paint systems.

[031] In one aspect of the invention, a treated surface of a substrate useful with the acid-base dye composition in the paint has a coating which has a material that is alkaline. The alkalinity of the treated surface interacts with the acid-base indicator dye(s) deposited by the paint to retain visible color on the treated surface. The composition can also include a binder for retaining the alkaline components on the substrate. For example, as a child or other user applies the painting composition to the treated surface, the color will remain on the surface and will not easily fade with exposure to air, pressure or water. In addition to retaining its color, the color is not easily transferred from the substrate. The present invention inhibits the permanent development of color marks on non-

treated surfaces like skin, clothing, or other unintended surfaces, since most surfaces are not alkaline. If, however, undesired stains are developed on household surfaces or other unintended surfaces, such stains can be readily removed via washing. The acid-base indicators are freely soluble in water, thus can be easily removed via washing.

[032] Typically the treated surface of a suitable substrate is coated with a chemical that imparts a desired pH to the surface or throughout the substrate. In one example, the substrate includes paper. In one embodiment, the pH of the treated surface, i.e., paper, can be acidic (a pH between 0 and about 7). In another embodiment, the pH of the paper is above 7, and in particular about 8.8.

[033] In one aspect, the bases useful with the paint systems of the invention are water soluble, non-toxic, and non-flammable. Many materials are weak bases due to the presence of an amino group ($-NH_2$) attached to an organic compound. Ammonia (water), dimethylamine, diethylamine, ethylamine, glycine and hydrazine, methylamine, trimethylamine, alanine, triethanolamine are examples of weak bases. Other examples of bases include alkali and alkaline hydroxides, such as sodium hydroxide, potassium hydroxide, rubidium hydroxide, cesium hydroxide, magnesium hydroxide, calcium hydroxide, strontium hydroxide, and barium hydroxide. The base can be impregnated throughout the substrate/surface or simply on the surface.

[034] The present invention surprisingly provides color changing, color disappearing bubble compositions, that have a uniform coloration about the bubble. Additionally, the present invention provides compositions that have film forming capabilities such that the resultant bubble can withstand physical contact with a surface. The film formed bubble can be colored, have a color changing composition, or can be without color.

[035] In one embodiment, the present invention provides an aqueous composition that includes a surfactant and a colorant. The compositions provide a bubble that begins as a uniformly colored bubble, but then changes coloration or the coloration disappears within a few seconds to within a few minutes. Suitable colorants include acid-base indicators, leuco dyes and/or metal salts. When a

leuco dye is included in the composition, an electron accepting compound or oxidizing agent is generally included. The compositions are non-toxic and/or washable, if necessary.

[036] In another embodiment, the present invention provides compositions that provide film forming bubbles. The film forming compositions include a film forming resin and, optionally, a colorant as described herein. Generally the film forming resin is a polymeric material that can form a film about the surface of the bubble, such that the resultant bubble can withstand contact with a surface. The film forming compositions can be adapted to provide substantially colorless bubbles, uniformly colored, or color changing bubbles. The compositions are non-toxic and/or washable, if necessary.

[037] In still another embodiment, the present invention provides methods to prepare compositions that provide the various bubble producing solutions used throughout the present specification.

[038] In still yet another embodiment, the present invention provides kits that include the compositions of the invention and instructions how to prepare bubbles from the compositions.

[039] The present invention provides marking systems, compositions, a methods to use the compositions that allow for the permanent marking of intended surfaces and the removal of color from unintended surfaces, which can be particularly useful for children.

[040] The present invention provides marking systems which includes acid-base indicator dyes compositions that can change color from a first color to colorless, a first color to a second color, or colorless to a color under appropriate conditions, and may or may not include a substrate which includes a treated surface. Writing with the marking instrument on the treated surface of the treated substrate produces color that will not fade with exposure to air. Application of the compositions to non-treated substrates produce a mark that's color will fade with pressure, water, or extended exposure to air. Little or no color mark will remain after pressure, water, or extended exposure to air on untreated substrates such as skin, clothing, carpeting, walls or other household surfaces.

[041] The marking instrument can be in any of a number of different forms, including a marker, pencil, crayon, spray-paint, chalk, nail polish, make-up compact, squirt gun, hair dye, lipstick, finger paint, splatter art, spray chalk, glue, cosmetics, paint, doll cosmetics, drawing, painting, decorating, styling and coloring purposes or the like. One or more additives, such as, for example, surfactants, antioxidants, buffers, basics, or glycerin, humectants, preservatives can be included in the marking composition.

[042] The treated surface of the substrate useful with the acid-base dye composition in the marker has a coating which has a material that is alkaline. The alkalinity operates chemically with the acid-base indicator dyes deposited by the marker to hold visible color on the surface of the treated surface. The coating can also include a binder for retaining the alkaline components on the substrate. As a child or other user applies the marking composition to the treated substrate surface, the color will remain on the surface and not easily fade with exposure to air, pressure or water. In addition to retaining its color, the color is not easily transferred from the substrate. The present invention inhibits the permanent development of color marks on non-treated surfaces like skin, clothing, or other unintended surfaces, since most surfaces are not alkaline. If, however, undesired stains are developed on household surfaces or other unintended surfaces, such stains can be readily removed via washing.

[043] Typically the substrate coating comprises a chemical that can effect the pH of the paper. In one instance, the pH of the paper could be acidic (a pH between 0 and about 7). Ideally, the pH of the paper is above 7, and in particular about 8.8.

[044] In one aspect, the bases are water soluble, non-toxic, and non-flammable. Many materials are weak bases due to the presence of an amino group (-NH₂) attached to an organic compound. Alanine, ammonia (water), dimethylamine, ethylamine, glycine and hydrazine, methylamine, trimethylamine, alanine are examples of weak bases. Other examples of bases include alkali and alkaline hydroxides, such as sodium hydroxide, potassium hydroxide, rubidium hydroxide, cesium hydroxide, magnesium hydroxide,

calcium hydroxide, strontium hydroxide, and barium hydroxide. The base can be impregnated throughout the paper or on the surface of the paper.

[045] The present invention also relates to cosmetic temporary coloring compositions which contain, as an active ingredient, at least one colorant, such as an acid-base indicator as described *vide infra*. The cosmetics include traditional facial cosmetics as well as hair care products.

[046] The present invention also relates to colored fog, colored squirt gun ammo, disappearing inks, disappearing messages, fake blood, secret messages that appear and disappear, splat ball ammo, hairspray highlights arts/crafts (bath tub foam, bath tub paint, bath tub tints, body/face paints, dry erase markers, finger paints, glue sticks, lawn paints, liquid glue, no-mess markers, pencils, sidewalk paint, sidewalk spray chalk, sidewalk stick chalk, splatter art, spray mount, stamp pads, temporary marker for sewing, temporary tattoos, water color paint) or entertainment (temporary field/golf course marking) colored compositions which contain, as an active ingredient, at least one colorant, such as an acid-base indicator as described *vide infra*.

[047] While multiple embodiments are disclosed, still other embodiments of the present invention will become apparent to those skilled in the art from the following detailed description. As will be apparent, the invention is capable of modifications in various obvious aspects, all without departing from the spirit and scope of the present invention. Accordingly, the detailed descriptions are to be regarded as illustrative in nature and not restrictive.

DETAILED DESCRIPTION

[048] Paint Applications

[049] Prior to the present invention, it was generally considered extremely difficult if not impossible to make color changing paint compositions. The present invention overcomes the drawbacks associated with paints and finger paints, especially for color change, washability and toxicity.

[050] Traditionally, paint compositions comprise a film forming polymer (a binder) which can be either an alkyd, vinyl, acrylic, epoxy, polyurethane, polyester, glycidyl esters, glycidyl ethers, one or more types of a non-film-forming solid which can be inorganic/organic pigments such as titanium oxide (dioxide), basic/food dyes, extenders, thickeners, and additives etc. These traditional paint compositions provide a specific color to the substrate and are not easily removed once dried, and thus leave residue/marks/stains on the painted surface.

[051] Children enjoy various finger painting colors, but most of the commercially available finger painting systems are not completely washable (removable), even though some are claimed as “washable”. The finger painting systems in the market thus leave stains/marks/residue on fingers, skin and cloths.

[052] Prior to the present invention, it has proven extremely difficult, if not impossible, to develop color changing paint compositions. The present invention surprisingly provides color changing paint compositions and methods to make and use the compositions. The present invention also provides color changing paint compositions that can be used for any type of paint applications and finger paints applications.

[053] The present invention, therefore, provides paint systems that advantageously minimize or eliminate messiness, i.e., inadvertent or stray marks, during use. The painting systems of the present invention comprise a composition composed of (A) an aqueous solution, that can include one or more organic solvent(s); (B) a coloring agent which is an acid-base indicator(s) as described herein, that changes color from colored to colorless, one color to another color, or colorless to colored under appropriate conditions; (C) a film forming agent/thickener, also known as a “binder”; optionally (D) one or more surface active agents (E); and/or, optionally, additives such as a preservative and/or a pigment, clay, etc. such as titanium dioxide.

[054] In certain embodiments, the paint composition includes a pigment, such as titanium dioxide, a clay, talc, calcium carbonate, mica and those known in the art. Pigments generally act as fillers and provide “hiding” capabilities for the

underlying color of the substrate. Pigments can also provide one or more of the following: UV protection, corrosion resistance, mildew resistance, stain resistance, weather resistance, prevents moisture permeability, helps promote adhesion and/or strength.

[055] Pigments can be inorganic or organic and can provide coloring to a paint. Suitable inorganic pigments can be white (e.g., titanium dioxide, Pigment White 6), colored or black. Titanium dioxide is generally available as rutile or anatase.

[056] Rutile titanium dioxide is used decorative paints, maintenance and industrial gloss finishes; decorative semi-gloss, eggshell and matt finishes; marine paints; undercoats; and emulsion paints for interior and exterior use. Anatase titanium dioxide used in industrial finishes where good whiteness is important but where weather resistance is not required, e.g., domestic and hospital equipment. Commercial products include Bayertitan (Bayer), Finntitan (Kemira), Tipure (DuPont), Tronox (Kerr McGee).

[057] Additional white inorganic pigments include Pigment White 1 (white lead), Pigment White 2 (basic lead sulfate), Pigment White 4 (zinc oxide), Pigment White 6, Pigment White 11 (antimony oxide), Pigment White 32 (zinc phosphate), barium compounds (barytes and blanc fixe or barium sulfate), calcium compounds (calcium carbonate, gypsum, calcium silicate), aluminum compounds (china clay, mica, bentonite), magnesium compounds (magnesium carbonate, asbestine, talc), silica (natural silica such as quartz, flint, kieselguhr, celite, diatomite and synthetic silica).

[058] Colored inorganic pigments include, for example, Pigment Yellow 31 (barium chromate), Pigment Yellow 32 (strontium chromate), Pigment Yellow 34/Pigment Red 104 (lead chromes), Pigment Yellow 36/36.1 (zinc chromes), Pigment Yellow 37/Pigment Red 108 (cadmium sulfide), Pigment Yellow 42, Pigment Red 101, Pigment Red 105 (red lead), Pigment Blue 23 (ultramarine blue), Pigment Blue 27 (prussian blue), Pigment Blue 29, Pigment Green 15 (chrome green), Pigment Green 17 (chromium oxide) and Pigment Green 18 (guignet's green).

[059] Luminous/Fluorescent inorganic pigments include, for example, zinc sulfide, cadmium sulfide, calcium sulfide, strontium sulfide and barium sulfide.

[060] Black pigments include, for example, Pigment Black 7 (carbon black), lamp (vegetable) black, drop (bone) black, graphite, iron oxide black, cobalt oxide black, nickel oxide black and mixed metal oxide black etc.

[061] Colored organic pigments include, for example, Pigment Yellow 1, Pigment Yellow 3, Pigment Yellow 5, Pigment Yellow 12, Pigment Yellow 13, Pigment Yellow 14, Pigment Yellow 16, Pigment Yellow 17, Pigment Yellow 34, 42, Pigment Yellow 74, Pigment Yellow 83, Pigment Yellow 106, Pigment Yellow 108, Pigment Yellow 113, Pigment Yellow 117, Pigment Yellow 126, Pigment Yellow 129, Pigment Yellow 185, Pigment Orange 5, Pigment Orange 13, Pigment Orange 16, Pigment Orange 34, Pigment Orange 36, Pigment Orange 43, Pigment Orange 67, Pigment Red 1, Pigment Red 3, Pigment Red 7, Pigment Red 9, Pigment Red 12, Pigment Red 48, Pigment Red 48.1, Pigment Red 48.4, Pigment Red 49, Pigment Red 49.1, Pigment Red 52.1, Pigment Red 53.1, Pigment Red 57, Pigment Red 83, Pigment Red 88, Pigment Red 104, 112, Pigment Red 122, Pigment Red 123, Pigment Red 146, Pigment Red 169, Pigment Red 170, Pigment Violet 19, Pigment Violet 23, Pigment Violet 27, Pigment Blue 1, Pigment Blue 15, Pigment Blue 15.1, Pigment Blue 15.3, Pigment Blue 15.6, Pigment Blue 16, Pigment Blue 61, Pigment Blue 62, Pigment Green 7, Pigment Green 8, Pigment Green 10, and Pigment Green 36.

[062] In one embodiment, a substrate can be provided with a suitable coating or impregnated with at least one color-maintaining material, e.g., an acid or a base. Upon application of the acid-base indicator dye to the treated surface or substrate, the dye pH level is maintained and thus the color is maintained. If, however, the colored paint is contacted with an unintended surface, the stain can be readily removed with the application of pressure, water, or extended exposure to air.

[063] In certain instances, the present invention provides the ability to have a temporary color that is easily removable from the surface/substrate is

desired. For example, when one is testing color samples on a wall. Typically, the wall coating is not alkaline. Treatment with a paint of the invention that is basic will not maintain color indefinitely. Advantageously, after the observer has viewed how the color looks on the wall, the paint composition can be easily removed with water or water with a detergent.

[064] Typically, the paint compositions of the invention can be applied by known methods and suitable instruments. The paint instruments include, but are not limited to, brushes, rollers, sprayers, writing instruments, e.g., felt-type writing instruments, wick-type writing instruments, spatulas, fingers and the like.

Paint Compositions of the Invention

[065] The compositions of the present invention generally contain between about 5 and about 70 parts water, in particular between about 10 and about 60, and more particularly between about 20 and about 50 percent based on a total weight percentage of the final composition. In one aspect, the water utilized can be ordinary tap water or spring water. In another aspect the water can be deionized water or water purified by reverse osmosis. Optionally, an organic solvent (alcohols, polyethers, glycol ethers, etc.) can also be used, alone or in combination with water.

[066] In one aspect the compositions of the invention include acid-base indicators that are generally colored under basic condition and change color or fade to clear in non-basic condition. Acid-base indicators which are colored on alkaline pH side ($\text{pH} > 7$) and turn clear on acidic pH ($\text{pH} < 7$) are most useful. Typically, the acid-base indicators are colored at pH between about 9 and about 10, and turn clear at pH between about 6 and about 8.

[067] Representative examples of acid-base indicators useful in the compositions of the present invention include, but are not limited to, picric acid, matius yellow, 2,6-dinitrophenol, 2,4-dinitrophenol, phenacetolin, 2,5-dinitrophenol, isopicramic acid, o-nitrophenol, m-nitrophenol, p-nitrophenol, 6,8-dinitro-2,4-(1H,3H)quinazolinedione, nitroamine, ethyl bis(2,4-dinitrophenyl)-acetate, 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene, 2,4,6-tribromobenzoic acid, 2-

(p-dimethylaminophenyl)azopyridine, metanil yellow, p-methyl red, 4-phenylazodiphenylamine, benzopurpurin 4B, tropaeolin OO, fast garnet GBC base, alizarin yellow R, benzyl orange, m-methyl red, 4-(m-tolyl)-azo-N,N-dimethyl-aniline, oil yellow II, methyl orange, ethyl orange, hessian purple N, congo red, N-pnehl-1-naphthyl-aminoazobenzene-p-sulfonic acid, 4-(4'-dimethylamino-1'-naphthyl)-azo-3-methoxy-benzenesulfonic acid, p-ethoxychrysoidine, α -naphthyl red, chrysoidine, 1-naphthylaminoazobenzene-p-sulfonic acid, methyl red, 2-(p-dimethylaminophenyl)-azopyridine, ethyl red, propyl red, N-phenyl-1-naphthyl-aminoazo-o-carboxybenzene, nitrazol yellow, brilliant yellow, brilliant yellow S, orange II, propyl-o-naphthyl orange, orange I, orange IV, hessian, Bordeaux, diazo violet, α -naphthol violet, alizarin yellow GG, chrome orange GR, sulfone acid blue R, lanacyl violet BF, tropaeolin O, orange G, crystal violet, methyl violet B, malachite green, brilliant green, ethyl violet, methyl violet 6B, ethyl/methyl green, basic fuchsine, acid, fuchsine, patent blue V, alkali blue, aniline blue, o-naphthol benzein, pentamethoxy red, hexamethoxy red, tetrabromophenolphthalein ethyl ester K salt, tetraiodophenolsulfophthlein, bromochlorophenol blue, bromocresol green, chlorocresol green, chlorophenol red, bromocresol purple, sulfonaphthyl red, bromophenol red, dibromophenol-tetrabromophenol-sulfophthlein, bromothymol blue, aurin, phenol red, o-cresol benzein, o-cresol red, α -naphtholphthlein, m-cresol purple, p-xylene blue, thymol blue, phenoltetrachlorophthlein, o-cresolphthalein, α -naphtholbenzein, phenoltetraiodophthlein, phenolphthalein, thymolphthlein, eosin Y, erythrosine B, erythrosine, galleon, brilliant cresyl blue, resazurin, lacmoid, litmus, azolitmus, azolitmin, neutral red, Nile blue 2B, Nile blue A, hematoxylin, quinaldine red, pinachrome, indo-oxine, quinoline blue, bis-5-bromovanillidenecyclohexanone, bis-(2'-hydroxystyryl)ketone, curcumin, bis-(4-hydroxy-3-ethoxy-benzylidene)-cyclohexanone, thiazole yellow G, alizarin blue B, alizarin red S, carminic acid, alizarin orange, alizarin, rufianic acid, rufianic blue, alizarin blue SWR, and indigocarmine.

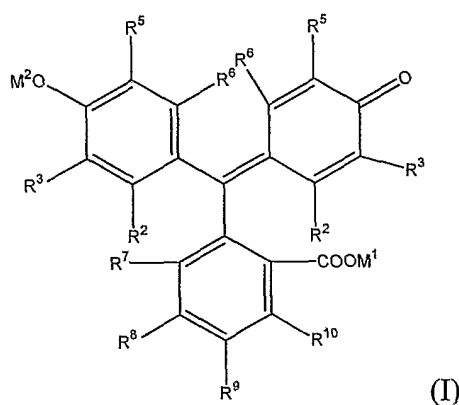
[068] With the suitable selection of acid-base indicators, it is possible to produce any color. The acid-base indicators are preferably in an acidic form, such

that when a paint is utilized with a base treated surface, for example, the treated area will change color. Additionally, combinations of two or more indicators may be used.

[069] Acid-base indicators are usually effective when present in small amounts in the compositions of the invention but generally are present in amounts from about 0.01% up to about 15% by weight, from about 0.05% to about 10% by weight and from about 0.1% to about 8% by weight of the total weight of the composition.

[070] It should be understood that the term “comprising” (or comprises) includes the more restrictive terms consisting of and consisting essentially of.

[071] Particular phthaleins useful in the invention, including paints, have the formula (I):



[072] wherein R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are each, independently of one another, selected from the group consisting of hydrogen, -OH, -SH, -CN, -NO₂, halo, fluoro, chloro, bromo, iodo, lower alkyl, substituted lower alkyl, lower heteroalkyl, substituted lower heteroalkyl, cycloalkyl, substituted cycloalkyl, cycloheteroalkyl, substituted cycloheteroalkyl, lower haloalkyl, monohalomethyl, dihalomethyl, trihalomethyl, trifluoromethyl, lower alkylthio, substituted lower alkylthio, lower alkoxy, substituted lower alkoxy, methoxy, substituted methoxy, lower heteroalkoxy, substituted lower heteroalkoxy, cycloalkoxy, substituted cycloalkoxy, cycloheteroalkoxy, substituted

cycloheteroalkoxy, lower haloalkoxy, monohalomethoxy, dihalomethoxy, trihalomethoxy, trifluoromethoxy, amino, lower di- or monoalkylamino, substituted lower di- or monoalkylamino, aryl, substituted aryl, aryloxy, substituted aryloxy, phenoxy, substituted phenoxy, arylalkyl, substituted arylalkyl, arylalkyloxy, substituted arylalkyloxy, benzyl, benzyloxy, heteroaryl, substituted heteroaryl, heteroaryloxy, substituted heteroaryloxy, heteroarylalkyl, substituted heteroarylalkyl, heteroarylalkyloxy, substituted heteroarylalkyloxy, carboxyl, lower alkoxycarbonyl, substituted lower alkoxycarbonyl, aryloxycarbonyl, substituted aryloxycarbonyl, arylalkyloxycarbonyl, substituted arylalkyloxycarbonyl, carbamate, substituted carbamate, carbamoyl, substituted carbamoyl, sulfamoyl or substituted sulfamoyl.

[073] Optionally, one of the carbons connected to R^2 , R^3 , R^5 or R^6 can be substituted with a nitrogen atom.

[074] Alternatively, R^2 and R^3 , R^5 and R^6 or R^2 and R^3 , and R^5 and R^6 can form cyclic ring structures that are heterocyclic, heteroaromatic, aromatic or nonaromatic and can contain one or more heteroatoms to form, for example, a quinoline, naphthalene, etc.

[075] Additionally, R^7 and R^8 , R^8 and R^9 , R^9 and R^{10} or combinations thereof can form cyclic ring structures that are heterocyclic, heteroaromatic, aromatic or nonaromatic and can contain one or more heteroatoms to form, for example, a quinoline, naphthalene, etc.

[076] M^1 and M^2 are each independently a hydrogen atom, a metal ion or an ammonium ion.

[077] In one aspect, the compound where R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms is excluded from the paint composition.

[078] In certain paint embodiments, R^2 is selected from the group consisting of hydrogen, nitro, amino and alkyl; R^3 is selected from the group consisting of hydrogen, phenyl, alkyl, nitro, acetamido and alkoxy; R^5 is selected from the group consisting of hydrogen, halo, and alkyl; and R^6 is selected from the group consisting of hydrogen and alkyl.

[079] In certain paint embodiments, R^2 is selected from the group consisting of hydrogen and methyl; R^3 is selected from the group consisting of hydrogen, phenyl, isopropyl, methyl, ethyl, sec-butyl, nitro and methoxy; R^5 is selected from the group consisting of hydrogen, bromo, methoxy, isopropyl and methyl; and R^6 is selected from the group consisting of hydrogen and methyl.

[080] In other paint embodiments, R^2 is hydrogen, R^3 is Me, and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is Me, R^3 is a hydrogen atom, R^5 is an iso-propyl group and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is Me, R^5 is Br and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is Me, R^3 is Br, R^5 is an isopropyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms. In certain embodiments, one or more of these compounds may be excluded from certain aspects of the invention.

[081] In still other paint embodiments, R^2 is H, R^3 is phenyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 and R^5 are isopropyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is methyl, R^5 is H, R^6 is methyl, R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 and R^5 are methoxy and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 and R^5 are methyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is ethyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is isopropyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is methoxide and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 , R^3 and R^5 are all methyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} are all hydrogen atoms and R^3 is sec-butyl, or R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} are all hydrogen atoms and R^3 is nitro.

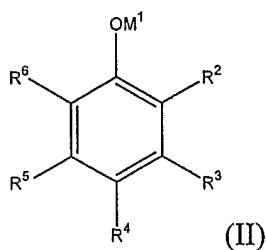
[082] In particular, at least one of M^1 or M^2 is a metal or an ammonium ion.

[083] It should be understood, that the salt form of the indicator can be isolated prior to use or prepared in situ. Ideally, the salt is formed as a mono-salt or a di-salt, meaning that excess base is not present and either 1 or 2 equivalents of base react with the acidic protons of the indicator.

[084] The following table provides phthaleins of particular interest.

R^2	R^3	R^5	R^6	Color
H	phenyl	H	H	purple
H	<i>i</i> -propyl	<i>i</i> -propyl	H	violet
H	Me	H	Me	blue
H	OMe	OMe	H	teal
H	Me	Me	H	purple
H	Et	H	H	magenta
H	<i>i</i> -propyl	H	H	pink
H	OMe	H	H	blue
Me	Me	Me	H	teal
H	Me	H	H	magenta
H	<i>i</i> -propyl	H	Me	blue
H	Me	Br	H	purple
H	<i>i</i> -propyl	Br	Me	teal
H	<i>sec</i> -butyl	H	H	pink
H	NO ₂	H	H	yellow

[085] In another aspect, the acid-base indicator can be a substituted phenol of formula (II):

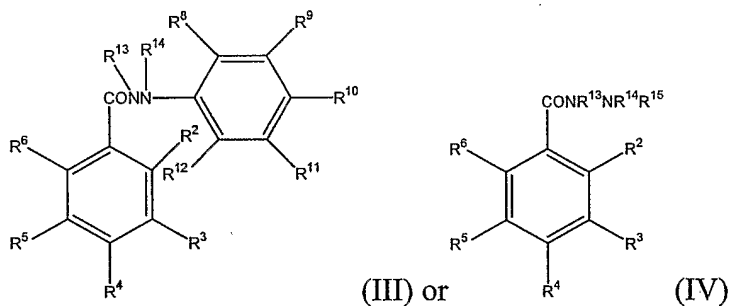


[086] wherein R^2 , R^3 , R^5 , R^6 and M^1 are as defined above and R^4 is selected from the same group as R^2 , R^3 , R^5 and R^6 .

[087] Alternatively, R^2 and R^3 , R^3 and R^4 , R^4 and R^5 , or R^5 and R^6 can form cyclic ring structures that are heterocyclic, heteroaromatic, aromatic or nonaromatic and can contain one or more heteroatoms to form, for example, a quinoline, naphthalene, etc.

[088] In one aspect, one or more of R^2 through R^6 , independently, is a nitro ($-NO_2$) group and the remaining R groups are selected from those provided above.

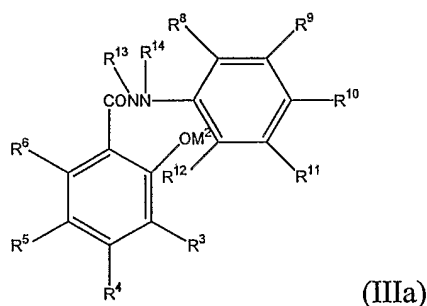
[089] Additionally, substituted hydrazides are useful in the compositions of the invention, including paint, and can have one of two formulae:



[090] wherein R^2 through R^6 are as defined above and R^8 through R^{12} are the same substituents as R^2 through R^6 . R^{13} , R^{14} and R^{15} (if present) are each, independently of one another, a hydrogen atom, an alkyl group, a substituted alkyl group, any aryl group or a substituted aryl group.

[091] In certain embodiments for compound formulae (II), R^{13} and R^{14} are hydrogen atoms and for compound formulae (III), R^{13} , R^{14} and R^{15} are all hydrogen atoms.

[092] In certain aspects, compounds of formulae (III) can have one or more hydroxyl groups, which can be deprotonated to form a salt. For example, formulae (IIIa) provides one isomer where a hydroxyl is present at the R^2 position as a salt. M^2 is as defined above for M^1 . It should be understood that one or more of R^2 through R^{12} could have a hydroxyl at that given position, and that hydroxyl could be in a salt form.



[093] “Alkyl,” by itself or as part of another substituent, refers to a saturated or unsaturated, branched, straight-chain or cyclic monovalent hydrocarbon radical derived by the removal of one hydrogen atom from a single carbon atom of a parent alkane, alkene or alkyne. Typical alkyl groups include, but are not limited to, methyl; ethyls such as ethanyl, ethenyl, ethynyl; propyls such as propan-1-yl, propan-2-yl, cyclopropan-1-yl, prop-1-en-1-yl, prop-1-en-2-yl, prop-2-en-1-yl (allyl), cycloprop-1-en-1-yl; cycloprop-2-en-1-yl, prop-1-yn-1-yl, prop-2-yn-1-yl, *etc.*; butyls such as butan-1-yl, butan-2-yl, 2-methyl-propan-1-yl, 2-methyl-propan-2-yl, cyclobutan-1-yl, but-1-en-1-yl, but-1-en-2-yl, 2-methyl-prop-1-en-1-yl, but-2-en-1-yl, but-2-en-2-yl, buta-1,3-dien-1-yl, buta-1,3-dien-2-yl, cyclobut-1-en-1-yl, cyclobut-1-en-3-yl, cyclobuta-1,3-dien-1-yl, but-1-yn-1-yl, but-1-yn-3-yl, but-3-yn-1-yl, *etc.*; and the like.

[094] The term “alkyl” is specifically intended to include groups having any degree or level of saturation, *i.e.*, groups having exclusively single carbon-carbon bonds, groups having one or more double carbon-carbon bonds, groups having one or more triple carbon-carbon bonds and groups having mixtures of single, double and triple carbon-carbon bonds. Where a specific level of saturation is intended, the expressions “alkanyl,” “alkenyl,” and “alkynyl” are used. Preferably, an alkyl group comprises from 1 to 15 carbon atoms (C₁-C₁₅ alkyl), more preferably from 1 to 10 carbon atoms (C₁-C₁₀ alkyl) and even more preferably from 1 to 6 carbon atoms (C₁-C₆ alkyl or lower alkyl).

[095] “Alkanyl,” by itself or as part of another substituent, refers to a saturated branched, straight-chain or cyclic alkyl radical derived by the removal of one hydrogen atom from a single carbon atom of a parent alkane. Typical alkanyl groups include, but are not limited to, methanyl; ethanyl; propanyls such as propan-1-yl, propan-2-yl (isopropyl), cyclopropan-1-yl, *etc.*; butanyls such as butan-1-yl, butan-2-yl (*sec*-butyl), 2-methyl-propan-1-yl (isobutyl), 2-methyl-propan-2-yl (*t*-butyl), cyclobutan-1-yl, *etc.*; and the like.

[096] “Alkenyl,” by itself or as part of another substituent, refers to an unsaturated branched, straight-chain or cyclic alkyl radical having at least one carbon-carbon double bond derived by the removal of one hydrogen atom from a single carbon atom of a parent alkene. The group may be in either the *cis* or *trans* conformation about the double bond(s). Typical alkenyl groups include, but are not limited to, ethenyl; propenyls such as prop-1-en-1-yl, prop-1-en-2-yl, prop-2-en-1-yl (allyl), prop-2-en-2-yl, cycloprop-1-en-1-yl; cycloprop-2-en-1-yl; butenyls such as but-1-en-1-yl, but-1-en-2-yl, 2-methyl-prop-1-en-1-yl, but-2-en-1-yl, but-2-en-1-yl, but-2-en-2-yl, buta-1,3-dien-1-yl, buta-1,3-dien-2-yl, cyclobut-1-en-1-yl, cyclobut-1-en-3-yl, cyclobuta-1,3-dien-1-yl, *etc.*; and the like.

[097] “Alkynyl,” by itself or as part of another substituent refers to an unsaturated branched, straight-chain or cyclic alkyl radical having at least one carbon-carbon triple bond derived by the removal of one hydrogen atom from a single carbon atom of a parent alkyne. Typical alkynyl groups include, but are

not limited to, ethynyl; propynyls such as prop-1-yn-1-yl, prop-2-yn-1-yl, etc.; butynyls such as but-1-yn-1-yl, but-1-yn-3-yl, but-3-yn-1-yl, *etc.*; and the like.

[098] “Alkyldiyl” by itself or as part of another substituent refers to a saturated or unsaturated, branched, straight-chain or cyclic divalent hydrocarbon group derived by the removal of one hydrogen atom from each of two different carbon atoms of a parent alkane, alkene or alkyne, or by the removal of two hydrogen atoms from a single carbon atom of a parent alkane, alkene or alkyne. The two monovalent radical centers or each valency of the divalent radical center can form bonds with the same or different atoms. Typical alkyldiyl groups include, but are not limited to, methandiyl; ethyldiyls such as ethan-1,1-diyl, ethan-1,2-diyl, ethen-1,1-diyl, ethen-1,2-diyl; propyldiyls such as propan-1,1-diyl, propan-1,2-diyl, propan-2,2-diyl, propan-1,3-diyl, cyclopropan-1,1-diyl, cyclopropan-1,2-diyl, prop-1-en-1,1-diyl, prop-1-en-1,2-diyl, prop-2-en-1,2-diyl, prop-1-en-1,3-diyl, cycloprop-1-en-1,2-diyl, cycloprop-2-en-1,2-diyl, cycloprop-2-en-1,1-diyl, prop-1-yn-1,3-diyl, *etc.*; butyldiyls such as, butan-1,1-diyl, butan-1,2-diyl, butan-1,3-diyl, butan-1,4-diyl, butan-2,2-diyl, 2-methyl-propan-1,1-diyl, 2-methyl-propan-1,2-diyl, cyclobutan-1,1-diyl; cyclobutan-1,2-diyl, cyclobutan-1,3-diyl, but-1-en-1,1-diyl, but-1-en-1,2-diyl, but-1-en-1,3-diyl, but-1-en-1,4-diyl, 2-methyl-prop-1-en-1,1-diyl, 2-methanylidene-propan-1,1-diyl, buta-1,3-dien-1,1-diyl, buta-1,3-dien-1,2-diyl, buta-1,3-dien-1,3-diyl, buta-1,3-dien-1,4-diyl, cyclobut-1-en-1,2-diyl, cyclobut-1-en-1,3-diyl, cyclobut-2-en-1,2-diyl, cyclobuta-1,3-dien-1,2-diyl, cyclobuta-1,3-dien-1,3-diyl, but-1-yn-1,3-diyl, but-1-yn-1,4-diyl, buta-1,3-diyn-1,4-diyl, *etc.*; and the like. Where specific levels of saturation are intended, the nomenclature alkanyldiyl, alkenyldiyl and/or alkynyldiyl is used. Where it is specifically intended that the two valencies are on the same carbon atom, the nomenclature “alkylidene” is used. In preferred embodiments, the alkyldiyl group comprises from 1 to 6 carbon atoms (C1-C6 alkyldiyl). Also preferred are saturated acyclic alkanyldiyl groups in which the radical centers are at the terminal carbons, *e.g.*, methandiyl (methano); ethan-1,2-diyl (ethano);

propan-1,3-diyl (propano); butan-1,4-diyl (butano); and the like (also referred to as alkylenos, defined *infra*).

[0099] “Alkyleno,” by itself or as part of another substituent, refers to a straight-chain saturated or unsaturated alkyl-diyl group having two terminal monovalent radical centers derived by the removal of one hydrogen atom from each of the two terminal carbon atoms of straight-chain parent alkane, alkene or alkyne. The locant of a double bond or triple bond, if present, in a particular alkyleno is indicated in square brackets. Typical alkyleno groups include, but are not limited to, methano; ethylenos such as ethano, etheno, ethyno; propylenos such as propano, prop[1]eno, propa[1,2]dieno, prop[1]yno, etc.; butylenos such as butano, but[1]eno, but[2]eno, buta[1,3]dieno, but[1]yno, but[2]yno, buta[1,3]diyno, etc.; and the like. Where specific levels of saturation are intended, the nomenclature alkano, alkeno and/or alkyno is used. In preferred embodiments, the alkyleno group is (C1-C6) or (C1-C3) alkyleno. Also preferred are straight-chain saturated alkano groups, *e.g.*, methano, ethano, propano, butano, and the like.

[0100] “Alkoxy,” by itself or as part of another substituent, refers to a radical of the formula -OR, where R is an alkyl or cycloalkyl group as defined herein. Representative examples alkoxy groups include, but are not limited to, methoxy, ethoxy, propoxy, isopropoxy, butoxy, tert-butoxy, cyclopropyloxy, cyclopentyloxy, cyclohexyloxy and the like.

[0101] “Alkoxy carbonyl,” by itself or as part of another substituent, refers to a radical of the formula -C(O)-alkoxy, where alkoxy is as defined herein.

[0102] “Alkylthio,” by itself or as part of another substituent, refers to a radical of the formula -SR, where R is an alkyl or cycloalkyl group as defined herein. Representative examples of Alkylthio groups include, but are not limited to, methylthio, ethylthio, propylthio, isopropylthio, butylthio, tert-butylthio, cyclopropylthio, cyclopentylthio, cyclohexylthio, and the like.

[0103] “Aryl,” by itself or as part of another substituent, refers to a monovalent aromatic hydrocarbon group derived by the removal of one hydrogen atom from a single carbon atom of a parent aromatic ring system, as defined

herein. Typical aryl groups include, but are not limited to, groups derived from aceanthrylene, acenaphthylene, acephenanthrylene, anthracene, azulene, benzene, chrysene, coronene, fluoranthene, fluorene, hexacene, hexaphene, hexalene, *as*-indacene, *s*-indacene, indane, indene, naphthalene, octacene, octaphene, octalene, ovalene, penta-2,4-diene, pentacene, pentalene, pentaphene, perylene, phenalene, phenanthrene, picene, pleiadene, pyrene, pyranthrene, rubicene, triphenylene, trinaphthalene and the like. Preferably, an aryl group comprises from 6 to 20 carbon atoms (C₆-C₂₀ aryl), more preferably from 6 to 15 carbon atoms (C₆-C₁₅ aryl) and even more preferably from 6 to 10 carbon atoms (C₆-C₁₀ aryl).

[0104] “Arylalkyl,” by itself or as part of another substituent, refers to an acyclic alkyl group in which one of the hydrogen atoms bonded to a carbon atom, typically a terminal or *sp*³ carbon atom, is replaced with an aryl group as, as defined herein. Typical arylalkyl groups include, but are not limited to, benzyl, 2-phenylethan-1-yl, 2-phenylethen-1-yl, naphthylmethyl, 2-naphthylethan-1-yl, 2-naphthylethen-1-yl, naphthobenzyl, 2-naphthophenylethan-1-yl and the like. Where specific alkyl moieties are intended, the nomenclature arylalkanyl, arylalkenyl and/or arylalkynyl is used. Preferably, an arylalkyl group is (C₆-C₃₀) arylalkyl, *e.g.*, the alkanyl, alkenyl or alkynyl moiety of the arylalkyl group is (C₁-C₁₀) alkyl and the aryl moiety is (C₆-C₂₀) aryl, more preferably, an arylalkyl group is (C₆-C₂₀) arylalkyl, *e.g.*, the alkanyl, alkenyl or alkynyl moiety of the arylalkyl group is (C₁-C₈) alkyl and the aryl moiety is (C₆-C₁₂) aryl, and even more preferably, an arylalkyl group is (C₆-C₁₅) arylalkyl, *e.g.*, the alkanyl, alkenyl or alkynyl moiety of the arylalkyl group is (C₁-C₅) alkyl and the aryl moiety is (C₆-C₁₀) aryl.

[0105] “Aryloxy,” by itself or as part of another substituent, refers to a radical of the formula -O-aryl, where aryl is as defined herein.

[0106] “Arylalkyloxy,” by itself or as part of another substituent, refers to a radical of the formula -O-arylalkyl, where arylalkyl is as defined herein.

[0107] “Aryloxycarbonyl,” by itself or as part of another substituent, refers to a radical of the formula -C(O)-O-aryl, where aryl is as defined herein.

[0108] “Carbamoyl,” by itself or as part of another substituent, refers to a radical of the formula $-C(O)NR'R''$, where R' and R'' are each, independently of one another, selected from the group consisting of hydrogen, alkyl and cycloalkyl as defined herein, or alternatively, R' and R'' , taken together with the nitrogen atom to which they are bonded, form a 5-, 6- or 7-membered cycloheteroalkyl ring as defined herein, which may optionally include from 1 to 4 of the same or different additional heteroatoms selected from the group consisting of O, S and N.

[0109] “Compounds of the invention” refers to compounds encompassed by the various descriptions and structural formulae disclosed herein. The compounds of the invention may be identified by either their chemical structure and/or chemical name. When the chemical structure and chemical name conflict, the chemical structure is determinative of the identity of the compound. The compounds of the invention may contain one or more chiral centers and/or double bonds and therefore may exist as stereoisomers, such as double-bond isomers (*i.e.*, geometric isomers), rotamers, enantiomers or diastereomers. Accordingly, when stereochemistry at chiral centers is not specified, the chemical structures depicted herein encompass all possible configurations at those chiral centers including the stereoisomerically pure form (*e.g.*, geometrically pure, enantiomerically pure or diastereomerically pure) and enantiomeric and stereoisomeric mixtures. Enantiomeric and stereoisomeric mixtures can be resolved into their component enantiomers or stereoisomers using separation techniques or chiral synthesis techniques well known to the skilled artisan. The compounds of the invention may also exist in several tautomeric forms including the enol form, the keto form and mixtures thereof. Accordingly, the chemical structures depicted herein encompass all possible tautomeric forms of the illustrated compounds. The compounds of the invention may also include isotopically labeled compounds where one or more atoms have an atomic mass different from the atomic mass conventionally found in nature. Examples of isotopes that may be incorporated into the compounds of the invention include, but are not limited to, ^2H , ^3H , ^{11}C , ^{13}C , ^{14}C , ^{15}N , ^{18}O , ^{17}O , ^{31}P , ^{32}P , ^{35}S , ^{18}F and ^{36}Cl . Compounds of the invention may exist in unsolvated forms as well as

solvated forms, including hydrated forms and as N-oxides. In general, the hydrated, solvated and N-oxide forms are within the scope of the present invention. Certain compounds of the present invention may exist in multiple crystalline or amorphous forms. In general, all physical forms are equivalent for the uses contemplated by the present invention and are intended to be within the scope of the present invention.

[0110] “Cycloalkyl,” by itself or as part of another substituent, refers to a saturated or unsaturated cyclic alkyl radical, as defined herein. Where a specific level of saturation is intended, the nomenclature “cycloalkanyl” or “cycloalkenyl” is used. Typical cycloalkyl groups include, but are not limited to, groups derived from cyclopropane, cyclobutane, cyclopentane, cyclohexane, and the like. Preferably, the cycloalkyl group comprises from 3 to 10 ring atoms (C₃-C₁₀ cycloalkyl) and more preferably from 3 to 7 ring atoms (C₃-C₇ cycloalkyl).

[0111] “Cycloheteroalkyl,” by itself or as part of another substituent, refers to a saturated or unsaturated cyclic alkyl radical in which one or more carbon atoms (and optionally any associated hydrogen atoms) are independently replaced with the same or different heteroatom. Typical heteroatoms to replace the carbon atom(s) include, but are not limited to, N, P, O, S, Si, *etc.* Where a specific level of saturation is intended, the nomenclature “cycloheteroalkanyl” or “cycloheteroalkenyl” is used. Typical cycloheteroalkyl groups include, but are not limited to, groups derived from epoxides, azirines, thiiranes, imidazolidine, morpholine, piperazine, piperidine, pyrazolidine, pyrrolidone, quinuclidine, and the like. Preferably, the cycloheteroalkyl group comprises from 3 to 10 ring atoms (3-10 membered cycloheteroalkyl) and more preferably from 5 to 7 ring atoms (5-7 membered cycloheteroalkyl).

[0112] A cycloheteroalkyl group may be substituted at a heteroatom, for example, a nitrogen atom, with a lower alkyl group. As specific examples, N-methyl-imidazolidinyl, N-methyl-morpholinyl, N-methyl-piperazinyl, N-methyl-piperidinyl, N-methyl-pyrazolidinyl and N-methyl-pyrrolidinyl are included within the definition of “cycloheteroalkyl.” A cycloheteralkyl group

may be attached to the remainder of the molecule *via* a ring carbon atom or a ring heteroatom.

[0113] “Dialkylamino” or “Monoalkylamino,” by themselves or as part of other substituents, refer to radicals of the formula $-NRR$ and $-NHR$, respectively, where each R is independently selected from the group consisting of alkyl and cycloalkyl, as defined herein. Representative examples of dialkylamino groups include, but are not limited to, dimethylamino, methylethylamino, di-(1-methylethyl)amino, (cyclohexyl)(methyl)amino, (cyclohexyl)(ethyl)amino, (cyclohexyl)(propyl)amino and the like. Representative examples of monalkylamino groups include, but are not limited to, methylamino, ethylamino, propylamino, isopropylamino, cyclohexylamino, and the like.

[0114] “Halogen” or “Halo,” by themselves or as part of another substituent, refer to a fluoro, chloro, bromo and/or iodo radical.

[0115] “Haloalkyl,” by itself or as part of another substituent, refers to an alkyl group as defined herein in which one or more of the hydrogen atoms is replaced with a halo group. The term “haloalkyl” is specifically meant to include monohaloalkyls, dihaloalkyls, trihaloalkyls, *etc.* up to perhaloalkyls. The halo groups substituting a haloalkyl can be the same, or they can be different. For example, the expression “(C₁-C₂) haloalkyl” includes 1-fluoromethyl, 1-fluoro-2-chloroethyl, difluoromethyl, trifluoromethyl, 1-fluoroethyl, 1, 1-difluoroethyl, 1, 2-difluoroethyl, 1,1,1-trifluoroethyl, perfluoroethyl, *etc.* “Haloalkyloxy,” by itself or as part of another substituent, refers to a group of the formula $-O\text{-haloalkyl}$, where haloalkyl is as defined herein.

[0116] “Heteroalkyl,” “Heteroalkanyl,” “Heteroalkenyl,” “Heteroalkynyl,” “Heteroalkyldiyl” and “Heteroalkyleno,” by themselves or as part of other substituents, refer to alkyl, alkanyl, alkenyl, alkynyl, alkyldiyl and alkylene groups, respectively, in which one or more of the carbon atoms (and optionally any associated hydrogen atoms), are each, independently of one another, replaced with the same or different heteroatoms or heteroatomic groups. Typical heteroatoms or heteroatomic groups which can replace the carbon atoms include, but are not limited to, O, S, N, Si, $-NH-$, $-S(O)-$, $-S(O)_2-$, $-S(O)NH-$,

-S(O)₂NH- and the like and combinations thereof. The heteroatoms or heteroatomic groups may be placed at any interior position of the alkyl, alkenyl or alkynyl groups. Examples of such heteroalkyl, heteroalkanyl, heteroalkenyl and/or heteroalkynyl groups include -CH₂-CH₂-O-CH₃, -CH₂-CH₂-NH-CH₃, -CH₂-CH₂-N(CH₃)-CH₃, -CH₂-S-CH₂-CH₃, -CH₂-CH₂-S(O)-CH₃, -CH₂-CH₂-S(O)₂-CH₃, -CH=CH-O-CH₃, -CH₂-CH=N-O-CH₃, and -CH₂-CH₂-O-C=CH. For heteroalkyldiyl and heteroalkyleno groups, the heteratom or heteratomic group can also occupy either or both chain termini. For such groups, no orientation of the group is implied.

[0117] “Heteroaryl,” by itself or as part of another substituent, refers to a monovalent heteroaromatic radical derived by the removal of one hydrogen atom from a single atom of a parent heteroaromatic ring systems, as defined herein. Typical heteroaryl groups include, but are not limited to, groups derived from acridine, β -carboline, chromane, chromene, cinnoline, furan, imidazole, indazole, indole, indoline, indolizine, isobenzofuran, isochromene, isoindole, isoindoline, isoquinoline, isothiazole, isoxazole, naphthyridine, oxadiazole, oxazole, perimidine, phenanthridine, phenanthroline, phenazine, phthalazine, pteridine, purine, pyran, pyrazine, pyrazole, pyridazine, pyridine, pyrimidine, pyrrole, pyrrolizine, quinazoline, quinoline, quinolizine, quinoxaline, tetrazole, thiadiazole, thiazole, thiophene, triazole, xanthene, and the like. Preferably, the heteroaryl group comprises from 5 to 20 ring atoms (5-20 membered heteroaryl), more preferably from 5 to 10 ring atoms (5-10 membered heteroaryl). Preferred heteroaryl groups are those derived from furan, thiophene, pyrrole, benzothiophene, benzofuran, benzimidazole, indole, pyridine, pyrazole, quinoline, imidazole, oxazole, isoxazole and pyrazine.

[0118] “Heteroarylalkyl” by itself or as part of another substituent refers to an acyclic alkyl group in which one of the hydrogen atoms bonded to a carbon atom, typically a terminal or *sp*³ carbon atom, is replaced with a heteroaryl group. Where specific alkyl moieties are intended, the nomenclature heteroarylalkanyl, heteroarylakenyl and/or heteroarylalkynyl is used. In preferred embodiments, the heteroarylalkyl group is a 6-21 membered heteroarylalkyl, *e.g.*, the alkanyl,

alkenyl or alkynyl moiety of the heteroarylalkyl is (C1-C6) alkyl and the heteroaryl moiety is a 5-15-membered heteroaryl. In particularly preferred embodiments, the heteroarylalkyl is a 6-13 membered heteroarylalkyl, *e.g.*, the alkanyl, alkenyl or alkynyl moiety is (C1-C3) alkyl and the heteroaryl moiety is a 5-10 membered heteroaryl.

[0119] “Parent Aromatic Ring System” refers to an unsaturated cyclic or polycyclic ring system having a conjugated π electron system. Specifically included within the definition of “parent aromatic ring system” are fused ring systems in which one or more of the rings are aromatic and one or more of the rings are saturated or unsaturated, such as, for example, fluorene, indane, indene, phenalene, *etc.* Typical parent aromatic ring systems include, but are not limited to, aceanthrylene, acenaphthylene, acephenanthrylene, anthracene, azulene, benzene, chrysene, coronene, fluoranthene, fluorene, hexacene, hexaphene, hexalene, *as*-indacene, *s*-indacene, indane, indene, naphthalene, octacene, octaphene, octalene, ovalene, penta-2,4-diene, pentacene, pentalene, pentaphene, perylene, phenalene, phenanthrene, picene, pleiadene, pyrene, pyranthrene, rubicene, triphenylene, trinaphthalene and the like.

[0120] “Parent Heteroaromatic Ring System” refers to a parent aromatic ring system in which one or more carbon atoms (and optionally any associated hydrogen atoms) are each independently replaced with the same or different heteroatom. Typical heteroatoms to replace the carbon atoms include, but are not limited to, N, P, O, S, Si, *etc.* Specifically included within the definition of “parent heteroaromatic ring system” are fused ring systems in which one or more of the rings are aromatic and one or more of the rings are saturated or unsaturated, such as, for example, benzodioxan, benzofuran, chromane, chromene, indole, indoline, xanthene, *etc.* Typical parent heteroaromatic ring systems include, but are not limited to, arsindole, carbazole, β -carboline, chromane, chromene, cinnoline, furan, imidazole, indazole, indole, indoline, indolizine, isobenzofuran, isochromene, isoindole, isoindoline, isoquinoline, isothiazole, isoxazole, naphthyridine, oxadiazole, oxazole, perimidine, phenanthridine, phenanthroline, phenazine, phthalazine, pteridine, purine, pyran, pyrazine, pyrazole, pyridazine,

pyridine, pyrimidine, pyrrole, pyrrolizine, quinazoline, quinoline, quinolizine, quinoxaline, tetrazole, thiadiazole, thiazole, thiophene, triazole, xanthene and the like.

[0121] “Metal ion” or “Metal Salt” refers to a salt of a compound of the invention which is made with counterions understood in the art to be generally acceptable for pharmaceutical uses and which possesses the desired pharmacological activity of the parent compound. Such salts include: (1) acid addition salts, formed with inorganic acids such as hydrochloric acid, hydrobromic acid, sulfuric acid, nitric acid, phosphoric acid, and the like; or formed with organic acids such as acetic acid, propionic acid, hexanoic acid, cyclopentanepropionic acid, glycolic acid, pyruvic acid, lactic acid, malonic acid, succinic acid, malic acid, maleic acid, fumaric acid, tartaric acid, citric acid, benzoic acid, 3-(4-hydroxybenzoyl) benzoic acid, cinnamic acid, mandelic acid, methanesulfonic acid, ethanesulfonic acid, 1,2-ethane-disulfonic acid, 2-hydroxyethanesulfonic acid, benzenesulfonic acid, 4-chlorobenzenesulfonic acid, 2-naphthalenesulfonic acid, 4-toluenesulfonic acid, camphorsulfonic acid, 4-methylbicyclo[2.2.2]-oct-2-ene-1-carboxylic acid, glucoheptonic acid, 3-phenylpropionic acid, trimethylacetic acid, tertiary butylacetic acid, lauryl sulfuric acid, gluconic acid, glutamic acid, hydroxynaphthoic acid, salicylic acid, stearic acid, muconic acid and the like; or (2) salts formed when an acidic proton present in the parent compound is replaced by a metal ion, *e.g.*, an alkali metal ion, an alkaline earth ion, or an aluminum ion; or coordinates with an organic base such as ethanolamine, diethanolamine, triethanolamine, N-methylglucamine, morpholine, piperidine, dimethylamine, diethylamine and the like. Also included are salts of amino acids such as arginates and the like, and salts of organic acids like glucurmic or galactunoric acids and the like (*see, e.g., Berge et al., 1977, J. Pharm. Sci. 66:1-19*).

[0122] “Pharmaceutically acceptable vehicle” refers to a diluent, adjuvant, excipient or carrier with which a compound of the invention is administered.

[0123] “Substituted,” when used to modify a specified group or radical, means that one or more hydrogen atoms of the specified group or radical are each,

independently of one another, replaced with the same or different substituent(s). Substituent groups useful for substituting saturated carbon atoms in the specified group or radical include, but are not limited to $-R^a$, halo, $-O^-$, $=O$, $-OR^b$, $-SR^b$, $-S^-$, $=S$, $-NR^cR^c$, $=NR^b$, $=N-OR^b$, trihalomethyl, $-CF_3$, $-CN$, $-OCN$, $-SCN$, $-NO$, $-NO_2$, $=N_2$, $-N_3$, $-S(O)_2R^b$, $-S(O)_2O^-$, $-S(O)_2OR^b$, $-OS(O)_2R^b$, $-OS(O)_2O^-$, $-OS(O)_2OR^b$, $-P(O)(O^-)_2$, $-P(O)(OR^b)(O^-)$, $-P(O)(OR^b)(OR^b)$, $-C(O)R^b$, $-C(S)R^b$, $-C(NR^b)R^b$, $-C(O)O^-$, $-C(O)OR^b$, $-C(S)OR^b$, $-C(O)NR^cR^c$, $-C(NR^b)NR^cR^c$, $-OC(O)R^b$, $-OC(S)R^b$, $-OC(O)O^-$, $-OC(O)OR^b$, $-OC(S)OR^b$, $-NR^bC(O)R^b$, $-NR^bC(S)R^b$, $-NR^bC(O)O^-$, $-NR^bC(O)OR^b$, $-NR^bC(S)OR^b$, $-NR^bC(O)NR^cR^c$, $-NR^bC(NR^b)R^b$ and $-NR^bC(NR^b)NR^cR^c$, where R^a is selected from the group consisting of alkyl, cycloalkyl, heteroalkyl, cycloheteroalkyl, aryl, arylalkyl, heteroaryl and heteroarylalkyl; each R^b is independently hydrogen or R^a ; and each R^c is independently R^b or alternatively, the two R^c s are taken together with the nitrogen atom to which they are bonded form a 5-, 6- or 7-membered cycloheteroalkyl which may optionally include from 1 to 4 of the same or different additional heteroatoms selected from the group consisting of O, N and S. As specific examples, $-NR^cR^c$ is meant to include $-NH_2$, $-NH$ -alkyl, N-pyrrolidinyl and N-morpholinyl.

[0124] Similarly, substituent groups useful for substituting unsaturated carbon atoms in the specified group or radical include, but are not limited to, $-R^a$, halo, $-O^-$, $-OR^b$, $-SR^b$, $-S^-$, $-NR^cR^c$, trihalomethyl, $-CF_3$, $-CN$, $-OCN$, $-SCN$, $-NO$, $-NO_2$, $-N_3$, $-S(O)_2R^b$, $-S(O)_2O^-$, $-S(O)_2OR^b$, $-OS(O)_2R^b$, $-OS(O)_2O^-$, $-OS(O)_2OR^b$, $-P(O)(O^-)_2$, $-P(O)(OR^b)(O^-)$, $-P(O)(OR^b)(OR^b)$, $-C(O)R^b$, $-C(S)R^b$, $-C(NR^b)R^b$, $-C(O)O^-$, $-C(O)OR^b$, $-C(S)OR^b$, $-C(O)NR^cR^c$, $-C(NR^b)NR^cR^c$, $-OC(O)R^b$, $-OC(S)R^b$, $-OC(O)O^-$, $-OC(O)OR^b$, $-OC(S)OR^b$, $-NR^bC(O)R^b$, $-NR^bC(S)R^b$, $-NR^bC(O)O^-$, $-NR^bC(O)OR^b$, $-NR^bC(S)OR^b$, $-NR^bC(O)NR^cR^c$, $-NR^bC(NR^b)R^b$ and $-NR^bC(NR^b)NR^cR^c$, where R^a , R^b and R^c are as previously defined.

[0125] Substituent groups useful for substituting nitrogen atoms in heteroalkyl and cycloheteroalkyl groups include, but are not limited to, $-R^a$, $-O^-$, $-OR^b$, $-SR^b$, $-S^-$, $-NR^cR^c$, trihalomethyl, $-CF_3$, $-CN$, $-NO$, $-NO_2$, $-S(O)_2R^b$, $-S(O)_2O^-$, $-S(O)_2OR^b$, $-OS(O)_2R^b$, $-OS(O)_2O^-$, $-OS(O)_2OR^b$, $-P(O)(O^-)_2$,

-P(O)(OR^b)(O⁻), -P(O)(OR^b)(OR^b), -C(O)R^b, -C(S)R^b, -C(NR^b)R^b, -C(O)OR^b, -C(S)OR^b, -C(O)NR^cR^c, -C(NR^b)NR^cR^c, -OC(O)R^b, -OC(S)R^b, -OC(O)OR^b, -OC(S)OR^b, -NR^bC(O)R^b, -NR^bC(S)R^b, -NR^bC(O)OR^b, -NR^bC(S)OR^b, -NR^bC(O)NR^cR^c, -NR^bC(NR^b)R^b and -NR^bC(NR^b)NR^cR^c, where R^a, R^b and R^c are as previously defined.

[0126] Substituent groups from the above lists useful for substituting other specified groups or atoms will be apparent to those of skill in the art.

[0127] The substituents used to substitute a specified group can be further substituted, typically with one or more of the same or different groups selected from the various groups specified above.

[0128] “Sulfamoyl,” by itself or as part of another substituent, refers to a radical of the formula -S(O)₂NR'R”, where R' and R” are each, independently of one another, selected from the group consisting of hydrogen, alkyl and cycloalkyl as defined herein, or alternatively, R' and R”, taken together with the nitrogen atom to which they are bonded, form a 5-, 6- or 7-membered cycloheteroalkyl ring as defined herein, which may optionally include from 1 to 4 of the same or different additional heteroatoms selected from the group consisting of O, S and N.

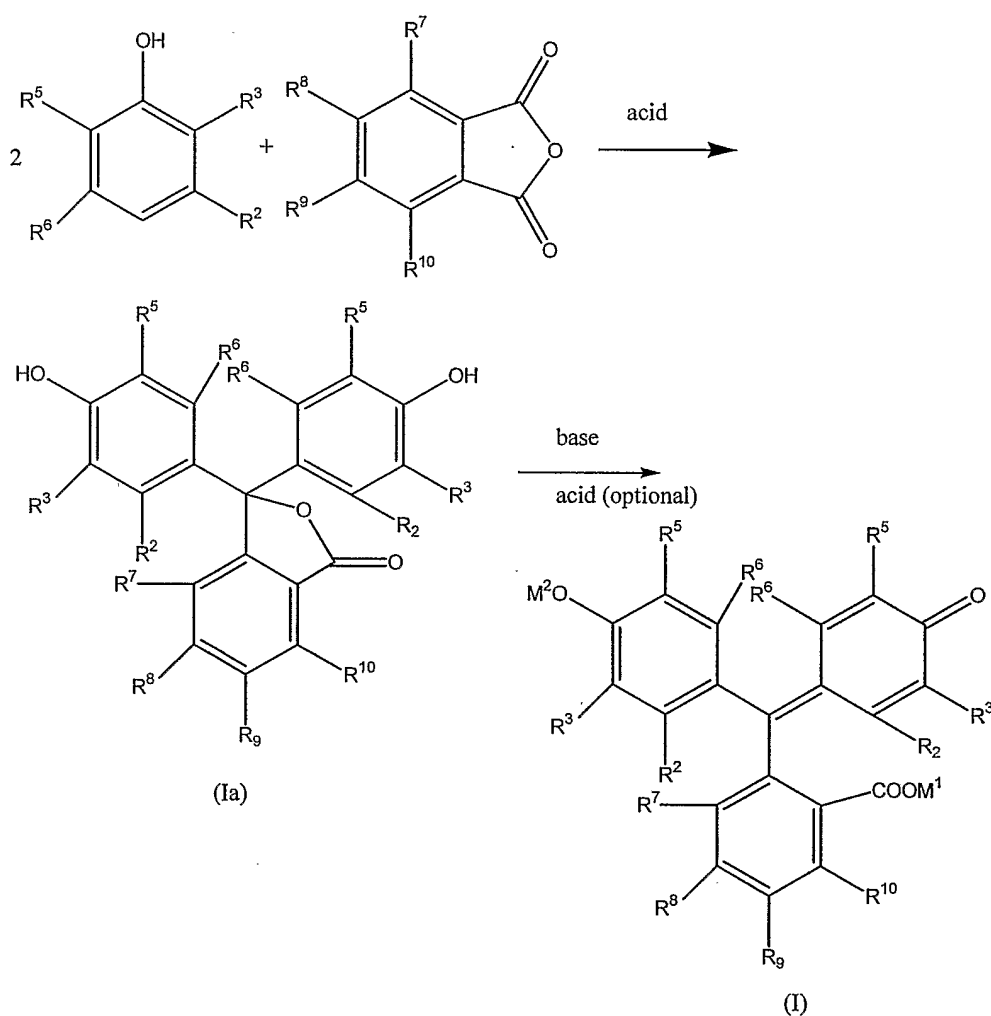
Methods of Synthesis

[0129] The particular phthaleins described above can be obtained *via* synthetic methods illustrated below. It should be understood that in R², R³, R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰, are as previously defined for structural formula (I).

[0130] Starting materials useful for preparing compounds of the invention and intermediates thereof are commercially available or can be prepared by well-known synthetic methods (*see, e.g.*, Harrison *et al.*, “Compendium of Synthetic Organic Methods”, Vols. 1-8 (John Wiley and Sons, 1971-1996); “Beilstein Handbook of Organic Chemistry,” Beilstein Institute of Organic Chemistry, Frankfurt, Germany; Feiser *et al.*, “Reagents for Organic Synthesis,” Volumes 1-21, Wiley Interscience; Trost *et al.*, “Comprehensive Organic Synthesis,” Pergamon Press, 1991; “Theilheimer’s Synthetic Methods of Organic Chemistry,”

Volumes 1-45, Karger, 1991; March, "Advanced Organic Chemistry," Wiley Interscience, 1991; Larock "Comprehensive Organic Transformations," VCH Publishers, 1989; Paquette, "Encyclopedia of Reagents for Organic Synthesis," 3d Edition, John Wiley & Sons, 1995). Other methods for synthesis of the compounds described herein and/or starting materials are either described in the art or will be readily apparent to the skilled artisan.

[0131] A typical synthesis is depicted in Scheme I, wherein 2 equivalents of a phenol or phenol equivalent are condensed with 1 equivalent of a phthalic anhydride or equivalent under essentially acid anhydrous conditions.



Scheme I

[0132] Generally, the phenol and anhydride are condensed in the presence of an acid under anhydrous conditions. For example, polyphosphoric acid and zinc chloride can be utilized. The carbon atom at 4-position -position with respect to the aromatic hydroxyl group must not be substituted as it is necessary for reaction. Polyphosphoric acid acts as a condensing agent as well as reaction medium. The reaction with only polyphosphoric acid afforded tarry products but when very small amount of zinc chloride was added to polyphosphoric acid, clean product was isolated. Very small amount of zinc chloride was found to increase yield and purity of the product. Polyphosphoric acid can be replaced with orthophosphoric acid, chlorosulfonic acid, methane sulfonic acid, trifluoroacetic acid or other acids under anhydrous conditions. Suitable solvents include non-protic solvents known in the art such as tetrahydrofuran, dioxane, methylene chloride, ether, etc.

[0133] The reaction proceeds with the formation of an isobenzofuranone (Ia), which is then treated with a base under aqueous conditions. The salt can be isolated or the solution can be acidified to produce the protonated phenol/carboxylic acid. For example, one molar equivalent of Ia was condensed with either two molar equivalent of sodium hydroxide in 85% ethanol or two molar equivalent of sodium ethoxide in ethanol. The products are generally solids and can be easily purified via filtration, crystallization, and other methods known in the art.

[0134] Suitable phenols include, but are not limited to 2-nitrophenol, 3-nitrophenol, 2-chlorophenol, 3-chlorophenol, 2-bromophenol, 3-bromophenol, 2-iodophenol, 3-iodophenol, 2-fluorophenol, 3-fluorophenol, 2-aminophenol, 3-aminophenol, 2-acetamidophenol, 3-acetamidophenol, 2-cyanophenol, 3-cyanophenol, 2-methylphenol, 3-methylphenol, 2-ethylphenol, 3-ethylphenol, 2-propylphenol, 3-propylphenol, 2-isopropylphenol, 3-isopropylphenol, 2-butylphenol, 3-butylphenol, 2-isobutylphenol, 3-isobutylphenol, 2-pentylphenol, 3-pentylphenol, 2-hexylphenol, 3-hexylphenol, 2-heptylphenol, 3-heptylphenol, 2-octylphenol, 3-octylphenol, 2-nonylphenol, 3-nonylphenol, 2-decylphenol, 3-

decylphenol, 2-decylphenol, 2-methoxyphenol, 3-methoxyphenol, 2-ethoxyphenol, 3-ethoxyphenol, 2-propoxyphenol, 3-propoxyphenol, 2-isopropoxyphenol, 3-isopropoxyphenol, 2-butoxyphenol, 3-butoxyphenol, 2-isobutoxyphenol, 3-isobutoxyphenol, 2-allylphenol, 3-allylphenol, 2-vinylphenol, 3-vinylphenol, 2-phenylphenol, 3-phenylphenol, 2-phenoxyphenol, 3-phenoxyphenol, 2-cyclopropylphenol, 3-cyclopropylphenol, 2-cyclobutylphenol, 3-cyclobutylphenol, 2-cyclopentylphenol, 3-cyclopentylphenol, 2-cyclohexylphenol, 3-cyclohexylphenol, 2-cycloheptylphenol, 3-cycloheptylphenol, 2-cyclooctylphenol, 3-cyclooctylphenol, 2-cyclononylphenol, 3-cyclononylphenol, 2-cyclodecylphenol, 3-cyclodecylphenol, 2,3-dinitrophenol, 2,5-dinitrophenol, 2,6-dinitrophenol, 2,3-dimethylphenol, 2,5-dimethylphenol, 2,6-dimethylphenol, 2,3-diethylphenol, 2,5-diethylphenol, 2,6-diethylphenol, 2,3-dipropylphenol, 2,5-dipropylphenol, 2,6-dipropylphenol, 2,3-diisopropylphenol, 2,5-diisopropylphenol, 2,6-diisopropylphenol, 2,3-dibutylphenol, 2,5-dibutylphenol, 2,6-dibutylphenol, 2,3-diisobutylphenol, 2,5-diisobutylphenol, 2,6-diisobutylphenol, 2,3-dipentylphenol, 2,5-dipentylphenol, 2,6-dipentylphenol, 2,3-dihexylphenol, 2,5-dihexylphenol, 2,6-dihexylphenol, 2,3-diheptylphenol, 2,5-diheptylphenol, 2,6-diheptylphenol, 2,3-dioctylphenol, 2,5-dioctylphenol, 2,6-dioctylphenol, 2,3-dinonylphenol, 2,5-dinonylphenol, 2,6-dinonylphenol, 2,3-didecylphenol, 2,5-didecylphenol, 2,6-didecylphenol, 2,3-dimethoxyphenol, 2,5-dimethoxyphenol, 2,6-dimethoxyphenol, 2,3-diethoxyphenol, 2,5-diethoxyphenol, 2,6-diethoxyphenol, 2,3-dipropoxyphenol, 2,5-dipropoxyphenol, 2,6-dipropoxyphenol, 2,3-diisopropoxyphenol, 2,5-diisopropoxyphenol, 2,6-diisopropoxyphenol, 2,3-dibutoxyphenol, 2,5-dibutoxyphenol, 2,6-dibutoxyphenol, 2,3-diisobutoxyphenol, 2,5-diisobutoxyphenol, 2,6-diisobutoxyphenol, 2,3-dipentoxyphenol, 2,5-dipentoxyphenol, 2,6-dipentoxyphenol, 2,3-dihexoxyphenol, 2,5-dihexoxyphenol, 2,6-dihexoxyphenol, 2,3-diheptoxyphenol, 2,5-diheptoxyphenol, 2,6-diheptoxyphenol, 2,3-dioctoxyphenol, 2,5-dioctoxyphenol, 2,6-dioctoxyphenol, 2,3-dinonoxoxyphenol, 2,5-dinonoxoxyphenol, 2,6-dinonoxoxyphenol, 2,3-didecyloxyphenol, 2,5-didecyloxyphenol, 2,6-didecyloxyphenol, 2,3-dichlorophenol, 2,5-dichlorophenol,

2,6-dichlorophenol, 2,3-dibromophenol, 2,5-dibromophenol, 2,6-dibromophenol, 2,3-diiodophenol, 2,5-diiodophenol, 2,6-diiodophenol, 2,3-difluorophenol, 2,5-difluorophenol, 2,6-difluorophenol, 2,3-diaminophenol, 2,5-diaminophenol, 2,6-diaminophenol, 2,3-diacetamidophenol, 2,5-diacetamidophenol, 2,6-diacetamidophenol, 2,3-dicyanophenol, 2,5-dicyanophenol, 2,6-dicyanophenol, 2,3-diallylphenol, 2,5-diallylphenol, 2,6-diallylphenol, 2,3-divinylphenol, 2,5-divinylphenol, 2,6-divinylphenol, 2,3-diphenylphenol, 2,5-diphenylphenol, 2,6-diphenylphenol, 2,3-diphenoxyphenol, 2,5-diphenoxyphenol, 2,6-diphenoxyphenol, 2,3-dicyclopropylphenol, 2,5-dicyclopropylphenol, 2,6-dicyclopropylphenol, 2,3-dicyclobutylphenol, 2,5-dicyclobutylphenol, 2,6-dicyclobutylphenol, 2,3-dicyclopentylphenol, 2,5-dicyclopentylphenol, 2,6-dicyclopentylphenol, 2,3-dicyclohexylphenol, 2,5-dicyclohexylphenol, 2,6-dicyclohexylphenol, 2,3-dicycloheptylphenol, 2,5-dicycloheptylphenol, 2,6-dicycloheptylphenol, 2,3-dicyclooctylphenol, 2,5-dicyclooctylphenol, 2,6-dicyclooctylphenol, 2,3-dicyclononylphenol, 2,5-dicyclononylphenol, 2,6-dicyclononylphenol, 2,3-dicyclodecylphenol, 2,5-dicyclodecylphenol, 2,6-dicyclodecylphenol, 2,3,5-trimethylphenol, 2,3,6-trimethylphenol, 2,3,5-triethylphenol, 2,3,6-triethylphenol, 2,3,5-tripropylphenol, 2,3,6-tripropylphenol, 2,3,5-tributylphenol, 2,3,6-tributylphenol, 2,3,5-trichlorophenol, 2,3,6-trichlorophenol, 2,3,5-tribromophenol, 2,3,6-tribromophenol, 2,3,5-triiodophenol, 2,3,6-triiodophenol, 2,3,5-trifluorophenol, 2,3,6-trifluorophenol, 2,3,5-trivinylphenol, 2,3,6-trivinylphenol, 2,3,5-triallylphenol, 2,3,6-triallylphenol, 2,3,5-triphenylphenol, 2,3,6-triphenylphenol, 2,3,5-triphenoxyphenol, 2,3,6-triphenoxyphenol, 2,3,5-trimethoxyphenol, 2,3,6-trimethoxyphenol, 2,3,5-triethoxyphenol, 2,3,6-triethoxyphenol, 2,3,5-tripropoxyphenol, 2,3,6-tripropoxyphenol, 2,3,5-tributoxyphenol, 2,3,6-tributoxyphenol, 2,3,5-trinitrophenol, 2,3,6-trinitrophenol, 2,3,5-triaminophenol, 2,3,6-triaminophenol, 2,3,5-triacetamidophenol, 2,3,6-triacetamidophenol, 2,3,5-tricyanophenol, 2,3,6-tricyanophenol, 3-(N,N-diethylamino)phenol, 2-tert-butyl-5-methylphenol, 2-tert-butyl-6-methylphenol, 3-methyl-2-nitrophenol, 5-methyl-2-nitrophenol, 6-methyl-2-nitrophenol, 3-ethyl-2-nitrophenol, 5-ethyl-2-nitrophenol, 6-ethyl-2-

nitrophenol, 3-methoxyl-2-nitrophenol, 5-methoxy-2-nitrophenol, 6-methoxy-2-nitrophenol, 1-naphthol, 2-naphthol, 2-nitro-1-naphthol, 3-nitro-1-naphthol, 5-nitro-1-naphthol, 6-nitro-1-naphthol, 7-nitro-1-naphthol, 8-nitro-1-naphthol, 2-methyl-1-naphthol, 3-methyl-1-naphthol, 5-methyl-1-naphthol, 6-methyl-1-naphthol, 7-methyl-1-naphthol, 8-methyl-1-naphthol, 2-methoxy-1-naphthol, 3-methoxy-1-naphthol, 5-methoxy-1-naphthol, 6-methoxy-1-naphthol, 7-methoxy-1-naphthol, 8-methoxy-1-naphthol, 2-chloro-1-naphthol, 3-chloro-1-naphthol, 5-chloro-1-naphthol, 6-chloro-1-naphthol, 7-chloro-1-naphthol, 8-chloro-1-naphthol, 2-bromo-1-naphthol, 3-bromo-1-naphthol, 5-bromo-1-naphthol, 6-bromo-1-naphthol, 7-bromo-1-naphthol, 8-bromo-1-naphthol, 2-iodo-1-naphthol, 3-iodo-1-naphthol, 5-iodo-1-naphthol, 6-iodo-1-naphthol, 7-iodo-1-naphthol, 8-iodo-1-naphthol, 2-fluoro-1-naphthol, 3-fluoro-1-naphthol, 5-fluoro-1-naphthol, 6-fluoro-1-naphthol, 7-bromo-1-naphthol, 8-fluoro-1-naphthol, 2-cyano-1-naphthol, 3-cyano-1-naphthol, 5-cyano-1-naphthol, 6-cyano-1-naphthol, 7-cyano-1-naphthol, 8-cyano-1-naphthol, 8-hydroxyquinaldine and 2-quinoxalinol.

[0135] The term “phenol equivalent” is intended to include those compounds where, as described above, R^2 and R^3 , for example, form an aromatic, heterocyclic, or non-aromatic ring. Suitable compounds include naphthols for example.

[0136] Suitable phthalic anhydrides include but are not limited to phthalic anhydride, 3-nitrophthalic anhydride, 4-nitrophthalic anhydride, 5-nitrophthalic anhydride, 6-nitrophthalic anhydride, 3-chlorophthalic anhydride, 4-chlorophthalic anhydride, 5-chlorophthalic anhydride, 6-chlorophthalic anhydride, 3-bromophthalic anhydride, 4-bromophthalic anhydride, 5-bromophthalic anhydride, 6-bromophthalic anhydride, 3-iodophthalic anhydride, 4-iodophthalic anhydride, 5-iodophthalic anhydride, 6-iodophthalic anhydride, 3-fluorophthalic anhydride, 4-fluorophthalic anhydride, 5-fluorophthalic anhydride, 6-fluorophthalic anhydride, 3-methylphthalic anhydride, 4-methylphthalic anhydride, 5-methylphthalic anhydride, 6-methylphthalic anhydride, 3-ethylphthalic anhydride, 4-ethylphthalic anhydride, 5-ethylphthalic anhydride, 6-ethylphthalic anhydride, 3-methoxyphthalic anhydride, 4-methoxyphthalic

anhydride, 5-methoxyphthalic anhydride, 6-methoxyphthalic anhydride, 3-cyanophthalic anhydride, 4-cyanophthalic anhydride, 5-cyanophthalic anhydride, 6-cyanophthalic anhydride, 3-aminophthalic anhydride, 4-aminophthalic anhydride, 5-aminophthalic anhydride, 6-aminophthalic anhydride, 3-acetamidophthalic anhydride, 4-acetamidophthalic anhydride, 5-acetamidophthalic anhydride, 6-acetamidophthalic anhydride, 3,4,5,6-tetrachlorophthalic anhydride, 3,4,5,6-tetrabromophthalic anhydride, 3,4,5,6-tetraiodophthalic anhydride, 3,4,5,6-tetrafluorophthalic anhydride, 3,4,5,6-tetranitrophthalic anhydride, 3,4,5,6-tetramethylphthalic anhydride, 3,4,5,6-tetraethylphthalic anhydride, 3,4,5,6-tetramethoxyphthalic anhydride, 3,4,5,6-tetracyanophthalic anhydride, 3,4,5,6-tetraaminophthalic anhydride, 3,4,5,6-tetraacetamidophthalic anhydride, naphthalic anhydride, 2-chloronaphthalic anhydride, 3-chloronaphthalic anhydride, 4-chloronaphthalic anhydride, 5-chloronaphthalic anhydride, 6-chloronaphthalic anhydride, 7-chloronaphthalic anhydride, 2-bromonaphthalic anhydride, 3-bromonaphthalic anhydride, 4-bromonaphthalic anhydride, 5-bromonaphthalic anhydride, 6-bromonaphthalic anhydride, 7-bromonaphthalic anhydride, 2-iodonaphthalic anhydride, 3-iodonaphthalic anhydride, 4-iodonaphthalic anhydride, 5-iodonaphthalic anhydride, 6-iodonaphthalic anhydride, 7-iodonaphthalic anhydride, 2-fluoronaphthalic anhydride, 3-fluoronaphthalic anhydride, 4-fluoronaphthalic anhydride, 5-fluoronaphthalic anhydride, 6-fluoronaphthalic anhydride, 7-fluoronaphthalic anhydride, 2-nitronaphthalic anhydride, 3-nitronaphthalic anhydride, 4-nitronaphthalic anhydride, 5-nitronaphthalic anhydride, 6-nitronaphthalic anhydride and 7-nitronaphthalic anhydride.

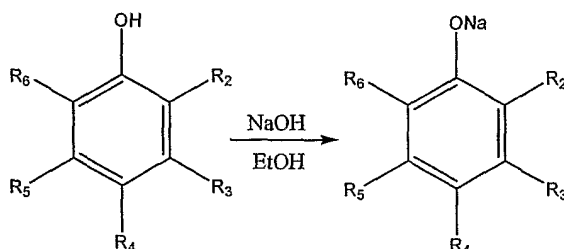
[0137] The term “phthalic anhydride equivalent” is intended to include those compounds where, as described above, R⁷ and R⁸, for example, form an aromatic, heterocyclic, or non-aromatic ring. Suitable compounds include naphthols for example.

Synthesis of Phenols and Hydrazides

[0138] The compounds of the invention may be obtained *via* synthetic methods illustrated below. It should be understood that in R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} and R^{15} are as previously defined for structural formulae (II), (III), (IIIa) and (IV).

[0139] Starting materials useful for preparing compounds of the invention and intermediates thereof are commercially available or can be prepared by well-known synthetic methods (*see, e.g.*, Harrison *et al.*, "Compendium of Synthetic Organic Methods", Vols. 1-8 (John Wiley and Sons, 1971-1996); "Beilstein Handbook of Organic Chemistry," Beilstein Institute of Organic Chemistry, Frankfurt, Germany; Feiser *et al.*, "Reagents for Organic Synthesis," Volumes 1-21, Wiley Interscience; Trost *et al.*, "Comprehensive Organic Synthesis," Pergamon Press, 1991; "Theilheimer's Synthetic Methods of Organic Chemistry," Volumes 1-45, Karger, 1991; March, "Advanced Organic Chemistry," Wiley Interscience, 1991; Larock "Comprehensive Organic Transformations," VCH Publishers, 1989; Paquette, "Encyclopedia of Reagents for Organic Synthesis," 3d Edition, John Wiley & Sons, 1995). Other methods for synthesis of the compounds described herein and/or starting materials are either described in the art or will be readily apparent to the skilled artisan.

[0140] A typical synthesis for substituted phenols is depicted in Scheme II, wherein a phenol is treated with a base to form the phenolic salt. Advantageously, the phenolic salts are water soluble, which is useful in the applications detailed throughout the specification.



Scheme II

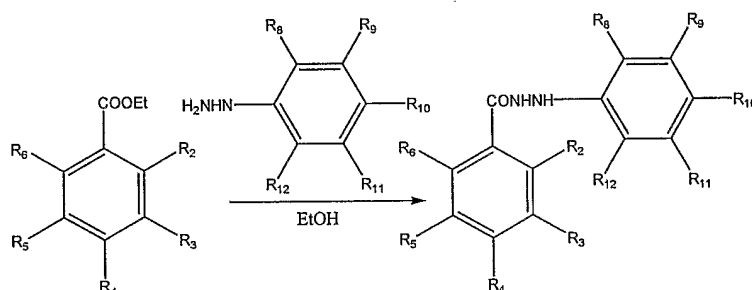
[0141] Generally, the phenol mixed with the base and the salt is formed. The solution may be heated to facilitate the rate of reaction.

[0142] Suitable phenols include, but are not limited to 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2-bromophenol, 3-bromophenol, 4-bromophenol, 2-iodophenol, 3-iodophenol, 4-iodophenol, 2-aminophenol, 3-aminophenol, 4-aminophenol, 2-cyanophenol, 3-cyanophenol, 4-cyanophenol, 2-vinylphenol, 3-vinylphenol, 4-vinylphenol, 2,3-dichlorophenol, 2,4-dichlorophenol, 2,5-dichlorophenol, 2,6-dichlorophenol, 2,3-dibromophenol, 2,4-dibromophenol, 2,5-dibromophenol, 2,6-dibromophenol, 2,3-diiodophenol, 2,4-diiodophenol, 2,5-diiodophenol, 2,6-diiodophenol, 2,3-diaminophenol, 2,4-diaminophenol, 2,5-diaminophenol, 2,6-diaminophenol, 2,3-dicyanophenol, 2,4-dicyanophenol, 2,5-dicyanophenol, 2,6-dicyanophenol, 2,3-divinylphenol, 2,4-divinylphenol, 2,5-divinylphenol, 2,6-divinylphenol, 2,3-diphenylphenol, 2,3,4-trichlorophenol, 2,3,5-trichlorophenol, 2,3,6-trichlorophenol, 2,3,4-tribromophenol, 2,3,5-tribromophenol, 2,3,6-tribromophenol, 2,3,4-triiodophenol, 2,3,5-triiodophenol, 2,3,6-triiodophenol, 2,3,4-trivinylphenol, 2,3,5-trivinylphenol, 2,3,6-trivinylphenol, 2,3,4-trinitrophenol, 2,3,5-trinitrophenol, 2,3,6-trinitrophenol, 2,3,4-triaminophenol, 2,3,5-triaminophenol, 2,3,6-triaminophenol, 2,3,4-tricyanophenol, 2,3,5-tricyanophenol, 2,3,6-tricyanophenol, 3-(N,N-diethylamino)phenol, 3-methyl-2-nitrophenol, 5-methyl-2-nitrophenol, 6-methyl-2-nitrophenol, 3-ethyl-2-nitrophenol, 5-ethyl-2-nitrophenol, 6-ethyl-2-nitrophenol, 3-methoxyl-2-nitrophenol, 5-methoxy-2-nitrophenol, 6-methoxy-2-nitrophenol, 2-nitro-1-naphthol, 3-nitro-1-naphthol, 4-nitro-1-naphthol, 5-nitro-1-naphthol, 6-nitro-1-naphthol, 7-nitro-1-naphthol, 8-nitro-1-naphthol, 2-chloro-1-naphthol, 3-chloro-1-naphthol, 4-chloro-1-naphthol, 5-chloro-1-naphthol, 6-chloro-1-naphthol, 7-chloro-1-naphthol, 8-chloro-1-naphthol, 2-bromo-1-naphthol, 3-bromo-1-naphthol, 4-bromo-1-naphthol, 5-bromo-1-naphthol, 6-bromo-1-naphthol, 7-bromo-1-naphthol, 8-bromo-1-naphthol, 2-iodo-1-naphthol, 3-iodo-1-naphthol, 4-iodo-1-naphthol, 5-iodo-1-naphthol, 6-iodo-1-naphthol, 7-iodo-1-naphthol, 8-

iodo-1-naphthol, 2-cyano-1-naphthol, 3-cyano-1-naphthol, 4-cyano-1-naphthol, 5-cyano-1-naphthol, 6-cyano-1-naphthol, 7-cyano-1-naphthol, 8-cyano-1-naphthol and 8-hydroxyquinoline.

[0143] The term “phenol equivalent” is intended to include those compounds where, as described above, R^2 and R^3 , for example, form an aromatic, heterocyclic, or non-aromatic ring. Suitable compounds include naphthols for example.

[0144] A typical synthesis of hydrazines is depicted in Scheme III, where a hydrazine (NH_2NH-R^{15} , wherein R^{15} can be a hydrogen atom or as described above) and an ester are condensed to form the hydrazide.



Scheme III

[0145] Typically the ester and the hydrazine are combined in a solvent, such as a protic solvent, e.g., an alcohol, such as ethanol, and heated, e.g., to reflux. Upon cooling, the hydrazide generally precipitates from solution and can be collected.

[0146] Suitable salicylic derivatives include, but not limited to salicylic acid, 3-methylsalicylic acid, 4-methylsalicylic acid, 5-methylsalicylic acid, 6-methylsalicylic acid, 3-ethylsalicylic acid, 4-ethylsalicylic acid, 5-ethylsalicylic acid, 6-ethylsalicylic acid, 3-propylsalicylic acid, 4-propylsalicylic acid, 5-propylsalicylic acid, 6-propylsalicylic acid, 3-isopropylsalicylic acid, 4-isopropylsalicylic acid, 5-isopropylsalicylic acid, 6-isopropylsalicylic acid, 3-butylsalicylic acid, 4-butylsalicylic acid, 5-butylsalicylic acid, 6-butylsalicylic acid, 3-isobutylsalicylic acid, 4-isobutylsalicylic acid, 5-isobutylsalicylic acid, 6-isobutylsalicylic acid, 3-methoxysalicylic acid, 4-methoxysalicylic acid, 5-

methoxysalicylic acid, 6-methoxysalicylic acid, 3-ethoxysalicylic acid, 4-ethoxysalicylic acid, 5-ethoxysalicylic acid, 6-ethoxysalicylic acid, 3-propoxysalicylic acid, 4-propoxysalicylic acid, 5-propoxysalicylic acid, 6-propoxysalicylic acid, 3-butoxysalicylic acid, 4-butoxysalicylic acid, 5-butoxysalicylic acid, 6-butoxysalicylic acid, 3-nitrosalicylic acid, 4-nitrosalicylic acid, 5-nitrosalicylic acid, 6-nitrosalicylic acid, 3-chlorosalicylic acid, 4-chlorosalicylic acid, 5-chlorosalicylic acid, 6-chlorosalicylic acid, 3-bromosalicylic acid, 4-bromosalicylic acid, 5-bromosalicylic acid, 6-bromosalicylic acid, 3-iodosalicylic acid, 4-iodosalicylic acid, 5-iodosalicylic acid, 6-iodosalicylic acid, 3-fluorosalicylic acid, 4-fluorosalicylic acid, 5-fluorosalicylic acid, 6-fluorosalicylic acid, 3-aminosalicylic acid, 4-aminosalicylic acid, 5-aminosalicylic acid, 6-aminosalicylic acid, 3-acetamidosalicylic acid, 4-acetamidosalicylic acid, 5-acetamidosalicylic acid, 6-acetamidosalicylic acid, 3-cyanosalicylic acid, 4-cyanosalicylic acid, 5-cyanosalicylic acid, 6-cyanosalicylic acid, 3-sulfosalicylic acid, 4-sulfosalicylic acid, 5-sulfosalicylic acid, 6-sulfosalicylic acid, 3,5-dimethylsalicylic acid, 3,5-diethylsalicylic acid, 3,5-dipropylsalicylic acid, 3,5-dibutylsalicylic acid, 3,5-dimethoxysalicylic acid, 3,5-diethoxysalicylic acid, 3,5-dipropoxysalicylic acid, 3,5-dibutoxysalicylic acid, 3,5-dichlorosalicylic acid, 3,5-dibromosalicylic acid, 3,5-diiodosalicylic acid, 3,5-difluorosalicylic acid, 3,5-dinitrosalicylic acid, 3,5-diaminosalicylic acid, 3,5-diacetamidosalicylic acid, 3,5-dicyanosalicylic acid, 3,5-disulfosalicylic acid, substituted/unsubstituted alkyl salicylic acid, substituted/unsubstituted alkoxy salicylic acid, substituted/unsubstituted aryl salicylic acid, substituted/unsubstituted cycloalkyl salicylic acid and substituted/unsubstituted hetaryl salicylic acid.

[0147] Suitable hydrazines include but not limited to hydrazine hydrate, 4-nitrophenylhydrazine, 3-nitrophenylhydrazine, 2-nitrophenylhydrazine, 4-nitrobenzoic hydrazide, 3-nitrobenzoic hydrazide, 2-nitrobenzoic hydrazide, p-toluenesulfonylhydrazide, m-toluenesulfonylhydrazide, o-toluenesulfonylhydrazide, 2,4-dinitrophenylhydrazine (2,4-DNP), 1-naphthoic hydrazide, 2-naphthoic hydrazide, nicotinic hydrazide, substituted/unsubstituted alkyl

hydrazide, substituted/unsubstituted alkoxy hydrazide, substituted/unsubstituted aryl hydrazide, substituted/unsubstituted cycloalkyl hydrazide and substituted/unsubstituted hetaryl hydrazide.

[0148] Where the painting composition is intended to be "colored", selection of an appropriate basic material is important for color change of acidic dye indicators in the colored compositions of the present invention. Desirable basic reagents, which should readily volatilize at ambient temperatures for use in the present compositions, include, but are not limited to, aminoalcohols, such as alkylamines, such as methylamine, dimethylamine, ethylamine, diethylamine, triethylamine, ethyleneamine, diethyleneamine, morpholine, ammonia, triethanolamine.

[0149] The selection of the kind and the amount of basic reagent used enables control of fading time of the color. Suitable basic reagents which readily volatilize at ambient temperatures, typically have a vapor pressure higher than about 10 mm Hg at 20°C. The selection of the base also depends on solubility in water, toxicity and odor. Therefore, aminoalcohols useful in the compositions of the present invention include, but are not limited to triethanolamine (TEA) and/or diethylamine. TEA, for example, is clear, non-toxic and does not emit a noxious odor. Some of the surface active agents, e.g., Colonial SLS, are alkaline nature and can serve as the basic reagent.

[0150] In painting compositions where color is not desired (clear to color), a base is not included in the composition, but is provided, for example) by the surface of the substrate written upon.

[0151] Alternatively, the painting composition can be basic and highly colored by use of a fugative base or a base that is not fugitive in nature, such as a metal hydroxide. The pH of the substrate will then determine whether the color of the painting composition is unchanged upon application, disappears or changes color. Therefore, by choice of dye and pH of the painting composition and pH of the surface of the substrate, painting compositions are provided that can be colored and remain so, can change from color to clear, or color to color, or uncolored to a color. It is the combination of the acid-base dye and the reactive

substrate surface that determines how the color change, or maintenance, is effected.

[0152] The painting compositions of the present invention generally include a resin which is water soluble, non-toxic, forms a film at room temperature and serves as thickener. The water soluble film forming agents provide the painting compositions with either low viscosity paints or high viscosity paints for a wide variety of applications.

[0153] Representative examples of typical film forming agents/thickeners (binders) employed in the paint compositions of the invention include, but are not limited to, polyvinylalcohol, polyvinylpyrrolidone, polyoxyethylene, polyvinyl acetate, gelatin, gum arabic, rosin, rosin-modified maleic acid resins, rosin-modified phenol resins, rosin esters, hydrogenated rosins, various cellulosic resins, methyl cellulose, ethyl cellulose, acetyl cellulose, propyl cellulose, butyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, higher alkyl cellulose, sodium carboxymethyl cellulose, cellulose ethers, cellulose esters, cellulose acetobutyrate, petroleum resins, various phenol resins, starches and derivatives thereof, acrylics such as polyacrylates and/or polymethacrylates, polyurethanes, styrenic polymers, acrylate/styrenic copolymers, methacrylate/styrenic copolymers, polyvinyl chloride, vinylchloride/styrenic copolymers, alkyds, polyesters, epoxy polymers, polyamides, polyimide, alkylated ureas, benzoguanamines, melamine-formaldehydes, phenolic resins and the like. Mixtures of two or more of these film forming agents can also be employed in the present invention.

[0154] Suitable polymerized vinyl containing materials include, for example, polyolefins, poly(vinyl halides), vinyl halide copolymers, poly(vinyl) esters, poly(vinyl) alcohol, poly(vinyl) acetals, poly(vinyl) acetate, poly(vinyl) chloride, poly(vinyl) formal, poly(vinyl) butyrals, poly(vinyl) ethers and polystyrenes.

[0155] Suitable alkyd resins include, for example, styrene modified alkyd resins, vinyl modified alkyd resins, silicon modified alkyd resins, thixotropic

alkyd resins, urethane alkyd resins, alkyd resins with highly branched carboxylic acids and waterborne alkyd resins.

[0156] In particular, film forming agents include, but are not limited to PVP K-15, PVP K-30, PVP K-90, polyvinylpyrrolidone, manufactured by ISP (International Specialty Products), Wayne, NJ, Elvanol 40-05, Elvanol 40-16, Elvanol 40-40, Elvanol 70-14, Elvanol 70-27, Elvanol 60-30, Elvanol 70-03, Elvanol 70-04, Elvanol 70-06, Elvanol 70-20, Elvanol 70-30, Elvanol 70-62, Elvanol 70-63, Elvanol 70-75, Elvanol 71-30, Elvanol 90-50, Elvanol 50-14, Elvanol 50-26, Elvanol 50-42, Elvanol 51-03, Elvanol 51-04, Elvanol 51-05, Elvanol 51-08, Elvanol 52-22, Elvanol 75-15, Elvanol 85-82, Elvanol 85-91, polyvinylalcohol, manufactured by DuPont, Wilmington, DE, Celvol 125, Celvol 165, Celvol 350, Celvol 325, Celvol 310, Celvol 305, Celvol 103, Celvol 107, Celvol 203, Celvol 205, Celvol 418, Celvol 425, Celvol 443, Celvol 502, Celvol 504, Celvol 508, Celvol 513, Celvol 518, Celvol 523, Celvol 530, Celvol 540, Celvol 805, Celvol 823, Celvol 840, polyvinylalcohol, manufactured by Celanese Chemicals, Dallas TX, Polyox WSR N-10, Polyox WSR N-80, Polyox WSR N-750, Polyox WSR N-3000, Polyox WSR 205, Polyox WSR -1105, Polyox WSR N-12K, Polyox WSR N-60K, Polyox WSR-301, Polyox WSR-303, Polyox WSR-308, polyethylene oxide, manufactured by Dow Chemical Co., Midland, MI, K4484, water soluble starch, manufactured by National Starch & Chemicals, Bridgewater, NJ, Dri-sweet 42, water soluble starch, manufactured by American Maize and ICB 3000, water soluble starch, manufactured by Staley.

[0157] The film forming agent/thickener present in the painting composition of the invention are generally in a range from about 2% up to about 99% by weight, in particular from about 5% to about 90% by weight and more particularly from about 10% to about 80% by weight.

[0158] In one aspect, film forming agents/thickeners useful in the painting compositions of the invention include, but are not limited to, cellulose ethers or mixtures with other surface-active agents, which are water soluble. Cellulose ether surface-active agents have unique thickening and film forming properties which make them ideal for color changing paint applications. Cellulose ethers

used in the present invention include methyl cellulose, ethyl cellulose, propyl cellulose, butyl cellulose, higher alkyl, aryl, alkoxy, cycloalkyl celluloses, hydroxypropyl cellulose, hydroxybutyl cellulose or mixtures thereof.

[0159] Commercial cellulose ether film forming agents/thickeners include, but are not limited to, Methocel A4M, methyl cellulose, Methocel F4M, hydroxypropyl methylcellulose, Methocel K4M, hydroxypropyl methylcellulose, manufactured by Dow Chemical Co., Midland, MI; Natrosol, hydroxyethyl cellulose, Klucel, hydroxypropyl cellulose, Aqualon Cellulose Gum, sodium carboxymethyl cellulose, Hercules Inc., Wilmington, DE; Elfacos CD 481, ethyl 2-hydroxyethyl ether cellulose, manufactured by Akzo Nobel, Chicago, IL.

[0160] Cellulose ether film forming agents/thickeners are generally present in amounts from about 2% up to about 99% by weight in the compositions of the invention. Suitable concentrations of cellulose ether surface-active agents are in the range of about 5% to about 90% by weight and from about 10% to about 80% by weight. A particularly useful cellulosic ether film forming agent in the painting compositions is Methocel A4M.

[0161] The painting compositions of the invention often include surface active agent(s) (surfactants). Suitable surface-active agents include anionic, cationic, nonionic or zwitterionic compounds and combinations thereof. The surface-active agent can be either polymeric or non-polymeric.

[0162] The term "surface active agent" is recognized in the relevant art to include those compounds which modify the nature of surfaces, e.g. reducing the surface tension of water. Surface active agents are generally classified into four types: cationic (e.g. modified onium salts, where part of the molecule is hydrophilic and the other consists of straight or branches long hydrocarbon chains such as hexadecyltrimethyl bromide), anionic, also known as amphiphatic agents (e.g., alkyl or aryl or alkylarylsulfonates, carboxylates, phosphates), nonionic (e.g., polyethylene oxides, alcohols) and ampholytic or amphoteric (e.g. dodecyl-beta-alanine, such that the surface-active agent contains a zwitterionic group). One or more surface-active agents can be used in the present invention.

[0163] Cationic surface-active agents useful as surface tension reducing agents in the present invention include long chain hydrocarbons which contain quaternarized heteroatoms, such as nitrogen. Suitable cationic surface-active agents include quaternary ammonium compounds in which typically one of the groups linked to the nitrogen atom is a C12-C18 alkyl group and the other three groups are short chained alkyl groups.

[0164] Anionic surface-active agents (amphiphatic agents) are characterized by a single lipophilic chain and a polar head group which can include sulfate, sulfonate, phosphate, phosphonate and carboxylate. Exemplary compounds include linear sodium alkyl benzene sulfonate (LAS), linear alkyl sulfates and phosphates, such as sodium lauryl sulfate (SLS) and linear alkyl ethoxy sulfates. Additional examples of anionic surface-active agents include substituted ammonium (e.g., mono-, di-, and tri-ethanolammonium), alkali metal and alkaline earth metal salts of C6-C20 fatty acids and rosin acids, linear and branched alkyl benzene sulfonates, alkyl ether sulfates, alkane sulfonates, olefin sulfonates, hydroxyalkane sulfonates, fatty acid monoglyceride sulfates, alkyl glyceryl ether sulfates, acyl sarcosinates, acyl N-methyltaurides, and alkylaryl sulfonated surface-active agents, such as alkylbenzene sulfonates.

[0165] Nonionic surface-active agents do not dissociate but commonly derive their hydrophilic portion from polyhydroxy or polyalkyloxy structures. Suitable examples of polyhydroxy (polyhydric) compounds include ethylene glycol, butylene glycol, 1,3-butylene glycol, propylene glycol, glycerine, 2-methyl-1,3-propane diol, glycerol, mannitol, corn syrup, beta-cyclodextrin, and amyloextrin. Suitable examples of polyalkyloxy compounds include diethylene glycol, dipropylene glycol, polyethylene glycols, polypropylene glycols and glycol derivatives.

[0166] Other suitable nonionic surface-active agents include other linear ethoxylated alcohols with an average length of 6 to 16 carbon atoms and averaging about 2 to 20 moles of ethylene oxide per mole of alcohol; linear and branched, primary and secondary ethoxylated, propoxylated alcohols with an average length of about 6 to 16 carbon atoms and averaging 0-10 moles of

ethylene oxide and about 1 to 10 moles of propylene oxide per mole of alcohol; linear and branched alkylphenoxy (polyethoxy) alcohols, otherwise known as ethoxylated alkylphenols, with an average chain length of 8 to 16 carbon atoms and averaging 1.5 to 30 moles of ethylene oxide per mole of alcohol; and mixtures thereof.

[0167] Additionally, suitable nonionic surface-active agents include polyoxyethylene carboxylic acid esters, fatty acid glycerol esters, fatty acid and ethoxylated fatty acid alkanolamides. Block copolymers of propylene oxide and ethylene oxide, and block polymers of propylene oxide and ethylene oxide with propoxylated ethylene diamine are also included as acceptable nonionic surface-active agents. Semi-polar nonionic surface-active agents like amine oxides, phosphine oxides, sulfoxides, and their ethoxylated derivatives are included within the scope of the invention.

[0168] Suitable amphoteric and zwitterionic surface-active agents which contain an anionic water-solubilizing group, a cationic group and a hydrophobic organic group include amino carboxylic acids and their salts, amino dicarboxylic acids and their salts, alkylbetaines, alkyl aminopropylbetaines, sulfobetaines, alkyl imidazolinium derivatives, certain quaternary ammonium compounds, certain quaternary phosphonium compounds and certain tertiary sulfonium compounds.

[0169] Examples of anionic, nonionic, cationic and amphoteric surface-active agents that are suitable for use in the present invention are described in Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, Volume 22, pages 347-387, and McCutcheon's Detergents and Emulsifiers, North American Edition, 1983, both of which are incorporated herein by reference.

[0170] Typical concentration ranges of surface-active agent that are useful in the present painting compositions are from about 0.1 parts by weight to about 15 parts by weight, from about 0.5 part by weight to about 10 parts by weight, and from about 1 parts by weight to about 5 parts by weight. Surface-active agents do not act as film forming agents.

[0171] In another aspect, alkanolamide or a mixture with other surface-active agents can be used in the compositions of the invention. Alkanolamides are commercially available and are the reaction products of one or more fatty acids having 12 or more carbon atoms and a lower alkanolamine. Typical alkanolamides are formed by reaction between stearic, myristic, lauric acid or mixtures thereof with mono-, di-, and/or iso-propanolamine.

[0172] Alkanolamides can be present in the painting compositions of the invention in the ranges generally described throughout the application but generally are present in amounts from about 0% up to about 10% by weight. Suitable ranges include from about 1% to about 6% by weight and in particular from about 1.5% to about 4% by weight.

[0173] In one embodiment, the alkanolamide surface-active agents of the present invention include, but are not limited to, Ninol 55LL, diethanolamine, Ninol 40CO, cocamide DEA, Ninol 30LL, lauramide DEA, manufactured by Stepan Co., Northfield, IL; Colamid C, cocamide DEA, Colamid 0071-J, alkanolamide, manufactured by Colonial Chemical Inc., S. Pittsburgh, TN. In one aspect, the alkanolamides are Ninol 55LL, and Colamid C.

[0174] Exemplary sulfosuccinates that can be employed in the present painting compositions include, but are not limited to, Stepan-Mild SL3-BA, disodium laureth sulfosuccinate, Stepan-Mild LSB, sodium lauryl sulfosuccinate, manufactured by Stepan Co., Northfield, IL, Lankropol 4161L, sodium fatty alkanolamide sulfosuccinate and Colamate-DSLS, disodium laureth sulfosuccinate, manufactured by Colonial Chemical Inc., S. Pittsburgh, TN.

[0175] Suitable betaines that can be employed in the present painting compositions include, but are not limited to, Miracare BC-27, cocamidopropyl betaine and Miranol Ultra C-37, sodium cocoampho acetate, manufactured by J & S Chemical Co., Weston, FL.

[0176] Suitable sulfates that can be employed in the present painting compositions include Rhodapex ES-2, sodium laureth sulfate, J & S Chemical Co., Weston, FL; Witcolate WAQ, sodium alkyl sulfate, manufactured by Akzo Nobel, Chicago, IL and Colonial-SLS, sodium lauryl sulfate, manufactured by

Colonial Chemical Inc., S. Pittsburgh, TN. Colonial-SLS surfactant is a combination of lauryl sulfate, C10-C16 alkyl alcohols, sodium salts and C10-C16 alcohols.

[0177] A suitable nonionic surface-active agent that can be employed in the present painting compositions is Triton H-66, alkyl aryl alkoxy potassium salt, manufactured by Dow Chemical Co., Midland, MI.

[0178] In another embodiment, the surface-active agent used is a combination of an alkanolamide and a mixture of an alkyl betaine and/or an alkyl sulfonate.

[0179] In a particular embodiment, the surface-active agent is a combination of Colamid C and Miracare BC27 which is a mixture of Surface-active agent blend include sodium tridecyl sulfate, water, PEG 80 sorbitant laurate, cocamidopropyl betaine, sodium lauroamphoacetate, PEG 150 distearate, sodium laureth-13 carboxylate, glycerin, citric acid, tetrasodium EDTA, quaternium-15. Generally, the combination of the alkanolamide and alkylsulfonate/betaine is in the range of between about 1:1 to about 1:7, more particularly between about 1:1 to about 2:7 and more particularly about 2:7. Generally, the combination of the two surface-active agents comprises a concentration between about 3 and about 10 percent by weight of the total weight of the composition, and more particularly between about 5 and about 10 percent by weight of the total weight of the composition, and in particular about 9 percent of the total weight of the composition.

[0180] The aqueous compositions throughout the specification can further include a solvent or other additives as described throughout the present application. Suitable solvents include, for example, alcohols having a carbon chain length of from about 1 carbon atom to about 12 carbon atoms. Typically, methanol and ethanol are not included due to their generally recognized properties, especially in view of use with children.

[0181] Suitable optional additives to the compositions mentioned throughout the invention include, preservatives, fragrance, etc.

[0182] Representative examples of preservatives useful with the compositions throughout the specification include, but are not limited to, glutaraldehyde, bicyclic oxazolidones, hydroxybenzoic acid esters, 3-iodo-2-propynyl butyl carbamate, methyl p-hydroxybenzoate, and a biocide comprising 2-methyl-4-isothiazolin-3-one and 5-chloro-2-methyl-4-isothiazolin-3-one. The preservatives often serves as both a bactericide and a fungicide.

[0183] In particular, compositions of the invention include preservatives that are selected from, but not limited to, Liquid Germall Plus, iodopropynyl butyl carbamate, Germall II, diazolidinyl urea, Nuosept 95, bicyclic oxazolidines solution, manufactured by ISP (International Specialty Products), Wayne, NJ, Troysan 395, dihydroxy-dimethyl hydantoin, manufactured by Troy Chemical Corporation, Florham park, NJ and Kathon PFM, isothiazolinones, manufactured by Rohm & Haas Co., Philadelphia, PA

[0184] Preservatives, when present in the compositions of the invention, are generally present in amounts from about 0.01% to about 10% by weight, in particular from about 0.05% to about 5% by weight, and particularly from about 0.1% to about 2.5% by weight. In one aspect, the preservative is one of Liquid Germall Plus, Tryosan 395 or Nuosept 95.

[0185] Representative fragrances include those pleasing to children such as flowers, candy, popcorn, fruit, bubble gum and the like. A fragrance, when present in the compositions of the invention, is generally present in amounts from about 0.1% to about 10% by weight of the total weight of the composition.

[0186] The present invention further includes kits that include the compositions of the invention and instructions how to use the compositions to perform painting. Typically, the painting devices include, but are not limited to, brushes, felt-type writing instruments, other wick-type writing instruments, by means of spatulas, with the fingers and the like. The painting solution is spread onto a surface of the substrate/paper with any of the painting devices. The painting systems of the invention are easily washable and are toxicologically safe.

[0187] It should be understood, that additional colorants described infra, are within the scope of the paint compositions. These colorants useful in paint applications, include, for example, leuco dyes, metal salts, etc. as described infra.

[0188] Bubbles

[0189] Prior to the present invention, it was generally considered extremely difficult if not impossible to make a colored bubble with uniform color intensity throughout the bubble: A bubbles wall is only a few millionths of an inch thick and up until the present invention was considered that the bubble wall was incapable of being colored. Generally, a bubble's rainbow color is the result of reflects color from its surroundings.

[0190] Traditionally, when a light wave hits the surface of a bubble, part of the light is reflected back to a viewer's eye from the outer surface and part of the light is reflected from the inner surface which is a few millionths of an inch further. As the two waves of light travel back, they interfere with one another causing what we visualize as color. When the waves reinforce each other, the color is more intense. When the waves get close to canceling each other out, there is almost no color. As a bubble wall gets thinner, either from a weakened solution or because gravity has pulled the additives to the bottom of the bubble, the distance between the inner surface and the outer surface of the bubble becomes less and less until the two reflected waves of light start to coincide and cancel each other out. The result is that the bubble loses its color and can become nearly invisible.

[0191] Prior to the present invention, it has proven extremely difficult, if not impossible, to develop a colored bubble composition with uniform color intensity throughout the bubble. When the dyes are added to the soap/bubble solution, they form colored solution but when the bubbles are blown, the resulting bubbles are colorless.

[0192] The present invention surprisingly provides coloration changing, color disappearing bubble compositions, that have substantially uniform

coloration about the bubble. Additionally, the present invention provides compositions that have film forming capabilities such that the resultant bubble can withstand physical contact with a surface. The film formed bubble can be colored, have a color changing composition, have a color disappearing composition, or can be without color. The bubbles can have a wide range of opacity, colors and scents. The compositions and resultant bubbles are non-toxic and/or washable.

[0193] The present invention further provides compositions and methods for producing bubbles, as described herein, having a wide range of opacities, ranging from essentially translucent to semi-transparent to opaque. The bubbles can be intrinsically colored; the composition from which the bubbles are formed itself is colored.

[0194] In some embodiments, the bubbles have substantially uniform color intensity. In other embodiments, the bubbles can have non-uniform color intensity and/or dispersion.

[0195] The phrases “substantially uniform” or “substantially uniformly” are intended to refer to coloration about the bubble such that the coloration intensity is approximately equal from the top of the bubble to the bottom of the bubble. In such an embodiment, the coloration in the bubble is dispersed evenly throughout the bubble and coloration streaking or having an increased concentration of color at the bottom of the bubble is substantially avoided.

[0196] The phrases “non-uniform” or “non-uniformly” are intended to refer to coloration about the bubble such that the coloration intensity is concentrated, for example, more at the top and bottom of the bubble. Such fanciful bubbles can be very interesting to children.

[0197] The phrase “colored bubble” is intended to refer to a bubble that can be uniformly or non-uniformly colored, as described herein, but does not have a change in coloration over a given period of time and does not have the coloration disappear from the bubble. Colored bubbles retain their coloration throughout the period of time the bubble exists, generally from about a few

seconds to about a few minutes. The colored bubbles related to the present invention are formed with film forming technology described herein.

[0198] In one aspect, the colored bubbles and compositions of the invention are excluded from those described in US Provisional Application 60/581,294, filed on June 17, 2004, by Tim Kehoe, entitled "Composition and Method for Producing Colored Bubbles", the contents of which are incorporated herein by reference in their entirety.

[0199] Color Changing or Color Disappearing Compositions and Bubbles

[0200] In one embodiment, the present invention pertains to an aqueous composition that includes a surfactant, an acid-base indicator and a base, such as a volatile base, such as an amine. The composition can be used to prepare bubbles that have color disappearing characteristics and/or color changing characteristics.

[0201] The phrase "color changing" refers to the ability of the dye or pigment to change coloration due to a change in physical propert(ies) of the dye or pigment. The change in color can be a result of oxidation, change in pH, or some other physical attribute of the dye or pigment that is altered upon, for example, the evaporation of water, solvent or some other component from the bubble surface. Alternatively, the change can occur when the concentration of an ingredient increases within the bubble surface due to loss of another component, for example, due to evaporation. Generally the color change occurs over a period between about 1 second and about 10 minutes, more particularly between about 2 seconds to about 5 minutes and more particularly between about 5 seconds and about 1 minute.

[0202] The phrase "color disappearing" refers to the ability of the dye or pigment to lose or have a diminishment in coloration due to a change in physical propert(ies). The disappearance of color can be a result of oxidation, change in pH, or some other physical attribute of the dye or pigment that is altered upon, for example, upon the evaporation of water, solvent or other component from the bubble surface. Alternatively, the coloration loss or diminishment can occur

when the concentration of an ingredient increases within the bubble surface due to loss of another component, for example, due to evaporation. Generally the coloration loss or diminishment occurs over a period between about 1 second and about 10 minutes, more particularly between about 2 seconds to about 5 minutes and more particularly between about 5 seconds and about 1 minute.

[0203] The aqueous solutions of the present invention generally contain between about 1 and about 90 parts water, in particular between about 10 and about 80, and more particularly between about 20 and about 70 percent based on a total weight percentage of the final composition. In one aspect, the water utilized can be ordinary tap water or spring water. In another aspect the water can be deionized water or water purified by reverse osmosis.

[0204] The compositions of the invention include a surfactant. Suitable surfactants include anionic, cationic, nonionic or zwitterionic compounds and combinations thereof described throughout the specification. The surfactant can be either polymeric or non-polymeric.

[0205] In one particular embodiment, the surfactant utilized to form the bubble is Colonial SLS.

[0206] Typical concentration ranges of surfactant that are useful in the preparation of bubble composition are from about 0.01 parts by weight to about 90 parts by weight, from about 0.5 part by weight to about 50 parts by weight, and from about 1 parts by weight to about 20 parts by weight.

[0207] In one aspect, surfactants useful in the bubble compositions of the invention include, but are not limited to, cellulose ethers or mixtures with other surfactants, which are water soluble. Cellulose ether surfactants have unique foaming and film forming properties which make them ideal of colored bubble applications. Cellulose ethers used in the present invention include methyl cellulose, ethyl cellulose, propyl cellulose, butyl cellulose, higher alkyl, aryl, alkoxy, cycloalkyl celluloses, hydroxypropyl cellulose, hydroxybutyl cellulose or mixtures thereof.

[0208] Cellulose ether surfactants are generally present in bubble composition in amounts from about 1% up to about 40% by weight in the

compositions of the invention. Suitable concentrations of cellulose ether surfactants are in the range of about 2% to about 30% by weight and from about 3% to about 8% by weight. A particularly useful cellulosic ether surfactant in the compositions is Methocel A4M.

[0209] Alkanolamides can be present in the bubble compositions of the invention in the ranges generally described throughout the application but generally are present in amounts from about 0% up to about 10% by weight. Suitable ranges include from about 1% to about 6% by weight and in particular from about 1.5% to about 4% by weight.

[0210] Suitable optional additives to the compositions of the invention include, humectants, preservatives, fragrance, dye blockers, cleaners, etc.

[0211] The term "humectant" is known and helps to retard the evaporation of water from the composition of the invention, thus avoiding premature drying during the application. Not to be limited by theory, it is believed that the presence of a humectant helps to strengthen the bubble formation, enhances even distribution of the dye throughout the bubble and increases life of bubble in the air.

[0212] Representative examples of humectants include, but are not limited to, glycerin, ethylene glycol, propylene glycol, diethylene glycol, polyethylene glycol, hydroxylated starches and mixtures of these materials. Any effective amount of humectant may be used although a generally useful concentration range for these humectants is from about 5% to about 35% by weight of the total composition. Particular ranges of the humectant include a range of from about 8% to about 30% by weight of the composition and from about 10% to about 25% by weight of the composition. In one particular aspect, the humectant is glycerin.

[0213] Preservatives, when present in the bubble compositions of the invention, are generally present in amounts from about 0.01% to about 6% by weight, in particular from about 0.05% to about 5% by weight, and particularly from about 0.1% to about 2.5% by weight. In one aspect, the preservative is one of Liquid Germall Plus, Tryosan 395 or Nuosept 95.

[0214] Representative fragrances include those pleasing to children such as flowers, candy, popcorn, fruit, bubble gum and the like. A fragrance, when present in the bubble compositions of the invention, is generally present in amounts from about 0.1% to about 10% by weight of the total weight of the composition.

[0215] Dye blockers or cleaners can be optionally added in the compositions of the invention, including bubbles, to remove dye from hard/porous surfaces such as wood, stone, brick, leather, cloth, concrete, skin, fabric, etc. Up until the present invention, contact with a solution having a dye could stain a surface.

[0216] Suitable dye blockers include, but are not limited to, Bio-Terge PAS-8S, sodium octane sulfonate, Stepanate SXS, sodium xylenesulfonate, Steposol DG, fatty alcohol ethoxylate, manufactured by Stepan Co., Northfield, IL, Dowfax 8390, disodium hexadecyldiphenyloxide disulfonate, Dowfax 2A1, benzene-1,1-oxybis-tetrapropylene sulfonated sodium, Dowfax 3B2, decyl-sulfophenoxy-benzenesulfonic acid-disodium, Dowfax C10L, decyl-sulfophenoxybenzenesulfonic acid disodium, Triton X-15, octylphenoxypolyethoxyethanol, manufactured by Dow Chemical Co., Midland, MI, Tamol SN, sodium salt of naphthalene-formaldehyde condensate, Tamol 731, sodium salt of carboxylated polyelectrolyte, manufactured by Rohm & Haas Co., Philadelphia, PA, Darvan 2, sodium lignin sulfonate, manufactured by R. T. Vanderbilt & Co., Norwalk, CT, Aqua-Cleen GP, polyethoxylated tert-dodecyl sulfur compound, TZ-Paint Prep, phosphorous/sulfur containing builders, and TAZ-B300, sulfur/oxygen/nitrogen containing surface active agents, manufactured by Chemical Products Industries, Oklahoma City, OK

[0217] Dye blockers or cleaners are usually effective in the compositions of the invention when present in any amount but generally are present in ranges from about 5% up to about 50% by weight, from 10% to about 40% by weight or from about 12% to about 25% by weight.

[0218] In one aspect the bubble compositions of the invention include acid-base indicators as described throughout the application. These acid-base

indicators used in the present invention are generally colored under basic condition and change color or fade to clear in non-basic condition. Acid-base indicators which are colored on alkaline pH side ($\text{pH} > 7$) and turn clear on acidic pH ($\text{pH} < 7$) are most useful. Typically, the acid-base indicators are colored at pH between about 9 and 10, and turn clear at pH between about 6 and 8.

[0219] Representative examples of acid-base indicators useful in the bubble compositions of the present invention include, but are not limited to those described herein. In particular, with reference for Formulae (I) and (Ia), R^2 is selected from the group consisting of hydrogen and methyl; R^3 is selected from the group consisting of hydrogen phenyl, isopropyl, methyl ethyl and methoxy; R^5 is selected from the group consisting of hydrogen, bromo, methoxy, isopropyl and methyl; and R^6 is selected from the group consisting of hydrogen and methyl.

[0220] In certain bubble embodiments, R^2 is selected from the group consisting of hydrogen, nitro, amino and alkyl; R^3 is selected from the group consisting of hydrogen, phenyl, alkyl, nitro, acetamido and alkoxy; R^5 is selected from the group consisting of hydrogen, halo, and alkyl; and R^6 is selected from the group consisting of hydrogen and alkyl.

[0221] In certain bubble embodiments, R^2 is selected from the group consisting of hydrogen and methyl; R^3 is selected from the group consisting of hydrogen, phenyl, isopropyl, methyl, ethyl, sec-butyl, nitro and methoxy; R^5 is selected from the group consisting of hydrogen, bromo, methoxy, isopropyl and methyl; and R^6 is selected from the group consisting of hydrogen and methyl.

[0222] In other bubble embodiments, $\text{R}^2, \text{R}^3, \text{R}^5, \text{R}^6, \text{R}^7, \text{R}^8, \text{R}^9$ and R^{10} are all hydrogen atoms; R^2 is hydrogen, R^3 is Me, and $\text{R}^5, \text{R}^6, \text{R}^7, \text{R}^8, \text{R}^9$ and R^{10} are all hydrogen atoms; R^2 is Me, R^3 is a hydrogen atom, R^5 is an iso-propyl group and $\text{R}^6, \text{R}^7, \text{R}^8, \text{R}^9$ and R^{10} are all hydrogen atoms; R^2 is H, R^3 is Me, R^5 is Br and $\text{R}^6, \text{R}^7, \text{R}^8, \text{R}^9$ and R^{10} are all hydrogen atoms; and R^2 is Me, R^3 is Br, R^5 is an isopropyl and $\text{R}^6, \text{R}^7, \text{R}^8, \text{R}^9$ and R^{10} are all hydrogen atoms. In certain embodiments, one or more of these compounds may be excluded from certain aspects of the invention.

[0223] In still other bubble embodiments, R^2 is H, R^3 is phenyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 and R^5 are isopropyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 is methyl, R^5 is H, R^6 is methyl, R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 and R^5 are methoxy and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 and R^5 are methyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 is ethyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 is isopropyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 is methoxide and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; and R^2 , R^3 and R^5 are all methyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} are all hydrogen atoms and R^3 is sec-butyl, or R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} are all hydrogen atoms and R^3 is nitro.

[0224] In particular, at least one of M^1 or M^2 is a metal or an ammonium ion.

[0225] Additionally, the phenols and hydrazines described throughout are useful in the bubble compositions as well. Additional colorants useful in the various compositions of the application (e.g., paints, bubbles, markers and cosmetics) include those listed throughout the application, including those which follow.

[0226] With the suitable selection of acid-base indicators, it is possible to produce any color. The acid-base indicators are preferably in the form of a salt, such as a sodium salt generated by reacting the indicator, such as a phthalein, with sodium hydroxide, so as to permit its solubilization into the present composition. Generally, 2 equivalents of base are added per mole of phthalein, however, less than 2 equivalents will produce a color, and it is possible that 1 equivalent will impart color to the phthalein salt. Additionally, combinations of two or more indicators may be used.

[0227] Acid-base indicators are usually effective when present in small amounts in the bubble compositions of the invention but generally are present in amounts from about 0.1% up to about 20% by weight, from about 0.5% to about

10% by weight and from about 0.8% to about 8% by weight of the total weight of the composition.

[0228] Selection of an appropriate basic material is important for color change of acidic dye indicators in the colored compositions of the present invention. Desirable basic reagents, which should readily volatilize at ambient temperatures for use in the present compositions, include, but are not limited to, aminoalcohols, such as alkylamines, such as methylamine, dimethylamine, ethylamine, diethylamine, triethylamine, ethyleneamine, diethyleneamine, morpholine, ammonia, triethanolamine.

[0229] The selection of the kind and the amount of basic reagent used enables control of fading time of the color after a colored bubble is blown. Suitable basic reagents which readily volatilize at ambient temperatures, typically have a vapor pressure higher than about 10 mm Hg at 20°C. The selection of the base also depends on solubility in water, toxicity and odor. Therefore, aminoalcohols useful in the compositions of the present invention include, but are not limited to triethanolamine (TEA) and/or diethylamine. TEA, for example, is clear, non-toxic and does not emit a noxious odor.

[0230] The basic reagent(s) is generally present in the bubble composition of the invention in an amount from about 0.1% up to about 20% by weight, from about 0.2% to about 10% by weight and from about 0.5% to about 5% by weight.

[0231] In another embodiment, the present invention pertains to aqueous bubble compositions that include a surfactant, leuco dye and an electron acceptor or oxidizing agent. The composition can be used to prepare bubbles that have color disappearing characteristics and/or color changing characteristics. Optionally, one or more of the above-identified solvents, humectants, preservatives, fragrances, etc. as described throughout the application can be included in the composition.

[0232] The bubble compositions can include one or more of the surfactant(s) described throughout the present application in combination with at least one leuco dye and an electron acceptor or oxidizing agent.

[0233] The term "leuco dye" is intended to mean a colorless or lightly colored dye which can be oxidized to a colored form. Leuco dyes are generally electron donating chromatic organic compounds which are generally colorless and produce color upon reaction with acidic materials.

[0234] Suitable examples of leuco dyes that can be incorporated into compositions of the invention include, but are not limited to, diaryl phthalide, polyarylcannabinols, leuco-auramines, acylauramines, arylauramines, rhodamine B lactams, indolines, spiropyrans, fluorans, phenothiazines, triarylmethanes, 3,3-bis(p-dimethylaminophenyl)-phthalide, 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide (crystal violet lactone), 3,3-bis(p-dimethylaminophenyl)-6-diethylaminophthalide, 3,3-bis(p-dimethylaminophenyl)-6-chlorophthalide, 3,3-bis(p-dibutylaminophenyl)-phthalide, 3-(2'-hydroxy-4'-dimethylaminophenyl)-3-(2'-methoxy-5'-chlorophenyl)-phthalide, 3-(2'-hydroxy-4'-dimethylaminophenyl)-3-(2'-methoxy-5'-nitrophenyl)-phthalide, 3-(2'-hydroxy-4'-diethylaminophenyl)-3-(2'-methoxy-5'-methylphenyl)-phthalide, 3-(2'-methoxy-4'-dimethylaminophenyl)-3-(2'-hydroxy-4'-chloro-5'-methylphenyl)-phthalide, malachite green lactone, mishler's hydrol, crystal violet carbinol, malachite green carbinol, N-(2,3-dichlorophenyl)-leuco auramine, N-benzoyl auramine, N-acetyl auramine, N-phenyl auramine, rhodamine B lactam, 2-(phenyliminoethylidene)-3,3-dimethylindoline, N-3,3-trimethyl-indolinobenzospiropyran, 8'-methoxy-N-3,3-trimethyl-indolino-benzospiropyran, 6'-chloro-8'-methoxy-benzoindolino-spiropyran, 6'-bromo-3'-methoxy-benzoindolino-spiropyran, 2[3,6-bis(diethylamino)-9-(o-chloroanilino)xanthylbenzoic acid lactam, benzoyl leuco methylene blue, 3-amino-5-phenyl-8-methylfluoran, 2-bromo-6-cyclohexylaminofluoran, 2-chloro-3-(N-methyltoluidino)-7-(p-n-butylanilino)fluoran, 3-cyclohexylamino-6-chlorofluoran, 3-dimethylamino-6-benzyloxyfluoran, 3-dimethylamino-5,7-dimethylfluoran, 3-diethylamino-7-methylfluoran, 3-diethylamino-7-methoxyfluoran, 3-diethylamino-7-chlorofluoran, 3-diethylamino-7-anilinofluoran, 3-diethylamino-7-acetamido-fluoran, 3-diethylamino-7-p-toluidino-fluoran, 3-diethylamino-7-piperidinofluoran, 3-diethylamino-7-(o-

chloroanilino)-fluoran, 3-diethylamino-7-(o-methoxycarbonylphenylamino)-fluoran, 3-diethylamino-7,8-benzofluoran, 6-diethylamino-1,2-benzofluoran, 3-diethylamino-6-methyl-7-chlorofluoran, 3-diethylamino-6-methyl-7-anilinofluoran, 3-diethylamino-6-methyl-7-mesidino-4',5'-benzofluoran, 3-diethylamino-6-methyl-7-(2',4'-dimethylanilino)fluoran, 3-diethylamino-6-methyl-7-(m-trichloroanilino)fluoran, 3-diethylamino-5-chloro-7-(N-benzyltrifluoromethyl-anilino)-fluoran, 3-diethylamino-5-chloro-7-(α -phenylethylamino)fluoran, 3-diethylamino-5-methyl-7-(α -phenylethylamino)fluoran, 3-dibutylamino-7-(o-chloroanilino)-fluoran, 2,3-dibutylene-6-di-n-butylaminofluoran, 2,7-dichloro-3-methyl-6-n-butylaminofluoran, 3,6-di-p-toluidino-4,5-dimethylfluoran-phenylhydrazide- γ -lactam, 3-N-ethyl-p-toluidino-7-(α -phenylethylamino)-fluoran, 3-N-methyl-N-amylamino-6-methyl-7-anilinofluoran, 3-N-methyl-N-cyclohexylamino-6-methyl-7-anilinofluoran, 3-(N-benzyl-N-cyclohexylamino)-5,6-benzo-7- α -naphthylamino-4'-bromofluoran, 3-(N-p-tolyl-N-ethylamino)-6-methyl-7-anilinofluoran, 2'-[N-(3'-trifluoromethylphenyl)amino]-6-diethylaminofluoran, 3-(N,N-diethylamino)-5-methyl-7-(N,N-dibenzylamino)fluoran, 3-morpholino-7-(N-propyltrifluoromethylanilino)fluoran, 3-pyrrolidino-6-methyl-7-anilinofluoran, 3-pyrrolidino-7-(di-p-chlorophenyl)-methylaminofluoran, 3-pyrrolidino-7-trifluoromethylanilinofluoran, and salts or mixtures thereof.

[0235] Typically the leuco dye concentration in the compositions of the invention range from about 0.1% up to about 20% by weight, in particular from about 0.5 to about 15 by weight, and most particular from about 1 to about 10 by weight.

[0236] As the color developers for use in combination with the above leuco dyes in the present invention, a variety of electron acceptors or oxidizing agents capable of inducing color formation with the leuco dyes can be employed.

[0237] Suitable examples of electron acceptors or oxidizing agents that can be incorporated into compositions of the invention include, but are not limited to, inorganic acids, organic acids, phenolic materials, phenolic resins, bentonite, zeolite, acidic terra alba, activated clay, silica gel, alkyl-monophenols, alkyl-

diphenols, thio-bis- alkyl-phenols, alkyl-phenylphenols, alkylcatechols, hydroxyl-alkylnaphthalenes, dihydroxyl-alkylnaphthalenes (any alkyl moiety having 1 to 12 carbon atoms), gallic acid alcohol esters, p-oxybenzoic acid alcohol esters, procatechuric acid alcohol esters, phenol-formaldehyde prepolymer, tert-butyl phenol, nonyl phenol, dodecyl phenol, styrenated phenol, 2,2'-methylene-bis-(4-methyl-6-tert-butyl phenol), α -naphthol, β -naphthol, hydroquinone monomethyl ether, guaiacol, eugenol, p-chlorophenol, p-bromophenol, o-chlorophenol, o-bromophenol, o-phenylphenol, p-phenylphenol, o-(o-chlorophenyl)phenol, p-(p-chlorophenyl)phenol, methyl p-hydroxybenzoate, ethyl p-hydroxybenzoate, propyl p-hydroxybenzoate, isopropyl p-hydroxybenzoate, octyl p-hydroxybenzoate, benzyl p-hydroxybenzoate, dodecyl phenol 3-isopropylcatechol, p-tert-butyl catechol, 4,4'-methylene diphenol, 4,4'-thio-bis-(6-tert-butyl-3-methylphenol), bisphenol A, 1,2-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, chlorocatechol, bromocatechol, 2,4-dihydroxybenzophenone, phenol, phthalein, o-cresol phthalein, methyl protocatechuate, ethyl protocatechuate, propyl protocatechuate, octyl protocatechuate, benzyl protocatechuate, dodecyl protocatechuate, 2,4,6-trihydroxymethylbenzene, methyl gallate, ethyl gallate, propyl gallate, butyl gallate, hexyl gallate, octyl gallate, dodecyl gallate, cetyl gallate, stearyl gallate, lauryl gallate, 2,4,6-trihydroxynaphthalene, tannic acid, phenol-formaldehyde prepolymers, resorcin, phloroglucin, 4,4'-isopropylidenebisphenol, 4,4'-isopropylidenebis-(o-methylphenol), 4,4'-isopropylidenebis-(2-tert-butylphenol), 4,4'- isopropylidenebis-(2-chlorophenol)phenol, 4,4'- sec-butylidene-bisphenol, 4,4'-cyclohexylidenebisphenol, 4,4'-butylidene-bis-(6-tert-butyl-2-methyl)phenol, 4,4'-thiobis- (6-tert-butyl-2-methyl)phenol, 2,2'-methylene-bis-(4-methyl-6-tert-butyl)phenol, 2,2'-methylene-bis-(4-ethyl-6-tert-butyl)phenol, 1,1,3-tris-(2-methyl-4-hydroxy-5-tert-butylphenyl)-butane, 1,1,3-tris-(2-methyl-4-hydroxy-5-cyclohexylphenyl)butane, 1,7-bis-(4-hydroxyphenylthio)-3,5-dioxaheptane, 1,5-bis-(4-hydroxyphenylthio)-3-oxapentane, 1,3-bis-(4-hydroxyphenylthio)-propane, 1,3-bis-(4-hydroxyphenylthio)-2-hydroxypropane, 2,2'-methylene-bis-(4-ethyl-6-tert-butylphenol), N,N'-diphenylthiourea, N,N'-di(m-chlorophenyl)thiourea,

salicylanilide, 5-chloro- salicylanilide, salicyl-o-chloroanilide, 2-hydroxy-3-naphthoic acid, 2-hydroxy-1-naphthoic acid, 1-hydroxy-2-naphthoic acid, zinc salt of 1-acetoxy-3-naphthoic acid, zinc hydroxynaphthoic acid, aluminum hydroxynaphthoic acid, calcium hydroxynaphthoic acid, bis(4-hydroxyphenyl)methyl acetate, bis(4-hydroxyphenyl)benzyl acetate, 1,3-bis(4-hydroxy)cumyl benzene, 1,4-bis(4-hydroxy)cumyl benzene, 4,4'-diphenylsulfone, 4,2'-diphenylsulfone, 2,4'-diphenylsulfone, 4,4'-diphenylsulfoxide, 3,3'-diallyl-4,4'-diphenylsulfone, 3,4-dihydroxy-4'-methyldiphenylsulfone, 4-isopropoxy-4'-hydroxydiphenylsulfone, 4-benzyloxy-4'-hydroxydiphenylsulfone, tetrabromobisphenol A, tetrabromobisphenol S and salts or mixtures thereof.

[0238] Typically the electron acceptor compound or oxidizing agent concentration in the compositions of the invention range from about 0.1% up to about 25% by weight, in particular from about 0.5 to about 15 by weight, and most particular from about 1 to about 10 by weight.

[0239] An additive which acts as a reaction medium or a solvent to help control the degree of color change is selected from long chain aliphatic alcohols. Specific examples used in the compositions of the present invention include, for example and are not limited to, 1-dodecanol, 1-decanol, 1-docosanol, 1-nonanol, 1-tetradecanol, 1-hexadecanol, 1-octadecanol, (2)-9-octadec-1-ol, 3-pentadecylcatechol and mixture thereof. Generally alcohols which have carbon atoms from 12 to 18 or having molecular weight greater than 100 are most useful. The reaction medium can also include polyvinyl alcohol which can be partially hydrolyzed (86-89 %), fully hydrolyzed (98-99 %) or super hydrolyzed (99.3+ %). The molecular weight range of the polyvinyl alcohol is from 50,000 to >186,000.

[0240] Typically the long chain aliphatic alcohol, is incorporated into the compositions of the invention range from about 1% up to about 90% by weight, in particular from about 2 to about 80 by weight, and most particular from about 5 to about 75 by weight.

[0241] An additional additive to the surfactant, leuco dye and electron acceptor or oxidizing agent can be an alcohol ester, with a molecular weight range

from 150 to about 1000. Suitable examples include, but are not limited to, octyl caprylate, decyl caprylate, octyl caprate, decyl caprate, cetyl caprate, stearyl caprate, butyl laurate, octyl laurate, lauryl laurate, stearyl laurate, butyl myristate, decyl myristate, myristyl myristate, cetyl myristate, octyl palmitate, butyl stearate, decyl stearate, lauryl stearate, stearyl stearate and 12-hydroxy stearic acid triglyceride.

[0242] Typically the alcohol ester, is incorporated into the compositions of the invention range from about 1% up to about 20% by weight, in particular from about 0.5 to about 15 by weight, and most particular from about 0.1 to about 5 by weight.

[0243] A typical ratio of long chain aliphatic alcohol to alcohol ester is about 9:1

[0244] In still another embodiment, the present invention pertains to an aqueous composition that includes a surfactant and a metal salt. The composition can be used to prepare bubbles that have color disappearing characteristics and/or color changing characteristics. Optionally, one or more of the above-identified solvents, humectants, preservatives, fragrances, etc. as described throughout the application can be included in the composition.

[0245] The compositions can include one or more of the surfactant(s) described throughout the present application in combination with at least one water soluble metal salt.

[0246] Typically the metallic salt is selected from transition metals. Transition elements, undergo a color change with the loss of a water of hydration or when complexes are formed with organic materials. Salts of transition metals include those salts formed from Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Ac, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th and Pa. For example, color change can occur upon heating the metallic salts with long chain alcohols or polyvinyl alcohols. Representative examples of suitable transition metal salts include, but are not limited to, cobalt (II) chloride, cobalt (III) chloride, cobalt (II) bromide, cobalt (III) bromide, cobalt (II) nitrate, cobalt (III) nitrate, nickel (II)

chloride, nickel (III) chloride, nickel (II) bromide, nickel (III) bromide, nickel (II) nitrate, nickel (III) nitrate, nickel (II) sulfate, nickel (II) sulfamate, nickel (II) oxalate, nickel (II) phthalocyanine, iron (II) chloride, iron (III) chloride, iron (II) bromide, iron (III) bromide, iron (II) nitrate, iron (III) nitrate, aluminium potassium sulfate.

[0247] Inorganic salts such as cobalt (II) chloride in combination with certain long chain alcohol produce the unusual effect of coloration due to the complex formation on heating and fade color on cooling. Specific examples of long chain alcohols that can interact with the transition metal to form a colored complex include, but are not limited to, 1-dodecanol, 1-tetradecanol, 1-hexadecanol, 1-docosanol, 1-decanol, 1-octadecanol, (2)-9-octadecen-1-ol, 1-nonanol, 3-pentadecylcatechol. Generally, suitable alcohols are those which have a carbon atom chain length from about 12 to about 18 carbon atoms or have molecular weight greater than 100. The reaction medium or solvent can also include polyvinyl alcohol which can be partially hydrolyzed (86-89 %), fully hydrolyzed (98-99 %) or super hydrolyzed (99.3+ %). The molecular weight range of polyvinyl alcohol is from 50,000 to >186,000.

[0248] For example, when metal salts are heated with a long chain aliphatic alcohol or a polyvinyl alcohol, colored complexes are formed, and hence generate color. The color fades away when they are cooled. The color either disappears (color to colorless) or changes color (one color to another color).

[0249] Colored, Color Disappearing or Color Changing Film Forming Compositions and Bubbles

[0250] The color changing and/or color disappearing compositions described herein can be combined with film forming technology as described infra. Additionally, substantially uniformly colored bubble compositions can be prepared with the film forming technology described infra. Suitable colored bubble compositions, such as those described in US Provisional Application No. 60/581,294, filed June 17, 2004, by Tim Kehoe, entitled "Composition and

Method for Producing Colored Bubbles”, the contents of which are incorporated herein in their entirety, can therefore be incorporated with the film forming technology described herein.

[0251] In one aspect, the present invention pertains to an aqueous film forming color changing composition that includes a surfactant, an acid-base indicator, a base, such as a volatile base, and a film forming resin. In one embodiment, the composition provides a film in which the color changes or the color disappears. In another embodiment, the composition provides a colored bubble in which the color changes or the color disappears.

[0252] In another aspect, the present invention pertains to an aqueous film forming color changing composition that includes a surfactant, a leuco dye, an electron acceptor or oxidizing agent and a film forming resin. In one embodiment, the composition provides a film in which the color changes or the color disappears. In another embodiment, the composition provides a colored bubble in which the color changes or the color disappears.

[0253] In still another aspect, the present invention pertains to an aqueous film forming color changing composition including a surfactant, a water soluble metal salt and a film forming resin. In one embodiment, the composition provides a film in which the color changes or the color disappears. In another embodiment, the composition provides a colored bubble in which the color changes or the color disappears.

[0254] In still yet another aspect, the present invention relates to an aqueous film forming colored composition that includes a surfactant, a colorant and a film forming resin. In one embodiment, the composition provides a substantially uniformly colored film. In another embodiment, the composition provides a substantially uniformly colored bubble.

[0255] In yet another aspect, the present invention relates to an aqueous film forming substantially colorless bubble composition that includes a surfactant and a film forming resin.

[0256] The surfactant(s), acid-base indicator(s), leuco dye(s), metal salt(s), base(s), dye blocker(s) and optional additives are as described herein.

[0257] The present invention provides the advantage(s) that a bubble that forms a strong film in the air permits the bubble to be caught, handled, stacked, and/or popped. The thin film of the bubble, for example, captures the color thus making the removal of the bubble or color from the bubble (if any) easy

[0258] The present invention further provides colored bubbles for films with uniform color intensity, large numbers of bubble, long lasting bubbles, bubbles that generate noise upon bursting, and in some cases, bubbles that are interconnected.

[0259] The compositions of the invention include a resin which is water soluble, non-toxic and forms a film at room temperature. The water soluble film forming resins provide the compositions with a suitable viscosity for generating films or bubbles.

[0260] Representative examples of typical film forming resins employed in the compositions of the invention include, but are not limited to, polyvinylalcohol, polyvinylpyrrolidone, polyoxyethylene, polyvinyl acetate, gelatin, gum arabic, rosin, rosin-modified maleic acid resins, rosin-modified phenol resins, rosin esters, hydrogenated rosins, various cellulosic resins, methyl cellulose, ethyl cellulose, acetyl cellulose, propyl cellulose, butyl cellulose, hydroxypropyl cellulose, higher alkyl cellulose, petroleum resins, various phenol resins, starches and derivatives thereof. Mixtures of two or more of these film forming agents can also be employed in the present invention.

[0261] In particular, film forming resin include, but are not limited to PVP K-15, PVP K-30, PVP K-90, polyvinylpyrrolidone, manufactured by ISP (International Specialty Products), Wayne, NJ, Elvanol 40-05, Elvanol 40-16, Elvanol 40-40, Elvanol 70-14, Elvanol 70-27, Elvanol 60-30, Elvanol 70-03, Elvanol 70-04, Elvanol 70-06, Elvanol 70-20, Elvanol 70-30, Elvanol 70-62, Elvanol 70-63, Elvanol 70-75, Elvanol 71-30, Elvanol 90-50, Elvanol 50-14, Elvanol 50-26, Elvanol 50-42, Elvanol 51-03, Elvanol 51-04, Elvanol 51-05, Elvanol 51-08, Elvanol 52-22, Elvanol 75-15, Elvanol 85-82, Elvanol 85-91, polyvinylalcohol, manufactured by DuPont, Wilmington, DE, Celvol 125, Celvol 165, Celvol 350, Celvol 325, Celvol 310, Celvol 305, Celvol 103, Celvol 107,

Celvol 203, Celvol 205, Celvol 418, Celvol 425, Celvol 443, Celvol 502, Celvol 504, Celvol 508, Celvol 513, Celvol 518, Celvol 523, Celvol 530, Celvol 540, Celvol 805, Celvol 823, Celvol 840, polyvinylalcohol, manufactured by Celanese Chemicals, Dallas TX, Polyox WSR N-10, Polyox WSR N-80, Polyox WSR N-750, Polyox WSR N-3000, Polyox WSR 205, Polyox WSR -1105, Polyox WSR N-12K, Polyox WSR N-60K, Polyox WSR-301, Polyox WSR-303, Polyox WSR-308, polyethylene oxide, manufactured by Dow Chemical Co., Midland, MI, K4484, water soluble starch, manufactured by National Starch & Chemicals, Bridgewater, NJ, Dri-sweet 42, water soluble starch, manufactured by American Maize and ICB 3000, water soluble starch, manufactured by Staley.

[0262] The film forming resin present in the composition of the invention are generally in a range from about 0.1% up to about 40% by weight, in particular from about 1% to about 35% by weight and more particularly from about 2% to about 30% by weight.

[0263] The combination of film forming resins, dye blockers and/or cleaners in the colored composition of the present invention provide enhanced washability on skin, fabrics, and hard surfaces such as finished/unfinished wood, stone, brick, leather, etc.

[0264] For films and bubbles that have a colorant that does not lose or changes color, various dyes and pigments can be incorporated into the compositions of the invention.

[0265] Suitable dyes can be selected from various dye classes that include, but are not limited to acid dyes, basic dyes, direct dyes, reactive dyes, sulfur dyes, fluorescent dyes, food dyes (FD&C) cosmetic dyes (D & C), solvent dyes and polymeric dyes.

[0266] The terms "acid dye" or "acidic dye" are recognized in the art and are intended to include those water soluble anionic dyes that are applied to a material from neutral to acid solution. Attachment to the material is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the material. Generally, acid dyes have functional groups such as azo,

triaryl methane or anthraquinone that include acid substituents such as nitro, carboxy or sulfonic acid groups.

[0267] Representative examples of acid dyes useful in the present compositions include, but are not limited to, Acid Black 1, Acid Black 2, Acid Black 24, Acid Black 48, Acid Blue 1, Acid Blue 7, Acid Blue 9, Acid Blue 25, Acid Blue 29, Acid Blue 40, Acid Blue 45, Acid Blue 74, Acid Blue 80, Acid Blue 83, Acid Blue 90, Acid Blue 92, Acid Blue 113, Acid Blue 120, Acid Blue 129, Acid Blue 147, Acid Green 1, Acid Green 3, Acid Green 5, Acid Green 25, Acid Green 27, Acid Green 50, Acid Orange 6, Acid Orange 7, Acid Orange 8, Acid Orange 10, Acid Orange 12, Acid Orange 51, Acid Orange 51, Acid Orange 63, Acid Orange 74, Acid Red 1, Acid Red 4, Acid Red 8, Acid Red 14, Acid Red 17, Acid Red 18, Acid Red 26, Acid Red 27, Acid Red 29, Acid Red 37, Acid Red 44, Acid Red 50, Acid Red 51, Acid Red 52, Acid Red 66, Acid Red 73, Acid Red 87, Acid Red 88, Acid Red 91, Acid Red 92, v Acid Red 94, Acid Red 97, Acid Red 103, Acid Red 114, Acid Red 150, Acid Red 151, Acid Red 183, Acid Violet 7, Acid Violet 9, Acid Violet 17, Acid Violet 19, Acid Yellow 1, Acid Yellow 3, Acid Yellow 9, Acid Yellow 11, Acid Yellow 17, Acid Yellow 23, Acid Yellow 25, Acid Yellow 29, Acid Yellow 34, Acid Yellow 36, Acid Yellow 42, Acid Yellow 54, Acid Yellow 73, Acid Yellow 76 and Acid Yellow 99.

[0268] The terms "base dye" or "basic dye" are recognized in the art and are intended to include those water soluble cationic dyes that are applied to a material from neutral to basic solution. Generally, basic dyes have functional groups such as sulfonium, oxonium, or quarternary ammonium functional groups. Attachment to the material is attributed, at least partly, to salt formation between cationic groups in the dyes and anionic groups in the material.

[0269] Representative examples of basic dyes useful in the present compositions include, but are not limited to, Basic Black 2, Basic Blue 3, Basic Blue 6, Basic Blue 7, Basic Blue 9, Basic Blue 11, Basic Blue 12, Basic Blue 16, Basic Blue 17, Basic Blue 24, Basic Blue 26, Basic Blue 41, Basic Blue 66, Basic Blue 140, Basic Brown 1, Basic Brown 4, Basic fuchsin, Basic Green 1, Basic

Green 4, Basic Green 5, Basic Orange 2, Basic Orange 14, Basic Orange 21, Basic Red 1, Basic Red 2, Basic Red 5, Basic Red 9, Basic Red 29, Basic Violet 1, Basic Violet 2, Basic Violet 3, Basic Violet 4, Basic Violet 10, Basic Yellow 1 and Basic Yellow 2.

[0270] The term “direct dye” is recognized in the art and is intended to include those water soluble dyes that adsorb onto a material. Bonding is believed to occur through hydrogen bonding and/or Van der Waals forces between the dye and the substrate.

[0271] Representative examples of direct dyes useful in the present compositions include, but are not limited to, Direct Blue 1, Direct Blue 14, Direct Blue 53, Direct Blue 71, Direct Red 2, Direct Red 23, Direct Red 28, Direct Red 75, Direct Red 80, Direct Red 81, Direct Violet 51, Direct Yellow 4, Direct Yellow 7, Direct Yellow 8, Direct Yellow 9, Direct Yellow 12, Direct Yellow 27, Direct Yellow 50, Direct Yellow 59, Direct Yellow 62.

[0272] The term “reactive dye” is recognized in the art and is intended to include those dyes that contain a reactive group, for example, either a haloheterocycle or an activated double bond, that, when applied to a surface in a weakly alkaline solution, forms a chemical bond with a hydroxyl or amino group on the substrate.

[0273] Representative examples of reactive dye compounds useful in the present compositions include, but are not limited to, Procion red, blue, orange and yellow (ICI), Levafix E Yellow (Bayer), Remazol Yellow (Hoechst), Cibacron (Ciba), Drimarene X, R, K (Sandoz), Reactive Black 5, Reactive Blue 2, Reactive Blue 4, Reactive Blue 13, Reactive orange 16 and Reactive Yellow 4.

[0274] The term “sulfur dye” is recognized in the art and is intended to include those dyes that contain sulfide linkages and are absorbed by a substrate and are insolubilised within or on the substrate by oxidation. During this process the sulfur dye forms complex larger molecules which are the basis of their good wash-fastness.

[0275] Representative examples of sulfur dyes useful in the present compositions include, but are not limited to, Sulfur Black 1 (Sulfur Black T) and Sulfur Blue (Patent Blue VF).

[0276] The term “fluorescent dye” is recognized in the art and is intended to include those dyes which give fluorescence either in solid phase or in liquid form. The color of compound can be different from the fluorescence in liquid form.

[0277] Representative examples of fluorescent dyes useful in the present compositions include, but are not limited to, Fluorescein, fluorescein diacetate, carboxyfluorescein, carboxyfluorescein diacetate, rhodamine B, sulforhodamine B, cotadecyl rhodamine B, rhodamine 6G, rhodamine 110, rhodamine 123, coumarine, resorufin, quinoxalines, pyrido[1,2-a]benzimidazoles, acridine, acriflavin, acridine orange, nonyl acridine orange, xanthene, eosin Y, pyronine Y, texas red, calcein, quinacrine, ethidium bromide, propidium iodide, resazurin, Nile, crystal violet, DiO6(3), JC-1, YOYO-1, DAPI, Hoechst 33342, FM 1-43, thiazole orange, primuline, thioflavin T, calcein blue, morin, and fura-2.

[0278] The term “solvent dye” is recognized in the art. Solubility in an organic solvent or solvents is a characteristic physical property of a solvent dye.

[0279] Representative examples of solvent dyes useful in the present compositions include, but are not limited to, Solvent Black 3, Solvent Black 5, Solvent Blue 14, Solvent Blue 35, Solvent Blue 38, Solvent Blue 43, Solvent Blue 59, Solvent Brown 1, Solvent Green 1, Solvent Green 3, Solvent Green 7, Solvent Green 11, Solvent Orange 1, Solvent Orange 2, Solvent Orange 7, Solvent Orange 15, Solvent Red 19, Solvent Red 23, Solvent Red 24, Solvent Red 26, Solvent Red 27, Solvent Red 41, Solvent Red 43, Solvent Red 45, Solvent Red 49, Solvent Red 72, Solvent Violet 8, Solvent Yellow 2, Solvent Yellow 3, Solvent Yellow 7, Solvent Yellow 14, Solvent Yellow 33, Solvent Yellow 94, manufactured by Sigma-Aldrich, St. Louis, MO; and Special Fluorescent Yellow 3G (Solvent Green 7), manufactured by Lanxess Corporation, Pittsburgh, PA.

[0280] The terms “FD&C” and “D&C” dyes are recognized in the art. In the United States, colorants for food, drugs and cosmetics are regarded as “color

additives". The Federal Food, Drug & Cosmetic (FD&C) Act of 1938 made food color additive certification mandatory. Since then the Food and Drug Administration (FDA) has been responsible for regulating all color additives used in food, drugs and cosmetics. Each batch to be sold in the United States has to be certified by the FDA. To avoid confusing color additives used in food with those manufactured for other uses, 3 categories of certifiable color additives were created: 1) FD&C (Food, Drug & Cosmetics) color additives with applications in food, drug & cosmetics; 2) D&C (Drug & Cosmetics) color additives with applications in drug & cosmetics; 3) External D&C (External Drug & Cosmetics) color additives with applications in externally applied drugs & in externally applied cosmetics. The use of all food colors approved for use in the United States are listed in 21 CFR (Code of Federal Regulation), parts 70 through 82 dealing with color additives.

[0281] Representative examples of FD&C dyes useful in compositions of the invention include, but are not limited to FD&C Blue 1, FD&C Blue 2, FD&C Green 3, FD&C Red 3, FD&C Red 40, FD&C Yellow 5, FD&C Yellow 6, Fast Emerald Green, and mixtures thereof, manufactured by Sensient Colors Inc., St. Louis, MO, Vitasyn Tetrazine X 90, Vitasyn Orange RGL 90, Vitasyn Quinoline Yellow 70, Vitasyn Ponceau 4RC 82, Vitasyn Blue AE 90, Vitasyn Patent Blue V 85 01, Sanolin Flavin 8GZ, Sanolin Yellow BG, Sanolin Red NBG, Sanolin Rhodamine B, Sanolin Violet E2R, Sanolin Violet FBL, Sanolin Blue NBL, Sanolin Blue EHRL, Sanolin Blue EHRL Liquid, and mixtures thereof, manufactured by Clariant Corp., Coventry, RI.

[0282] The term "polymeric colorant" is recognized in the art and polymeric colorants are a group of intermediate or high molar mass compounds that are intrinsically colored. Polymeric dyes may be defined through their applications as polymers and dyes, which possess suitably high tinctorial strength. Polymeric dyes are characterized by having polymeric chains covalently bonded to a chromophore (dye) molecule.

[0283] Representative examples of polymeric dyes useful in compositions of the invention include, but are not limited to , Palmer Orange B113, Palmer

Blue B232, Palmer Magenta, Palmer Fluorescent Red, Palmer Yellow R, Palmer Scarlett, Palmer Black B57, Palmer Patent Blue, LiquiTone Magenta 418, Polytint Violet X80LT, Polytint Orange X96, Polytint Yellow X15, Polytint Black X41LV, Polytint Red X64, Polytint Blue X3LV, & mixtures thereof, manufactured by Milliken & Co., Spartanburg, SC.

[0284] Alternatively, pigments can be incorporated into the compositions of the invention. Suitable examples of pigments include those known as Hydrus™ (available from Salis International Inc./Dr. Ph. Martin's). Currently there are 24 Hydrus™ colors that can be used within the scope of the present invention.

[0285] Colorants (dyes and pigments) that do not change color or have color dissipation are included in the compositions of the invention in ranges from about 1% to about 50% by weight, more particularly from about 3% to about 30% by weight and in particular from about 5% to about 15% by weight.

[0286] The compositions of the present invention can be used with any simple or complex bubble making device, apparatus or machine to generate bubbles.

[0287] The compositions of the present invention provide bubbles that have at least average bubble integrity and lifespan. In particular embodiments, the compositions that do not contain a film forming resin, resultant bubbles maintain integrity and/or lifespan for 1 second to about 30 minutes, more particularly from about 2 seconds to about 20 minutes and most particularly from about 5 seconds to about 5 minutes. In particular embodiments, where the compositions include a film forming resin, resultant bubbles maintain integrity and/or lifespan for 1 second to about 30 days, more particularly from about 2 seconds to about 25 days and most particularly from about 5 seconds to about 20 days.

[0288] The compositions of the present invention can be prepared by the following general method. Either 1%, 3% or 5% indicator, 2 equivalent of sodium hydroxide, 16g Colonial SLS (30%) solution with the remainder being remaining DI water to make total 100g. When polyvinyl alcohol was added,

heating was required but otherwise reaction was stirred at room temperature. Additional additives such as deionized water, surfactant, preservatives, amine, dye blockers and polyvinyl alcohol solution (in case of film forming bubbles) are added and the reaction mixture further stirred for 2 hours at room temperature.

[0289] In certain experiments were polyvinyl alcohol in prepared in situ, the following procedure can be used. Polyvinyl alcohol is added with stirring to deionized water at room temperature. After the addition is complete, the mixture is heated at 90°C for 30 min, cooled to room temperature followed by addition of dye, humectant (glycerin or triethanolamine), surfactant, base, dye blockers and/or preservatives.

[0290] After cooling, the compositions may be bottled. Alternately, the solution may be bottled without cooling.

[0291] The present invention further includes kits that include the compositions of the invention and instructions how to use the compositions to form films or bubbles. Typically, the solution is spread onto a surface to form a film or a suitable object is dipped into the solution and subjected to air flow to form a bubble or bubbles.

[0292] Markers

[0293] The present invention also provides compositions that are useful in no mess markers as described herein. The compositions include the various colorants (phthaleins, hydrazines, phenols, leuco dyes, etc.) described throughout the application, including in particular, the acid-base indicators described herein.

[0294] The present invention, therefore, provides marking systems that advantageously minimize or eliminate messiness, i.e., inadvertent or stray marks, during use. The marking system comprises a marking composition composed of an acid-base indicator(s) as described herein, that change color from a first color to colorless, a first color to a second color, or colorless to a color under appropriate conditions.

[0295] The marking instrument can be utilized to store the marking composition and/or apply the marking composition to a desired substrate. The substrate can be provided with a coating or impregnated with at least one color-maintaining material, e.g., an acid or a base. Upon application of the acid-base indicator dye to the substrate, the dye pH level is maintained and thus the color is maintained. If, however, color is marked on an intended or unintended surface, thereby resulting in undesired color or the desire for temporary color, the stain can be readily removed with the application of pressure, water, or extended exposure to air.

[0296] The marking instruments include, but are not limited to, markers, pencils, crayons, stamps, stamp pads, pens, spray bottles, brushes, pads, sponges, squirt guns and the like.

[0297] In one aspect the compositions of the invention include acid-base indicators that are generally colored under basic condition and change color or fade to clear in non-basic condition. Acid-base indicators which are colored on alkaline pH side (pH >7) and turn clear on acidic pH (pH <7) are most useful. Typically, the acid-base indicators are colored at pH between about 9 and about 10, and turn clear at pH between about 6 and about 8.

[0298] Acid-base indicators are usually effective when present in small amounts in the marker compositions of the invention but generally are present in amounts from about 0.01% up to about 20% by weight, from about 0.05% to about 10% by weight and from about 0.1% to about 8% by weight of the total weight of the composition.

[0299] Representative examples of acid-base indicators useful in the marker compositions of the present invention include, but are not limited to those described herein. In particular, with reference for Formulae (I) and (Ia), R² is selected from the group consisting of hydrogen and methyl; R³ is selected from the group consisting of hydrogen phenyl, isopropyl, methyl ethyl and methoxy; R⁵ is selected from the group consisting of hydrogen, bromo, methoxy, isopropyl and methyl; and R⁶ is selected from the group consisting of hydrogen and methyl.

[0300] In one aspect, the compound where R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms is excluded from marker compositions.

[0301] In certain marker compositions, R^2 is selected from the group consisting of hydrogen, nitro, amino and alkyl; R^3 is selected from the group consisting of hydrogen, phenyl, alkyl, nitro, acetamido and alkoxy; R^5 is selected from the group consisting of hydrogen, halo, and alkyl; and R^6 is selected from the group consisting of hydrogen and alkyl.

[0302] In certain marker compositions, R^2 is selected from the group consisting of hydrogen and methyl; R^3 is selected from the group consisting of hydrogen, phenyl, isopropyl, methyl, ethyl, sec-butyl, nitro and methoxy; R^5 is selected from the group consisting of hydrogen, bromo, methoxy, isopropyl and methyl; and R^6 is selected from the group consisting of hydrogen and methyl.

[0303] In other marker compositions, R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; R^2 is hydrogen, R^3 is Me, and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; R^2 is Me, R^3 is a hydrogen atom, R^5 is an iso-propyl group and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 is Me, R^5 is Br and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; and R^2 is Me, R^3 is Br, R^5 is an isopropyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms. In certain embodiments, one or more of these compounds may be excluded from certain aspects of the invention.

[0304] In still other marker composition embodiments, R^2 is H, R^3 is phenyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 and R^5 are isopropyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 is methyl, R^5 is H, R^6 is methyl, R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 and R^5 are methoxy and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 and R^5 are methyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 is ethyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 is isopropyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 is methoxide and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms; and R^2 , R^3 and R^5 are all methyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 , R^3 ,

R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} are all hydrogen atoms and R^3 is sec-butyl, or R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} are all hydrogen atoms and R^3 is nitro.

[0305] In particular, at least one of M^1 or M^2 is a metal or an ammonium ion.

[0306] In another embodiment M^1 and M^2 can be hydrogen atoms for marker compositions. In this way, a basic substrate would react with the marker composition when acted upon by the marker. In this manner, "clear" marker would provide a color to an otherwise uncolored surface that has slightly basic characteristics.

[0307] It should be understood that the marker compositions can include any of the components described throughout the application including humectants, solvents, fragrances, etc.

[0308] In particular embodiment, there are surfactants which play a significant role in flow, color uniformity and viscosity of marker inks. These surfactants include, but are not limited to Triton X100, TritonX102, Tergitol 15-S-2 (90% aqueous), manufactured by Dow Chemical Co., Midland, MI; Dow Corning 190, Dow Corning 193, manufactured by Dow Corning, Midland, MI and Coatosil 1211, Silwet L7604, manufactured by GE Silicones. In particular, surfactants used in the invention are Triton X100, octylphenol ethoxylate and Dow Corning 190 fluid, poly(oxyethylene.oxypropylene)-methyl polysiloxane copolymer.

[0309] Surfactants are usually effective when present in small amounts in the marker compositions of the invention but generally are present in amounts from about 0.01% up to about 25% by weight, from about 0.05% to about 15% by weight and from about 0.1% to about 5% by weight of the total weight of the composition.

[0310] Cosmetic Compositions

[0311] The present invention also provides cosmetic temporary coloring compositions which include a cosmetically acceptable support and at least one of the colorants as described herein, and in particular, acid-based indicator(s).

[0312] In one aspect the cosmetic compositions of the invention include acid-base indicators. These acid-base indicators used in the present invention are generally colored under basic condition and change color or fade to clear in non-basic condition. Acid-base indicators which are colored on alkaline pH side (pH >7) and turn clear on acidic pH (pH <7) are most useful. Typically, the acid-base indicators are colored at pH between about 9 and 10, and turn clear at pH between about 6 and 8.

[0313] Representative examples of acid-base indicators useful in the cosmetic compositions of the present invention include, but are not limited to those described herein. In particular, with reference for Formulae (I) and (Ia), R² is selected from the group consisting of hydrogen and methyl; R³ is selected from the group consisting of hydrogen phenyl, isopropyl, methyl ethyl and methoxy; R⁵ is selected from the group consisting of hydrogen, bromo, methoxy, isopropyl and methyl; and R⁶ is selected from the group consisting of hydrogen and methyl.

[0314] In one aspect, the compound where R², R³, R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms is excluded from cosmetic compositions.

[0315] In certain cosmetic embodiments, R² is selected from the group consisting of hydrogen, nitro, amino and alkyl; R³ is selected from the group consisting of hydrogen, phenyl, alkyl, nitro, acetamido and alkoxy; R⁵ is selected from the group consisting of hydrogen, halo, and alkyl; and R⁶ is selected from the group consisting of hydrogen and alkyl.

[0316] In certain cosmetic embodiments, R² is selected from the group consisting of hydrogen and methyl; R³ is selected from the group consisting of hydrogen, phenyl, isopropyl, methyl, ethyl, sec-butyl, nitro and methoxy; R⁵ is selected from the group consisting of hydrogen, bromo, methoxy, isopropyl and methyl; and R⁶ is selected from the group consisting of hydrogen and methyl.

[0317] In other cosmetic embodiments, R² is hydrogen, R³ is Me, and R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms; R² is Me, R³ is a hydrogen atom,

R^5 is an iso-propyl group and R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 is Me, R^5 is Br and R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms; and R^2 is Me, R^3 is Br, R^5 is an isopropyl and R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms. In certain embodiments, one or more of these compounds may be excluded from certain aspects of the invention.

[0318] In still other cosmetic embodiments, R^2 is H, R^3 is phenyl and R^5, R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 and R^5 are isopropyl and R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 is methyl, R^5 is H, R^6 is methyl, R^7, R^8, R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 and R^5 are methoxy and R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 and R^5 are methyl and R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 is ethyl and R^5, R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 is isopropyl and R^5, R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms; R^2 is H, R^3 is methoxide and R^5, R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms; and R^2, R^3 and R^5 are all methyl and R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms, or $R^2, R^3, R^5, R^6, R^7, R^8, R^9, R^{10}$ are all hydrogen atoms and R^3 is sec-butyl, or $R^2, R^3, R^5, R^6, R^7, R^8, R^9, R^{10}$ are all hydrogen atoms and R^3 is nitro.

[0319] In particular, at least one of M^1 or M^2 is a metal or an ammonium ion.

[0320] Additionally, the phenols and hydrazines described throughout are useful in the cosmetic compositions as well. Additional colorants useful in the various cosmetic compositions of the application include those listed throughout the application.

[0321] Acid-base indicators are usually effective in cosmetics when present in small amounts in the compositions of the invention but generally are present in amounts from about 0.01% up to about 20% by weight, from about 0.05% to about 10% by weight and from about 0.1% to about 5% by weight of the total weight of the composition.

[0322] If the cosmetic compositions according to the invention are intended for temporary coloring keratin fibers such as human hair and nails, especially human hair, the acid-base indicators are generally present in a

proportion of from 0.005% to 10%, and preferably of from 0.02% to 8%, by weight relative to the total weight of the composition. The pH of the composition is preferably from 5 to 11, and more preferably from 6 to 10. The compositions according to the invention used in this manner are preferably applied for 1 to 45 minutes, more preferably 5 to 30 minutes, although for lotions applied as a hair rinse, there is not treatment time, the said lotions being applied and then dried.

[0323] The cosmetic compositions according to the invention can also be used in the form of colored lacquers, optionally in aerosol form using a propellant.

[0324] The cosmetic compositions according to the invention can be used in direct dyeing and can contain, in addition to the acid-base indicators, other colorants, in particular direct dyes such as azo dyes, anthraquinone dyes, nitrated dyes of the benzene series, 2,5-diaminoquinones, indophenols, indoanilines and indamines.

[0325] The cosmetic compositions according to the invention can also contain alkalization or acidification agents and/or solvents and/or polymers and/or treatment products of cationic character and/or amides and/or thickeners and/or surfactants and/or additives commonly used in capillary cosmetics, such as sun filters, optical blues, antioxidants, sequestering agents and perfumes.

[0326] The alkalization agents which may be present in the cosmetic compositions according to the invention can be, for example, mono- or triethanolamine, ammonia, sodium phosphate or sodium carbonate. The acidification agents which may be present in the composition according to the invention can be, for example, phosphoric, hydrochloric, lactic, tartaric, acetic or citric acid. These alkalization or acidification agents are intended for adjusting the pH of the tinctorial composition to the desired value.

[0327] The solvents present in the cosmetic compositions according to the invention may be alcohols of 2 to 4 carbon atoms, such as ethyl or isopropyl alcohol or glycols such as ethylene glycol, propylene glycol, or butylene glycol, or glycol ethers such as the methyl, ethyl or butyl ether of ethylene glycol. The solvent is preferably present in an amount of from 0.5 to 50% by weight,

preferably from 1 to 15% by weight, relative to the total weight of the composition.

[0328] The polymers which may be present in the cosmetic composition are cosmetically acceptable polymers known to a person skilled in the art.

[0329] These polymers may be used at concentrations of from 0.1 to 4% by weight, preferably from 0.3 to 2% by weight, relative to the total weight of the composition.

[0330] The amides which may be present in the cosmetic compositions according to the invention can be mono- or diethanolamides of fatty acids, optionally oxyethyleneated.

[0331] The thickeners may be cellulose derivatives such as carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose and those described herein.

[0332] The surfactants may be anionic, cationic, non-ionic or amphoteric surfactants, such as those described throughout the application.

[0333] The cosmetic compositions according to the invention may be in many forms, for example in the form of a gel, cream, foaming liquid or milky liquid, and can be packaged in, for example, bottles, tubes or aerosols.

[0334] If cosmetic compositions according to the invention are treatment and/or make-up products for the skin surface, the acid-base indicator derivatives have the function of coloring the composition itself or the skin surface, and they can simultaneously confer on the latter the treatment effect and protection effect due to the presence of the protein chains.

[0335] The cosmetic compositions according to the invention intended for application to the skin preferably contain the acid-base indicator(s) in an amount of from 0.01 to 10% by weight, relative to the total weight of the composition.

[0336] The cosmetic make-up compositions according to the invention may, for example, take the form of sticks, pastes, emulsions, suspensions, dispersions, powders or solutions, and may form lipsticks, mascaras, lip glosses, blushers, eye shadows, make-up foundations, eyeliners or powders.

[0337] The colorant, such as an acid-base indicator, can be associated with inorganic or organic pigments, and especially with lacquers such as those commonly used.

[0338] The inorganic pigments are, in general, iron oxides (red, brown, black and yellow), chromium oxides, the ultramarines (aminosilicate polysulphides), titanium dioxide, manganese pyrophosphate and Prussian Blue (ferric ferrocyanide). These various compounds alone or mixed together are generally employed at concentrations of from 0.1 to 40% by weight with respect to the total weight of the cosmetic composition.

[0339] The cosmetic compositions can also contain agents imparting pearlescence such as bismuth oxychloride, titanium mica and guanine crystals.

[0340] When the cosmetic compositions take the form of sticks, especially lipstick, eye shadow, blusher and make-up foundation, a significant part of the compositions may consist of a fatty substance which can comprise one or more waxes, for example ozokerite, lanolin, lanolin alcohol, hydrogenated lanolin, acetylated lanolin, lanolin wax, beeswax, candellila wax, microcrystalline wax, carnauba wax, cetyl alcohol, stearyl alcohol, cocoa butter, lanolin fatty acids, petrolatum, vaselines, mono-, di- and triglycerides solid at 25°C., fatty esters solid at 25°C., silicone waxes such as methyloctadecane-oxypolysiloxane and poly(dimethyl-siloxy) stearoxysiloxane, stearic acid monoethanolamide, colophony and its derivatives such as glycol abietate and glycerol abietate, hydrogenated oils solid at 25°C., sucroglycerides, and calcium, magnesium, zirconium and aluminum oleates, myristates, lanolates, stearates or dihydroxystearates.

[0341] The fatty substance may also consist of a mixture of at least one wax and at least one oil, for example: paraffin oil, purcellin oil, perhydrosqualene, sweet-almond oil, avocado oil, oil of calophyllum, castor oil, sesame oil, jojoba oil, mineral oils having a boiling point between 310 and 410°C., silicone oils such as dimethylpolysiloxanes, linoleyl alcohol, linolenyl alcohol, oleyl alcohol, the oil of cereal seeds such as wheatgerm oil, isopropyl lanolate, isopropyl palmitate, isopropyl myristate, butyl myristate, cetyl myristate, hexadecyl stearate, butyl

stearate, decyl oleate, acetylglycerides, octanoates and decanoates of such alcohols and polyalcohols as glycol and glycerol, the ricinoleates of alcohols and polyalcohols such as cetyl ricinoleate, isostearyl alcohol, isocetyl lanolate, isopropyl adipate, hexyl laurate or octyldodecanol.

[0342] In general, the fatty substance in these compositions in stick form may represent up to 99.9% by weight of the total weight of the composition.

[0343] The cosmetic compositions may also contain other ingredients such as glycols, polyethylene glycols, polypropylene glycols, monoalkanolamides, uncolored polymers, inorganic or organic fillers, preservatives, UV filters or other additives common in cosmetics.

[0344] The cosmetic compositions in stick form may contain a quantity of water, generally not exceeding 40% relative to the total weight of the cosmetic composition.

[0345] When the cosmetic compositions according to the invention are semi-solid in form, that is, in the form of pastes or creams, they may be used as a mascara, an eyeliner, a make-up foundation, a blusher, an eye shadow, a lipstick, or a concealer.

[0346] These pastes or creams may be emulsions of the water-in-oil or oil-in-water type, in which the fatty phase preferably represents from 1 to 98.8% by weight and the water phase preferably represents from 1 to 98.8% by weight and the emulsifier preferably represents from 0.1 to 30% by weight.

[0347] The cosmetic compositions can also contain other conventional ingredients such as perfumes, antioxidants, preservatives, gelling agents, UV filters, colorings, pigments, agents imparting pearlescence, uncolored polymers and inorganic or organic fillers.

[0348] When the cosmetic compositions take the form of a powder, they may consist essentially of an inorganic or organic filler such as talc, kaolin, starches, polyethylene powders or polyamide powders, as well as additives such as binders, colorings and the like.

[0349] Such cosmetic compositions can also contain various additives commonly used in cosmetics such as perfumes, antioxidants and preservatives as described throughout the application.

[0350] Aspects of the present teachings can be further understood in light of the following examples, which should not be construed as limiting the scope of the present teachings in any way.

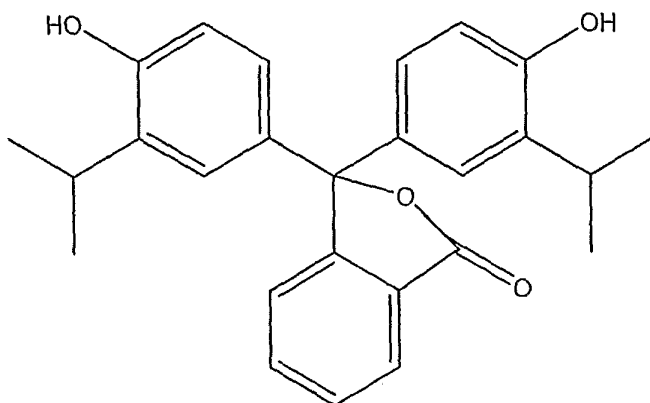
[0351] Examples

Synthesis of acid-base indicators:

EXAMPLE 1

Synthesis of 3,3-bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone

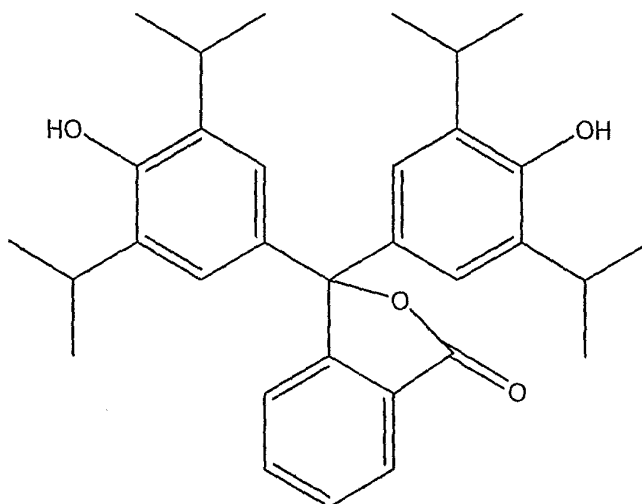
A mixture of 2-isopropylphenol (0.2M), phthalic anhydride (0.1M), polyphosphoric acid (0.25M), and zinc chloride (0.01M), was stirred and heated at 100C for 3 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from ethanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone in 96% yield.



EXAMPLE 2

Synthesis of 3,3-bis-(4-hydroxy-3,5-diisopropylphenyl)-1-(3H)- isobenzofuranone

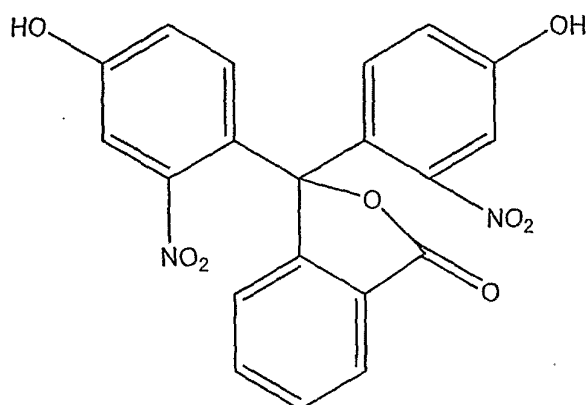
A mixture of 2,6-diisopropylphenol (0.2M), phthalic anhydride (0.1M), polyphosphoric acid (0.25M), and zinc chloride (0.01M), was stirred and heated at 100C for 3 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from ethanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-3,5-diisopropylphenyl)-1-(3H)-isobenzofuranone in 98% yield.



EXAMPLE 3

Synthesis of 3,3-bis-(4-hydroxy-2-nitrophenyl)-1-(3H)-isobenzofuranone

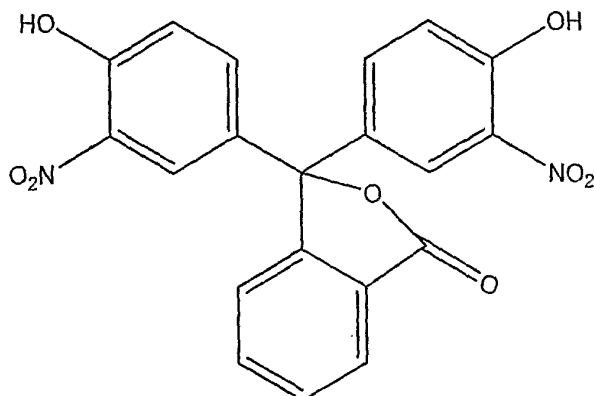
A mixture of 3-nitrophenol (0.2M), phthalic anhydride (0.1M), polyphosphoric acid (0.25M), and zinc chloride (0.01M), was stirred and heated at 100C for 3 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from ethanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-2-nitrophenyl)-1-(3H)-isobenzofuranone in 81% yield.



EXAMPLE 4

Synthesis of 3,3-bis-(4-hydroxy-3-nitrophenyl)-1-(3H)-isobenzofuranone

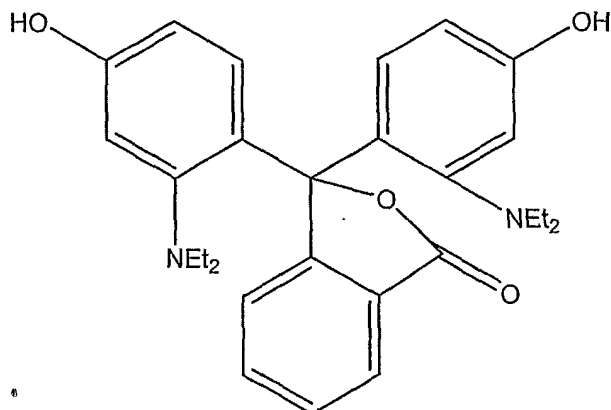
A mixture of 2-nitrophenol (0.2M), phthalic anhydride (0.1M), polyphosphoric acid (0.25M), and zinc chloride (0.01M), was stirred and heated at 100C for 3 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from ethanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-3-nitrophenyl)-1-(3H)-isobenzofuranone in 89% yield.



EXAMPLE 5

Synthesis of 3,3-bis-[4-hydroxy-2-(N,N-diethylamino)phenyl]-1-(3H)- isobenzofuranone

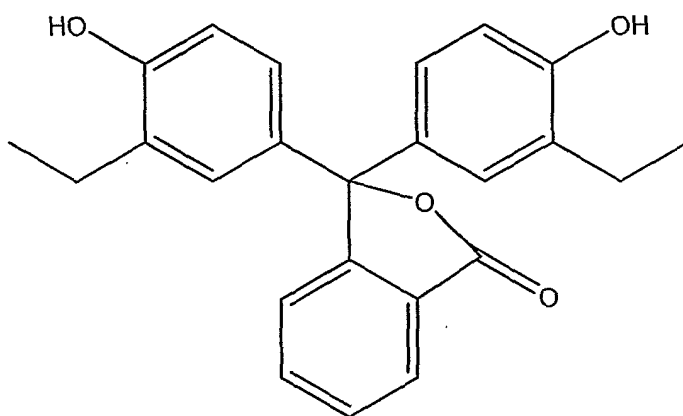
A mixture of 3-(N,N-diethylamino)phenol (0.2M), phthalic anhydride (0.1M), polyphosphoric acid (0.25M), and zinc chloride (0.01M), was stirred and heated at 100C for 3 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from ethanol with charcoal treatment furnished pure 3,3-bis-[4-hydroxy-2-(N,N-diethylamino)phenyl]-1-(3H)-isobenzofuranone in 93% yield.



EXAMPLE 6

Synthesis of 3,3-bis-(4-hydroxy-3-ethylphenyl)-1-(3H)-isobenzofuranone

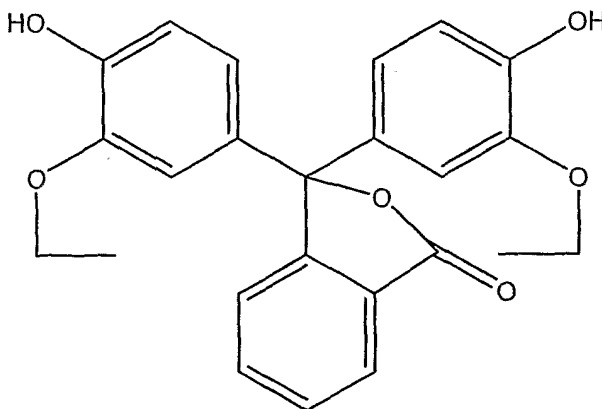
A mixture of 2-ethylphenol (0.2M), phthalic anhydride (0.1M), polyphosphoric acid (0.25M), and zinc chloride (0.01M), was stirred and heated at 100C for 3 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from ethanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-3-ethylphenyl)-1-(3H)-isobenzofuranone in 92% yield.



EXAMPLE 7

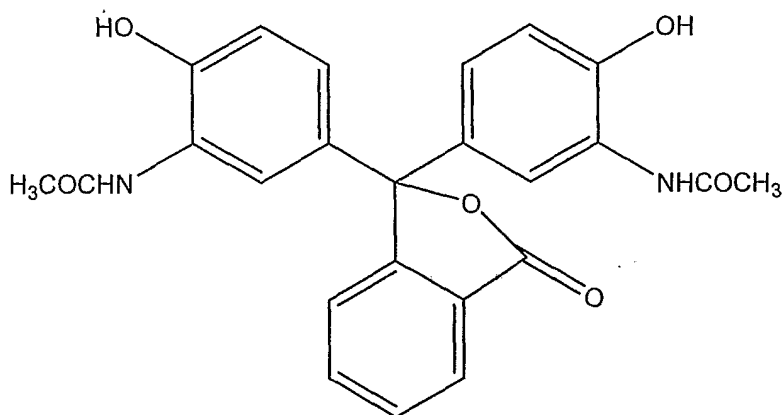
Synthesis of 3,3-bis-(4-hydroxy-3-ethoxyphenyl)-1-(3H)-isobenzofuranone

A mixture of 2-ethoxyphenol (0.2M), phthalic anhydride (0.1M), polyphosphoric acid (0.25M), and zinc chloride (0.01M), was stirred and heated at 100C for 3 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from ethanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-3-ethoxyphenyl)-1-(3H)-isobenzofuranone in 85% yield.

**EXAMPLE 8****Synthesis of 3,3-bis-(4-hydroxy-3-acetamidophenyl)-1-(3H)-isobenzofuranone**

A mixture of 2-acetamidophenol (0.2M), phthalic anhydride (0.1M), polyphosphoric acid (0.25M), and zinc chloride (0.01M), was stirred and heated at 100C for 3 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from ethanol

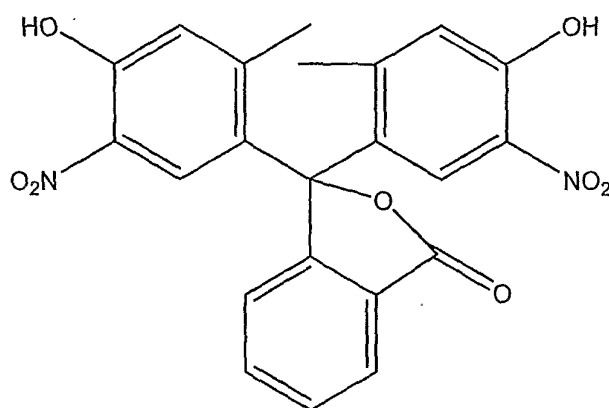
with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-3-acetamidophenyl)-1-(3H)-isobenzofuranone in 83% yield.



EXAMPLE 9

Synthesis of 3,3-bis-(4-hydroxy-6-methyl-3-nitrophenyl)-1-(3H)-isobenzofuranone

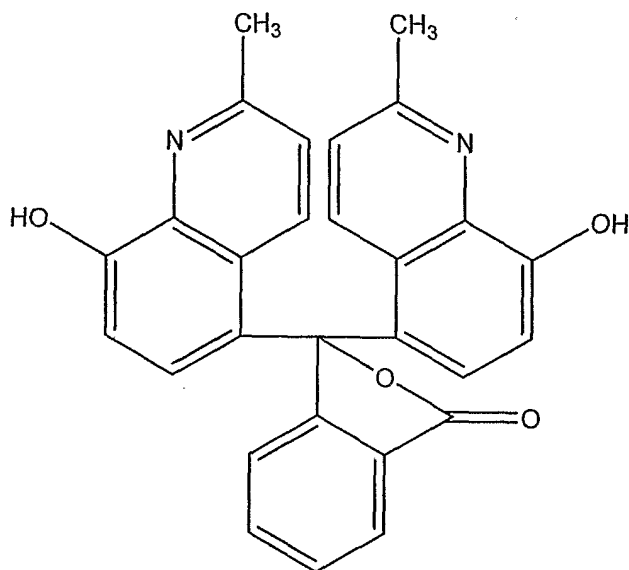
A mixture of 5-methyl-2-nitrophenol (0.2M), phthalic anhydride (0.1M), polyphosphoric acid (0.25M), and zinc chloride (0.01M), was stirred and heated at 100C for 3 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from ethanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-6-methyl-3-nitrophenyl)-1-(3H)-isobenzofuranone in 81% yield.



EXAMPLE 10

Synthesis of 3,3-bis-(4-hydroxy-6-methyl-5-quinolin-1-yl)-1-(3H)- isobenzofuranone

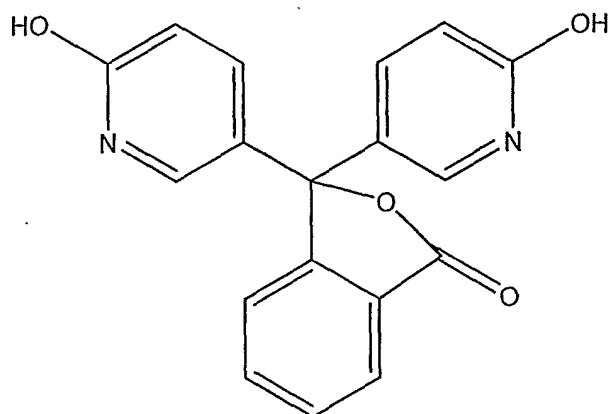
A mixture of 8-hydroxyquinaldine (0.2M), phthalic anhydride (0.1M), polyphosphoric acid (0.25M), and zinc chloride (0.01M), was stirred and heated at 100C for 3 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from ethanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-6-methyl-5-quinolin-1-yl)-1-(3H)-isobenzofuranone in 88% yield.



EXAMPLE 11

Synthesis of 3,3-bis-(4-hydroxy-3-pyridin-1-yl)-1-(3H)-isobenzofuranone

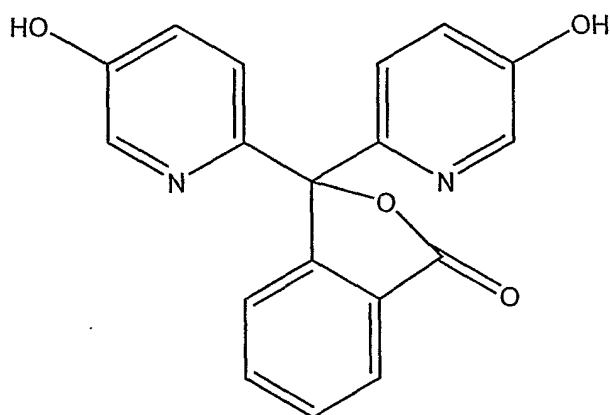
A mixture of 2-hydroxypyridine (0.2M), phthalic anhydride (0.1M), polyphosphoric acid (0.25M), and zinc chloride (0.01M), was stirred and heated at 100C for 3 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from ethanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-3-pyridin-1-yl)-1-(3H)-isobenzofuranone in 80% yield.



EXAMPLE 12

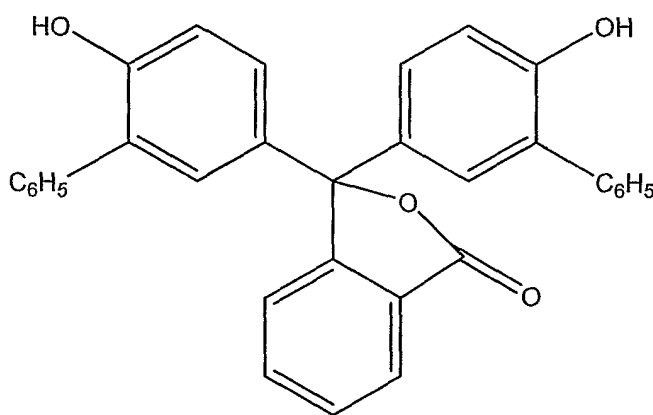
Synthesis of 3,3-bis-(4-hydroxy-2-pyridin-1-yl)-1-(3H)-isobenzofuranone

A mixture of 3-hydroxypyridine (0.2M), phthalic anhydride (0.1M), polyphosphoric acid (0.25M), and zinc chloride (0.01M), was stirred and heated at 100C for 3 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from ethanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-2-pyridin-1-yl)-1-(3H)-isobenzofuranone in 82% yield.



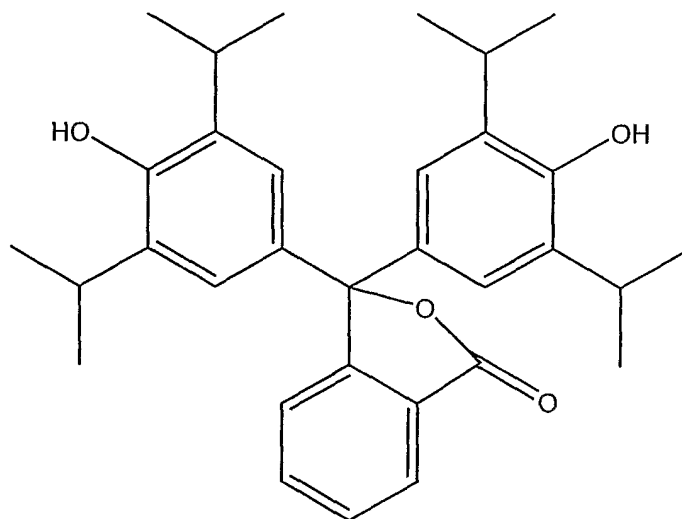
EXAMPLE 13**Synthesis of 3,3-bis-(4-hydroxy-3-phenylphenyl)-1-(3H)-isobenzofuranone**

A mixture of 2-phenylphenol (0.133mol), phthalic anhydride (0.074mol), reaction medium (0.416mol), and Lewis acid (0.029mol), was stirred and heated at 90°C for 5 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from methanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-3-phenylphenyl)-1-(3H)-isobenzofuranone as white crystals in 94% yield. ¹H-NMR (DMSO-d₆, 300MHz): δ 9.89 (s, 2H, 2OH), 6.97-7.18 (m, 6H, aromatic), 7.26-7.47 (m, 10H, aromatic), 7.63-7.92 (m, 4H, aromatic) ppm. Mass spectra: m/z 470 (M⁺).

**EXAMPLE 14****Synthesis of 3,3-bis-(4-hydroxy-3,5-diisopropylphenyl)-1-(3H)-isobenzofuranone**

A mixture of 2,6-diisopropylphenol (0.133mol), phthalic anhydride (0.074mol), reaction medium (0.416mol), and Lewis acid (0.029mol), was stirred

and heated at 90°C for 5 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from methanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-3,5-diisopropylphenyl)-1-(3H)-isobenzofuranone as white crystals in 89% yield. IR (KBr): 3506, 1734, 1609 cm^{-1} . $^1\text{H-NMR}$ (DMSO-d_6): δ 9.56 (s, 2H, 2OH), 1.02-1.05 (dd, 24H, 8 CH_3), 3.22-3.31 (heptate, 4H, 4CH), 6.74-7.00 (m, 4H, aromatic), 7.59-7.92 (m, 4H, aromatic) ppm. Mass spectra: m/z 486 (M^+).

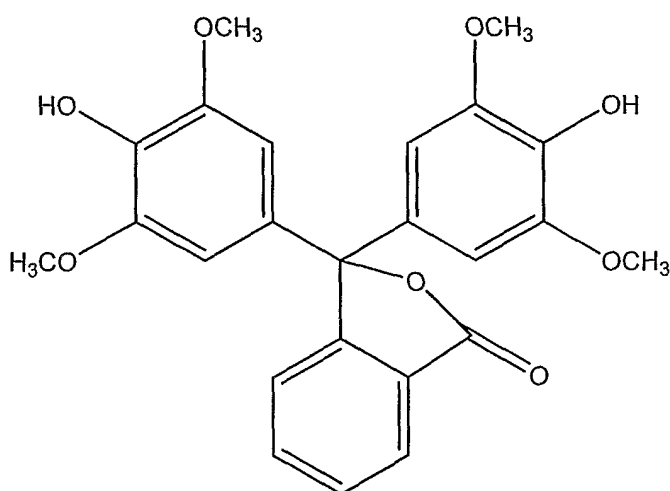


EXAMPLE 15

Synthesis of 3,3-bis-(4-hydroxy-3,5-dimethoxyphenyl)-1-(3H)-isobenzofuranone

A mixture of 2,6-dimethoxyphenol (0.133mol), phthalic anhydride (0.074mol), reaction medium (0.416mol), and Lewis acid (0.029mol), was stirred and heated at 90°C for 5 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The

product was filtered, thoroughly washed with water and dried. Recrystallization from methanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-3,5-dimethoxyphenyl)-1-(3H)-isobenzofuranone as white crystals in 84% yield. IR (KBr): 3388, 1769, 1606, 1369 cm^{-1} . $^1\text{H-NMR}$ (DMSO-d_6): δ 8.71 (s, 2H, 2OH), 3.66 (s, 12H, 4OCH₃), 7.65-7.68 (m, 4H, aromatic), 7.83-7.96 (m, 4H, aromatic) ppm. Mass spectra: m/z 438 (M^+).

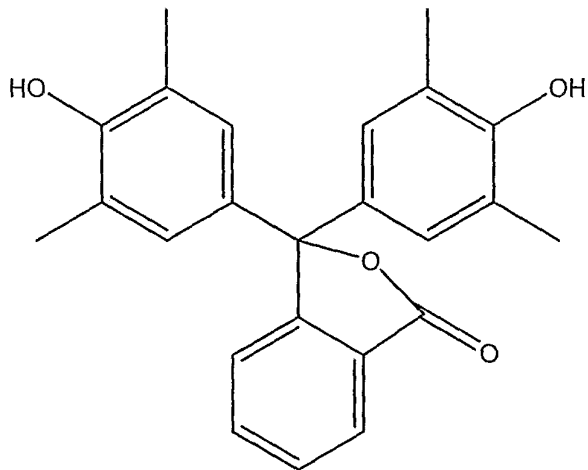


EXAMPLE 16

Synthesis of 3,3-bis-(4-hydroxy-3,5-dimethylphenyl)-1-(3H)-isobenzofuranone

A mixture of 2,6-dimethylphenol (0.133mol), phthalic anhydride (0.074mol), reaction medium (0.416mol), and Lewis acid (0.029mol), was stirred and heated at 90°C for 5 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from methanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-3,5-

dimethylphenyl)-1-(3H)-isobenzofuranone as white crystals in 91% yield. IR (KBr): 3582, 3386, 1746, 1605 cm^{-1} . $^1\text{H-NMR}$ (DMSO-d_6): δ 8.45 (s, 2H, 2OH), 2.10 (s, 12H, 4CH₃), 7.58-7.63 (m, 4H, aromatic), 7.78-7.87 (m, 4H, aromatic) ppm. Mass spectra: m/z 374 (M^+).

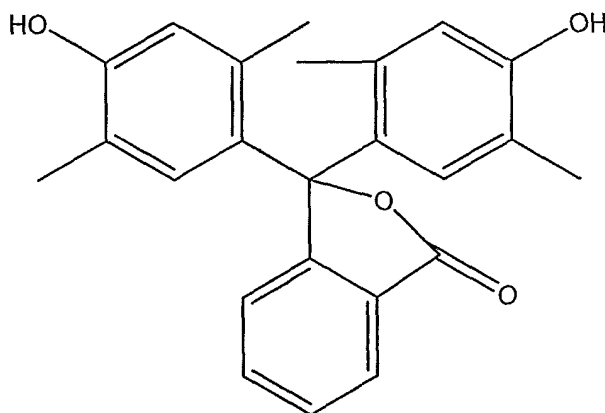


EXAMPLE 17

Synthesis of 3,3-bis-(4-hydroxy-3,6-diimethylphenyl)-1-(3H)-isobenzofuranone

A mixture of 2,5-dimethylphenol (0.133mol), phthalic anhydride (0.074mol), reaction medium (0.416mol), and Lewis acid (0.029mol), was stirred and heated at 90°C for 5 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from methanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-3,6-diimethylphenyl)-1-(3H)-isobenzofuranone as pale yellow crystals in 85% yield. IR (KBr): 3393, 1729, 1611 cm^{-1} . $^1\text{H-NMR}$ (DMSO-d_6): δ 9.40 (s, 2H, 2OH),

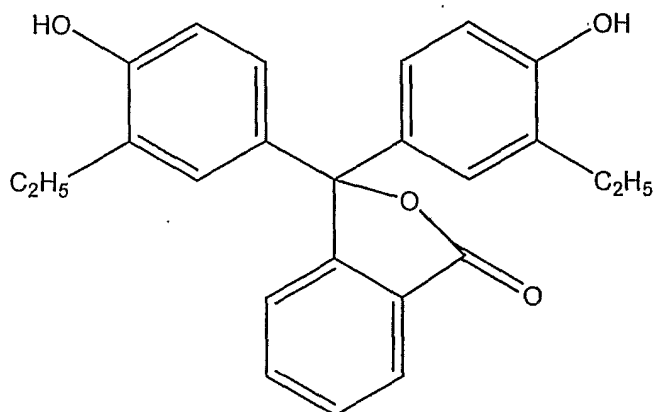
1.95 (s, 12H, 4CH₃), 6.59-6.63 (m, 4H, aromatic), 7.46-7.91 (m, 4H, aromatic) ppm. Mass spectra: m/z 374 (M⁺).



EXAMPLE 18

Synthesis of 3,3-bis-(4-hydroxy-3-ethylphenyl)-1-(3H)-isobenzofuranone

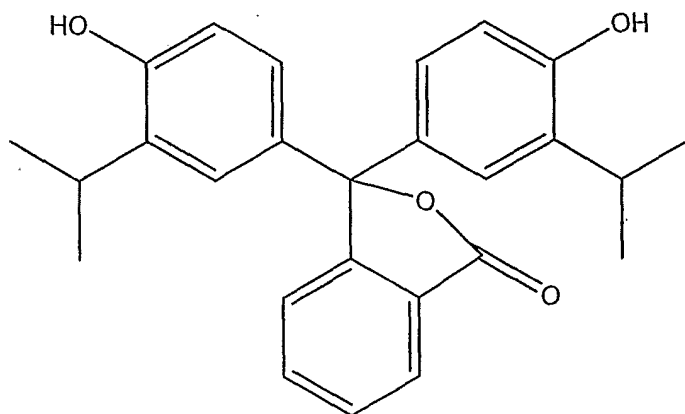
A mixture of 2-ethylphenol (0.133mol), phthalic anhydride (0.074mol), reaction medium (0.416mol), and Lewis acid (0.029mol), was stirred and heated at 90°C for 5 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from ethyl acetate:petroleum ether (1:1) with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-3-ethylphenyl)-1-(3H)-isobenzofuranone as white crystals in 81% yield. IR (KBr): 3389, 1783, 1718, 1605 cm⁻¹. ¹H-NMR (DMSO-d₆): δ 9.54 (s, 2H, 2OH), 2.43-2.50 (q, 4H, 2CH₂), 1.00-1.05 (t, 6H, 2CH₃), 6.74-6.96 (m, 6H, aromatic), 7.57-7.89 (m, 4H, aromatic) ppm. Mass spectra: m/z 374 (M⁺).



EXAMPLE 19

Synthesis of 3,3-bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone

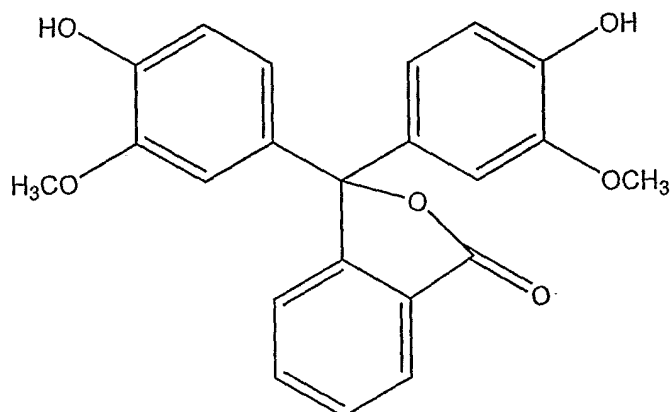
A mixture of 2-isopropylphenol (0.133mol), phthalic anhydride (0.074mol), reaction medium (0.416mol), and Lewis acid (0.029mol), was stirred and heated at 90°C for 5 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from methanol:water (1:1) with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone as white crystals in 83% yield. IR (KBr): 3383, 1733, 1608 cm^{-1} . $^1\text{H-NMR}$ (DMSO-d_6): δ 9.57 (s, 2H, 2OH), 1.05-1.07 (dd, 12H, 4 CH_3), 3.11-3.18 (heptate, 2H, 2CH), 6.75-7.01 (m, 6H, aromatic), 7.59-7.90 (m, 4H, aromatic) ppm. Mass spectra: m/z 402 (M^+).



EXAMPLE 20

Synthesis of 3,3-bis-(4-hydroxy-3-methoxyphenyl)-1-(3H)-isobenzofuranone

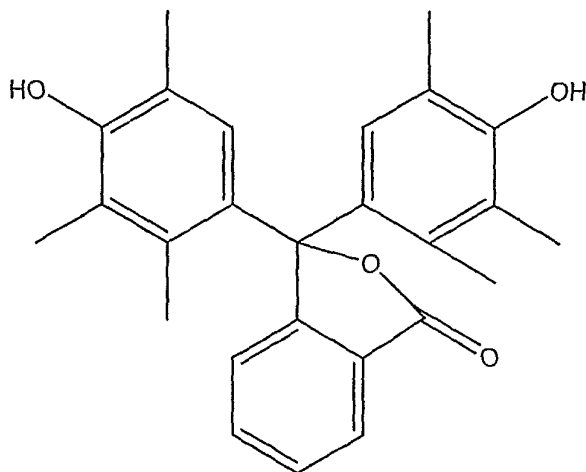
A mixture of 2-methoxyphenol (0.133mol), phthalic anhydride (0.074mol), reaction medium (0.416mol), and Lewis acid (0.029mol), was stirred and heated at 90°C for 5 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from methanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-3-methoxyphenyl)-1-(3H)-isobenzofuranone as white crystals in 79% yield. IR (KBr): 3517, 1747, 1701, 1279 cm^{-1} . $^1\text{H-NMR}$ (DMSO-d_6): δ 9.27 (s, 2H, 2OH), 3.66 (s, 6H, 2OCH₃), 6.65-6.78 (m, 6H, aromatic), 7.61-7.90 (m, 4H, aromatic) ppm. Mass spectra: m/z 378 (M^+).



EXAMPLE 21

Synthesis of 3,3-bis-(4-hydroxy-2,3,5-trimethylphenyl)-1-(3H)-isobenzofuranone

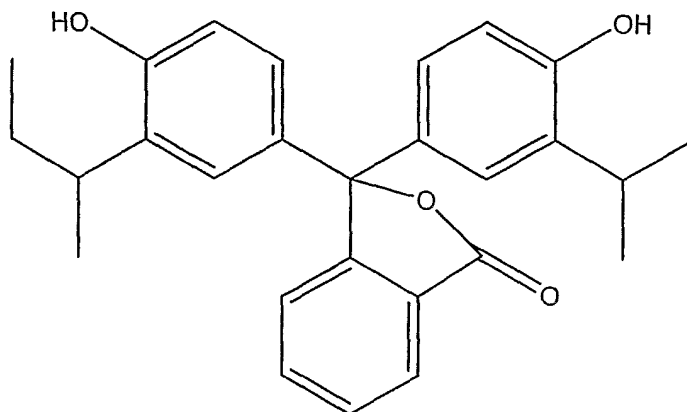
A mixture of 2,3,6-trimethylphenol (0.133mol), phthalic anhydride (0.074mol), reaction medium (0.416mol), and Lewis acid (0.029mol), was stirred and heated at 90°C for 5 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from methanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-2,3,5-trimethylphenyl)-1-(3H)-isobenzofuranone as white crystals in 73% yield. IR (KBr): 3510, 3390, 1746, 1609, cm^{-1} . $^1\text{H-NMR}$ (DMSO-d_6): δ 9.44 (s, 2H, 2OH), 2.05 (s, 18H, 6CH₃), 6.55 (s, 2H, aromatic), 7.46-7.90 (m, 4H, aromatic) ppm. Mass spectra: m/z 402 (M^+).



EXAMPLE 22

Synthesis of 3,3-bis-(4-hydroxy-3-sec-butylphenyl)-1-(3H)-isobenzofuranone

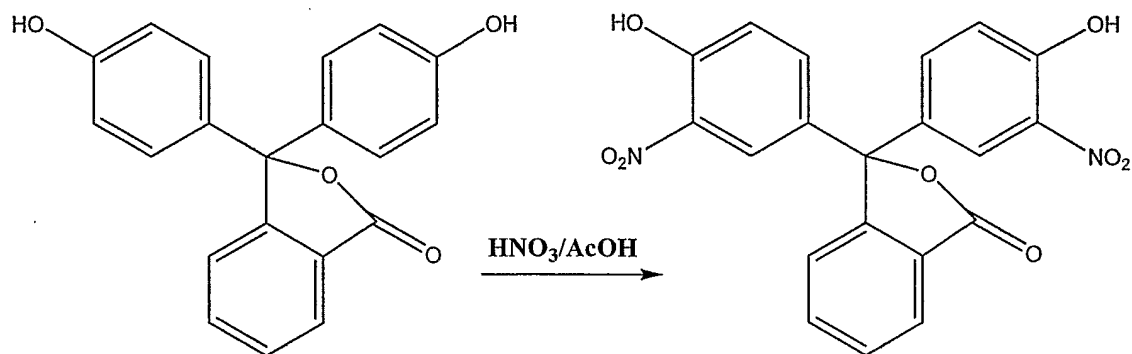
A mixture of 2-sec-butylphenol (0.133mol), phthalic anhydride (0.074mol), reaction medium (0.416mol), and Lewis acid (0.029mol), was stirred and heated at 90°C for 5 hours. The reaction mixture was cooled to room temperature and added to ice-water mixture when the product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from methanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-3-sec-butylphenyl)-1-(3H)-isobenzofuranone as white crystals in 77% yield. IR (KBr): 3400, 1722, 1607 cm^{-1} . $^1\text{H-NMR}$ (DMSO-d_6): δ 9.50 (s, 2H, 2OH), 0.80 (t, 6H, 2CH₃), 1.35-1.39 (p, 4H, 2CH₂), 1.22 (d, 6H, 2CH₃), 2.89-2.97 (sextate, 2H, 2CH), 6.73-6.93 (m, 6H, aromatic), 7.59-7.90 (m, 4H, aromatic) ppm. Mass spectra: m/z 430 (M^+).



EXAMPLE 23

Synthesis of 3,3-bis-(4-hydroxy-3-nitrophenyl)-1-(3H)-isobenzofuranone

A mixture of phenolphthalein (0.062mol) in acetic acid (290mL) was stirred at 15°C. Concentrated nitric acid (0.136mol, 65%) in acetic acid (10mL) was slowly added to stirring mixture at 15°C. The reaction mixture was further stirred for 6 hours at room temperature and added to ice-water mixture when the yellow colored product precipitated. The product was filtered, thoroughly washed with water and dried. Recrystallization from ethanol with charcoal treatment furnished pure 3,3-bis-(4-hydroxy-3-nitrophenyl)-1-(3H)-isobenzofuranone as pale yellow crystals in 78% yield. IR (KBr): 3262, 1766, 1627, 1538, 1423 cm^{-1} . $^1\text{H-NMR}$ (DMSO-d_6): δ 9.67 (s, 2H, 2OH), 6.71-7.16 (m, 6H, aromatic), 7.46-7.98 (m, 4H, aromatic) ppm. Mass spectra: m/z 408 (M^+).

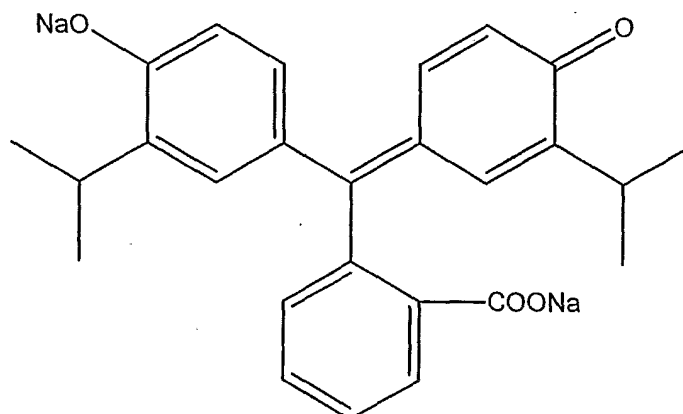


Synthesis of disodium salts of acid-base indicators for water based systems:

EXAMPLE 1

Synthesis of disodium salt of 3,3-bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone

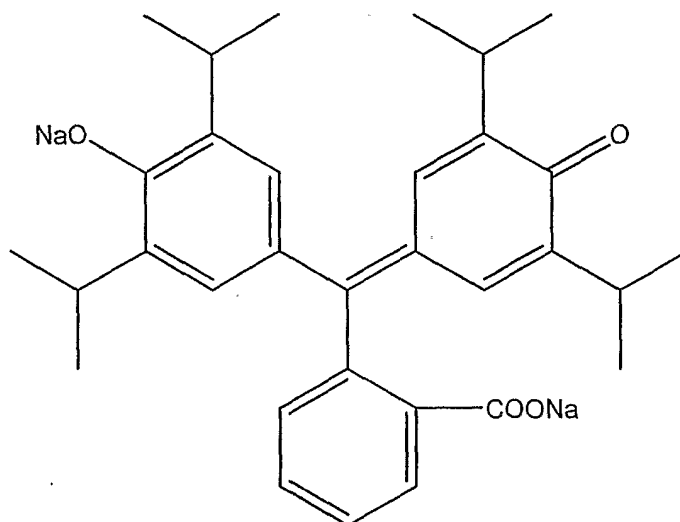
A mixture of 3,3-bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone (0.01M) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02M) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 98% yield.



EXAMPLE 2

Synthesis of disodium salt of 3,3-bis-(4-hydroxy-3,5-diisopropylphenyl)-1-(3H)-isobenzofuranone

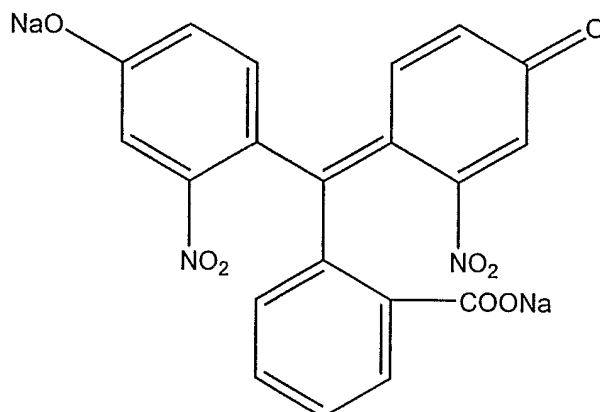
A mixture of 3,3-bis-(4-hydroxy-3,5-diisopropylphenyl)-1-(3H)-isobenzofuranone (0.01M) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02M) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 94% yield.



EXAMPLE 3

Synthesis of disodium salt of 3,3-bis-(4-hydroxy-2-nitrophenyl)-1-(3H)- isobenzofuranone

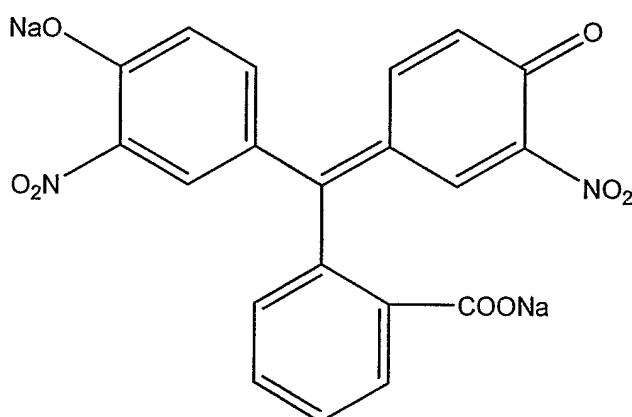
A mixture of 3,3-bis-(4-hydroxy-2-nitrophenyl)-1-(3H)-isobenzofuranone (0.01M) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02M) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 88% yield.



EXAMPLE 4

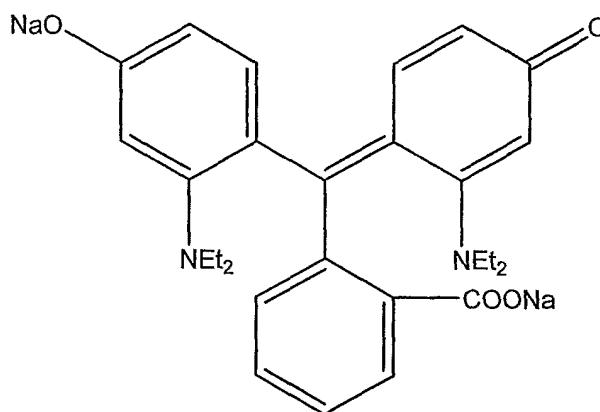
Synthesis of disodium salt of 3,3-bis-(4-hydroxy-3-nitrophenyl)-1-(3H)-isobenzofuranone

A mixture of 3,3-bis-(4-hydroxy-3-nitrophenyl)-1-(3H)-isobenzofuranone (0.01M) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02M) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 91% yield.



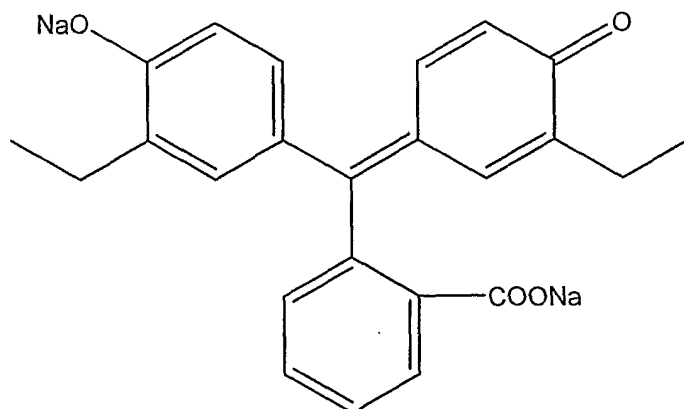
EXAMPLE 5**Synthesis of disodium salt of 3,3-bis-[4-hydroxy-2-(N,N-diethylamino)phenyl]-1-(3H)-isobenzofuranone**

A mixture of 3,3-bis-[4-hydroxy-2-(N,N-diethylamino)phenyl]-1-(3H)-isobenzofuranone (0.01M) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02M) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure, disodium salt in 89% yield.

**EXAMPLE 6****Synthesis of disodium salt of 3,3-bis-(4-hydroxy-3-ethylphenyl)-1-(3H)-isobenzofuranone**

A mixture of 3,3-bis-(4-hydroxy-3-ethylphenyl)-1-(3H)-isobenzofuranone (0.01M) in ethanol (50mL, 85%) was stirred followed by addition of sodium

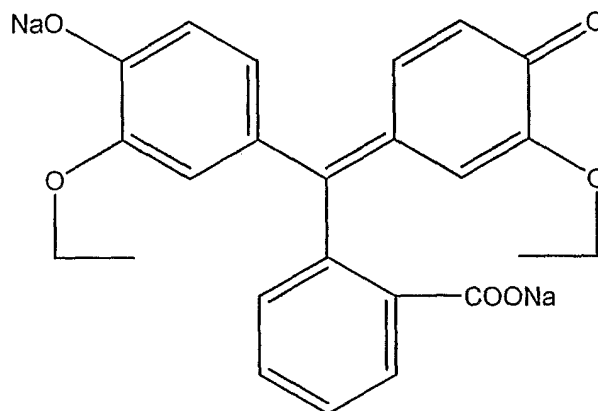
hydroxide (0.02M) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 97% yield.



EXAMPLE 7

Synthesis of disodium salt of 3,3-bis-(4-hydroxy-3-ethoxyphenyl)-1-(3H)-isobenzofuranone

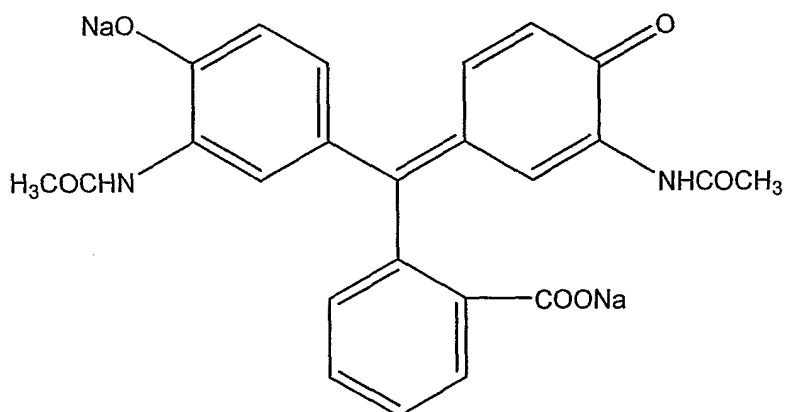
A mixture of 3,3-bis-(4-hydroxy-3-ethoxyphenyl)-1-(3H)-isobenzofuranone (0.01M) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02M) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 94% yield.



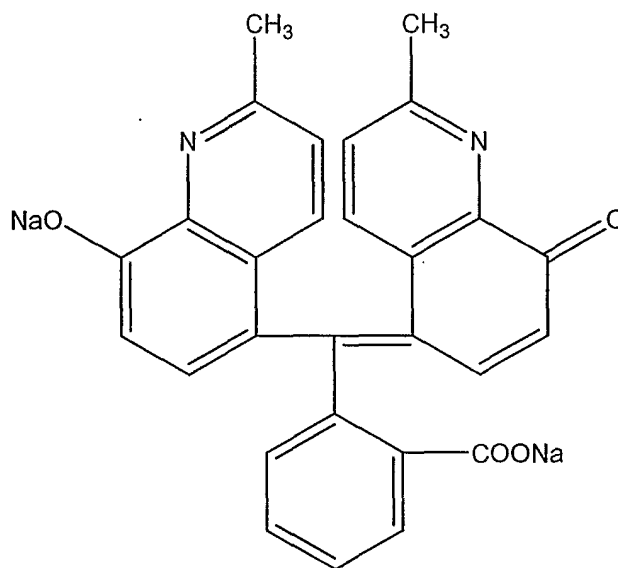
EXAMPLE 8

Synthesis of disodium salt of 3,3-bis-(4-hydroxy-3-acetamidophenyl)-1-(3H)-isobenzofuranone

A mixture of 3,3-bis-(4-hydroxy-3-acetamidophenyl)-1-(3H)-isobenzofuranone (0.01M) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02M) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 92% yield.



addition of sodium hydroxide (0.02M) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 94% yield.

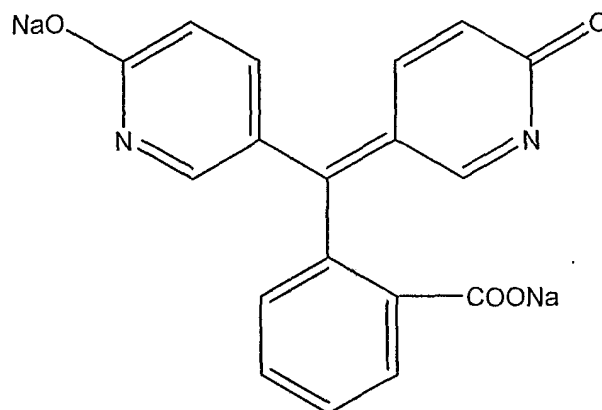


EXAMPLE 11

Synthesis of disodium salt of 3,3-bis-(4-hydroxy-3-pyridin-1-yl)-1-(3H)-isobenzofuranone

A mixture of 3,3-bis-(4-hydroxy-3-pyridin-1-yl)-1-(3H)-isobenzofuranone (0.01M) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02M) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on

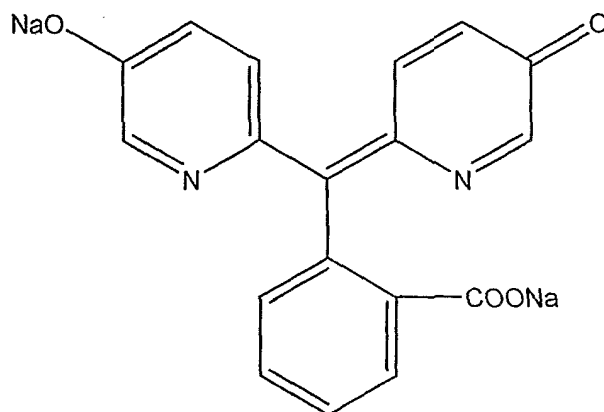
rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 81% yield.



EXAMPLE 12

Synthesis of disodium salt of 3,3-bis-(4-hydroxy-2-pyridin-1-yl)-1-(3H)-isobenzofuranone

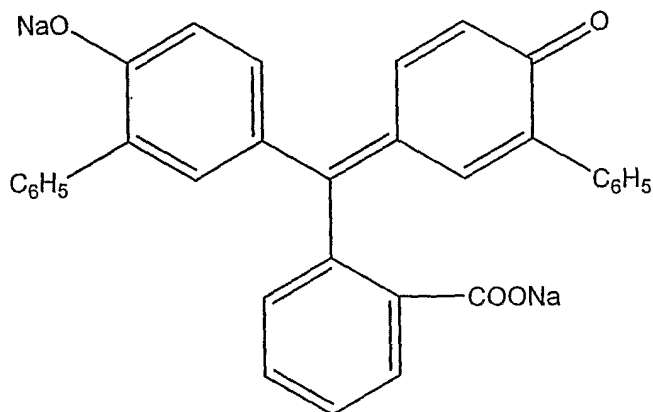
A mixture of 3,3-bis-(4-hydroxy-2-pyridin-1-yl)-1-(3H)-isobenzofuranone (0.01M) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02M) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 84% yield.



EXAMPLE 13

Synthesis of disodium salt of 3,3-bis-(4-hydroxy-3-phenylphenyl)-1-(3H)-isobenzofuranone

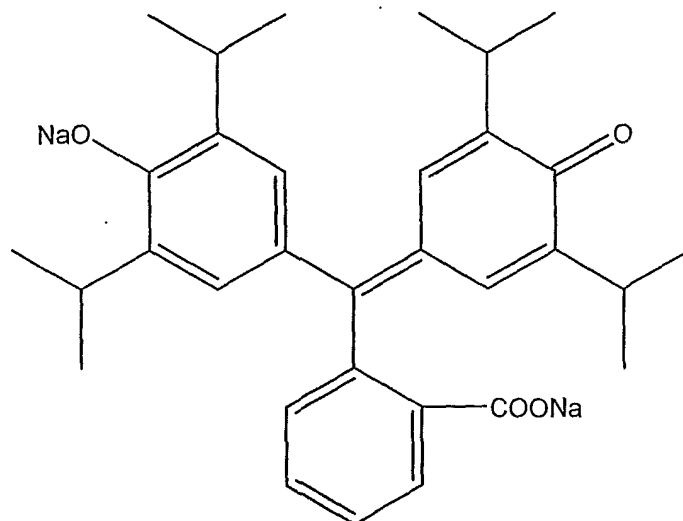
A mixture of 3,3-bis-(4-hydroxy-3-phenylphenyl)-1-(3H)-isobenzofuranone (0.01mol) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02mol) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 96% yield. ^1H -NMR (DMSO- d_6 , 300MHz): δ 6.25-6.74 (m, 6H, aromatic), 6.88-7.45 (m, 10H, aromatic), 7.53-7.84 (m, 4H, aromatic) ppm. Mass spectra: m/z 514 (M^+).



EXAMPLE 14

Synthesis of disodium salt of 3,3-bis-(4-hydroxy-3,5-diisopropylphenyl)-1-(3H)-isobenzofuranone

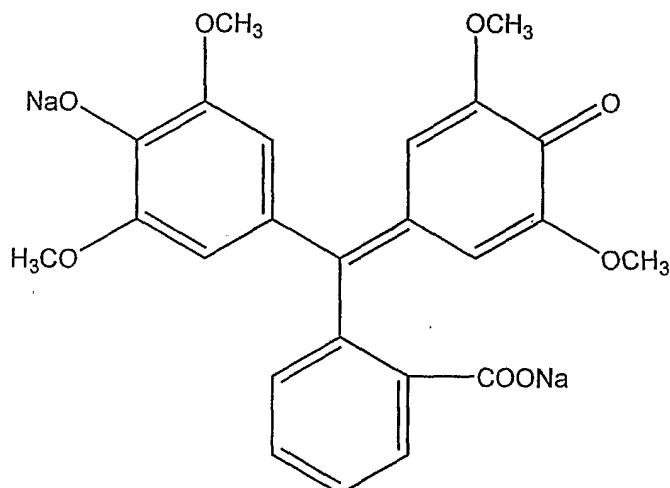
A mixture of 3,3-bis-(4-hydroxy-3,5-diisopropylphenyl)-1-(3H)-isobenzofuranone (0.01mol) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02mol) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 92% yield. ^1H -NMR (DMSO- d_6): δ 1.00-1.21 (dd, 24H, 8CH₃), 3.06-3.36 (heptate, 4H, 4CH), 6.74-6.96 (m, 4H, aromatic), 7.05-7.83 (m, 4H, aromatic) ppm. Mass spectra: m/z 530 (M^+).



EXAMPLE 15

Synthesis of disodium salt of 3,3-bis-(4-hydroxy-3,5-dimethoxyphenyl)-1-(3H)-isobenzofuranone

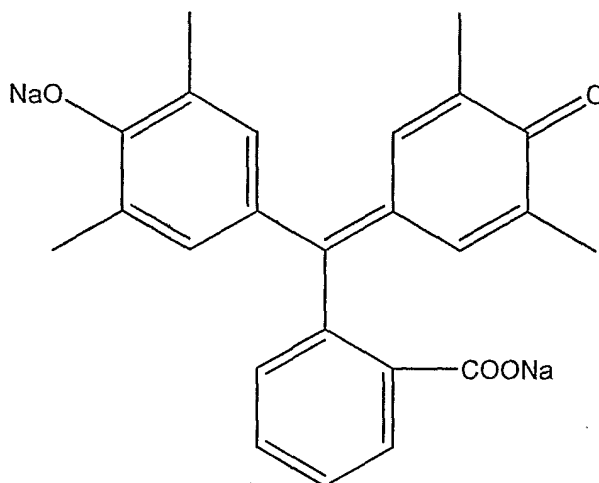
A mixture of 3,3-bis-(4-hydroxy-3,5-dimethoxyphenyl)-1-(3H)-isobenzofuranone (0.01mol) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02mol) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 90% yield. ^1H -NMR (DMSO- d_6): δ 3.61 (s, 12H, 4OCH₃), 6.45-6.52 (m, 4H, aromatic), 7.04-7.78 (m, 4H, aromatic) ppm. Mass spectra: m/z 482 (M^+).



EXAMPLE 16

Synthesis of disodium salt of 3,3-bis-(4-hydroxy-3,5-dimethylphenyl)-1-(3H)-isobenzofuranone

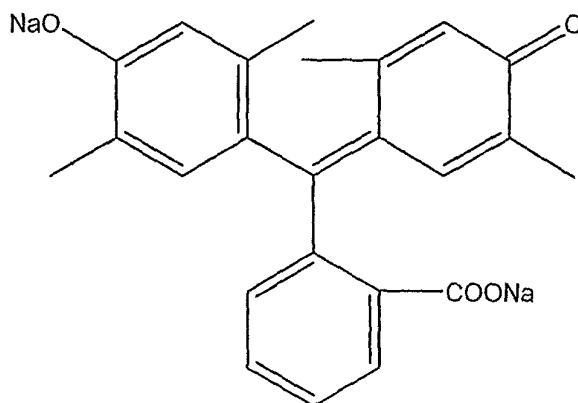
A mixture of 3,3-bis-(4-hydroxy-3,5-dimethylphenyl)-1-(3H)-isobenzofuranone (0.01mol) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02mol) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 95% yield. ^1H -NMR (DMSO- d_6): δ 2.11 (s, 12H, 4CH₃), 6.81-6.87 (m, 4H, aromatic), 7.23-7.84 (m, 4H, aromatic) ppm. Mass spectra: m/z 418 (M^+).



EXAMPLE 17

Synthesis of disodium salt of 3,3-bis-(4-hydroxy-3,6-dimethylphenyl)-1-(3H)-isobenzofuranone

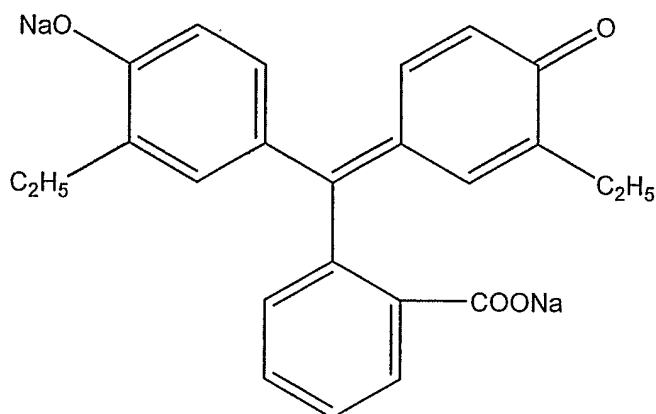
A mixture of 3,3-bis-(4-hydroxy-3,6-dimethylphenyl)-1-(3H)-isobenzofuranone (0.01mol) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02mol) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 88% yield. ^1H -NMR (DMSO- d_6): δ 2.01 (s, 12H, 4CH₃), 6.04-6.82 (m, 4H, aromatic), 7.10-7.72 (m, 4H, aromatic) ppm. Mass spectra: m/z 418 (M^+).



EXAMPLE 18

Synthesis of disodium salt of 3,3-bis-(4-hydroxy-3-ethylphenyl)-1-(3H)-isobenzofuranone

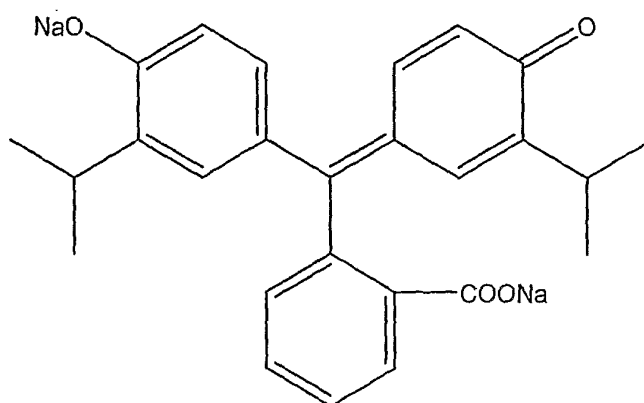
A mixture of 3,3-bis-(4-hydroxy-3-ethylphenyl)-1-(3H)-isobenzofuranone (0.01mol) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02mol) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 86% yield. $^1\text{H-NMR}$ (DMSO-d_6): δ 2.30-2.51 (q, 4H, 2CH_2), 1.00-1.10 (t, 6H, 2CH_3), 6.20-6.75 (m, 6H, aromatic), 7.12-7.84 (m, 4H, aromatic) ppm. Mass spectra: m/z 418 (M^+).



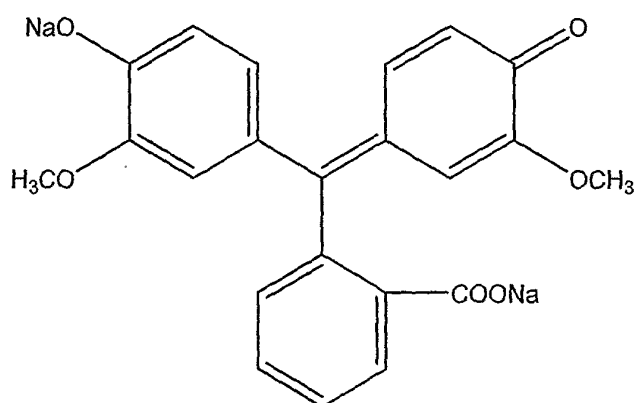
EXAMPLE 19

Synthesis of disodium salt of 3,3-bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone

A mixture of 3,3-bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone (0.01mol) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02mol) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 81% yield. ^1H -NMR (DMSO- d_6): δ 1.02-1.14 (dd, 12H, 4CH₃), 3.12-3.45 (heptate, 2H, 2CH), 6.32-6.76 (m, 6H, aromatic), 7.30-7.83 (m, 4H, aromatic) ppm. Mass spectra: m/z 446 (M^+).

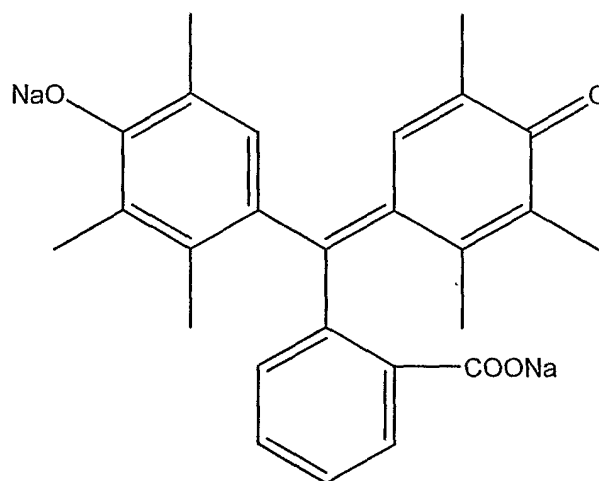
**EXAMPLE 20****Synthesis of disodium salt of 3,3-bis-(4-hydroxy-3-methoxyphenyl)-1-(3H)-isobenzofuranone**

A mixture of 3,3-bis-(4-hydroxy-3-methoxyphenyl)-1-(3H)-isobenzofuranone (0.01mol) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02mol) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 88% yield.



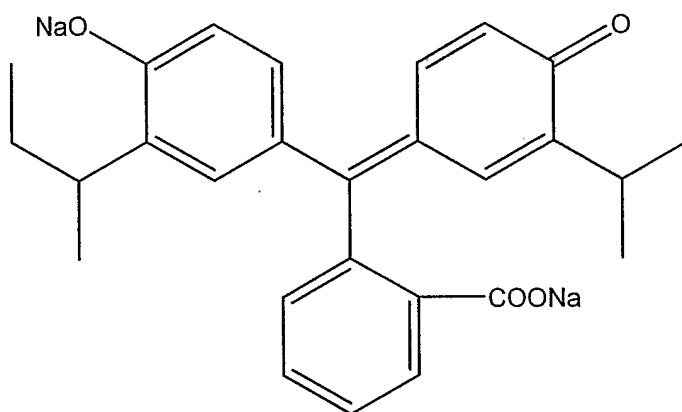
EXAMPLE 21**Synthesis of disodium salt of 3,3-bis-(4-hydroxy-2,3,5-trimethylphenyl)-1-(3H)-isobenzofuranone**

A mixture of 3,3-bis-(4-hydroxy-2,3,5-trimethylphenyl)-1-(3H)-isobenzofuranone (0.01mol) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02mol) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 80% yield.

**EXAMPLE 22****Synthesis of disodium salt of 3,3-bis-(4-hydroxy-3-sec-butylphenyl)-1-(3H)-isobenzofuranone**

A mixture of 3,3-bis-(4-hydroxy-3-sec-butylphenyl)-1-(3H)-isobenzofuranone (0.01mol) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02mol) in ethanol (50mL, 85%). The reaction

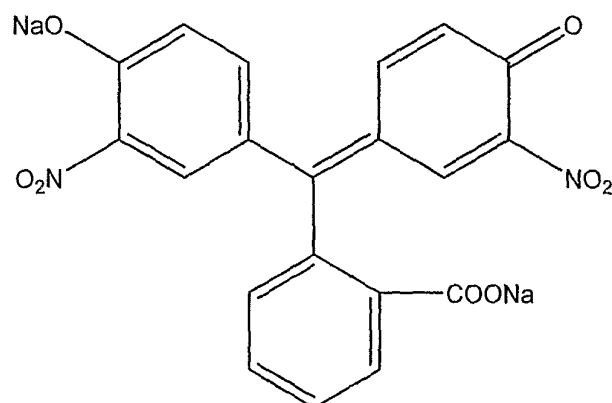
mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 82% yield. ^1H -NMR (DMSO-d_6): δ 0.80 (t, 6H, 2CH_3), 1.29-1.37 (p, 4H, 2CH_2), 1.20 (d, 6H, 2CH_3), 2.88-2.96 (sextate, 2H, 2CH), 6.08-6.75 (m, 6H, aromatic), 7.37-7.81 (m, 4H, aromatic) ppm.



EXAMPLE 23

Synthesis of disodium salt of 3,3-bis-(4-hydroxy-3-nitrophenyl)-1-(3H)-isobenzofuranone

A mixture of 3,3-bis-(4-hydroxy-3-nitrophenyl)-1-(3H)-isobenzofuranone (0.01mol) in ethanol (50mL, 85%) was stirred followed by addition of sodium hydroxide (0.02mol) in ethanol (50mL, 85%). The reaction mixture was stirred and refluxed for 2 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude product and dried. Recrystallization from ethanol furnished pure disodium salt in 92% yield.

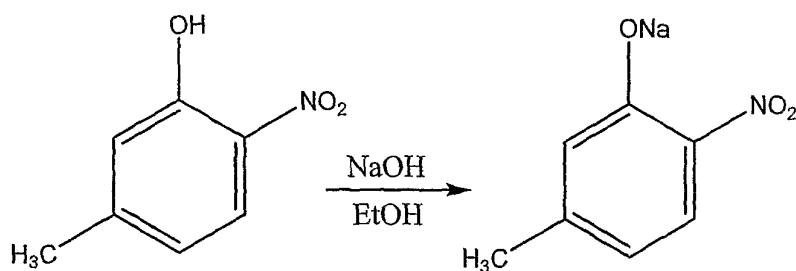


Synthesis of Phenol and Hydrazine Acid-Base Indicators

EXAMPLE 1

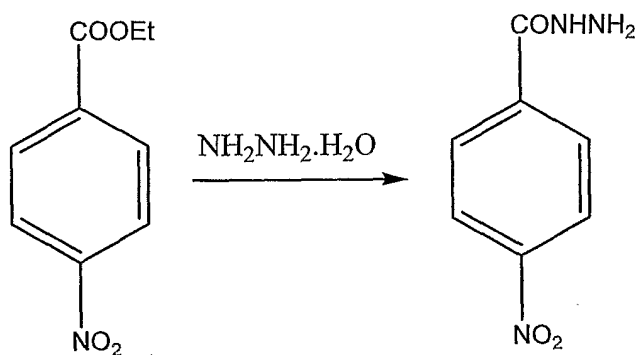
Synthesis of sodium salt of 5-methyl-2-nitrophenol

A mixture of 5-methyl-2-nitrophenol (0.1M) in ethanol (25mL, 85%) was stirred followed by addition of sodium hydroxide (0.1M) in ethanol (25mL, 85%). The reaction mixture was stirred at room temperature for 2 hours. The separated golden yellow solid was filtered, washed with ethanol and dried. Recrystallization from ethanol furnished pure sodium salt in 96% yield.

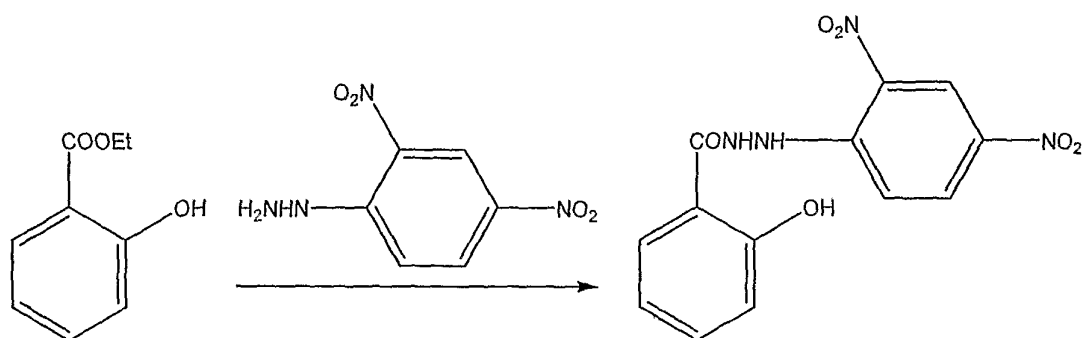


EXAMPLE 2**Synthesis of p-nitrobenzhydrazide**

A mixture of ethyl p-nitrobenzoate (0.1M), hydrazine hydrate (0.11M) in ethanol (100mL) was stirred at room temperature for 2 hours. The separated pale yellow solid was filtered, washed with ethanol and dried. Recrystallization from ethanol furnished pure hydrazide in 88% yield.

**EXAMPLE 3****Synthesis of hydrazide**

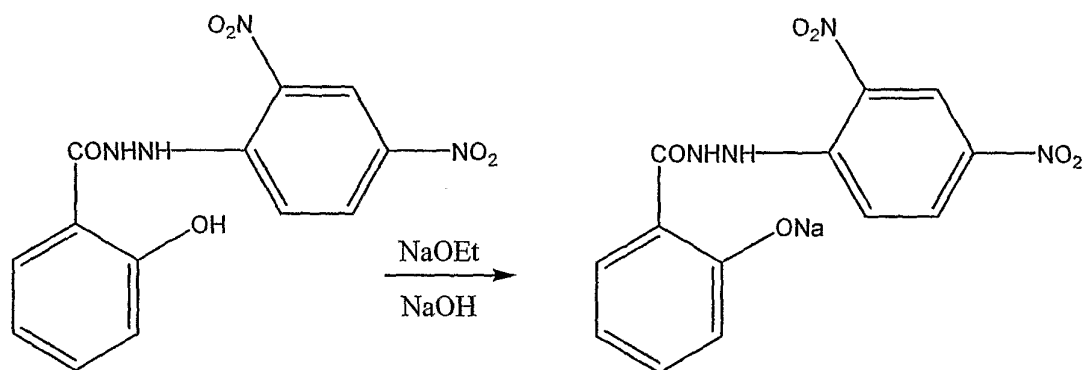
A mixture of ethyl salicylate (0.1M), 2,4-dinitrophenylhydrazine (0.1M) in ethanol (150mL) was stirred at room temperature for 2 hours. The separated orange solid was filtered, washed with ethanol and dried. Recrystallization from ethanol furnished pure hydrazide in 94% yield.



EXAMPLE 4

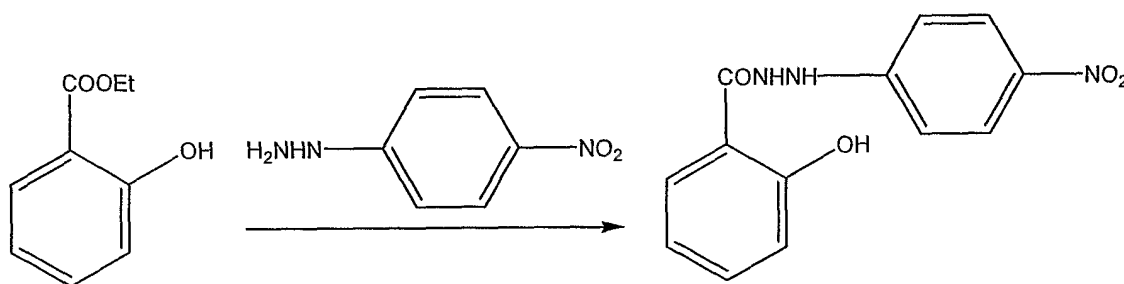
Synthesis of sodium salt of hydrazide

A mixture of hydrazide (0.1M) in ethanol (25mL) was stirred followed by addition of sodium ethoxide (0.1M) in ethanol (25mL). The reaction mixture was stirred and refluxed at for 4 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude yellow product and dried. Recrystallization from ethanol furnished pure sodium salt in 92% yield.

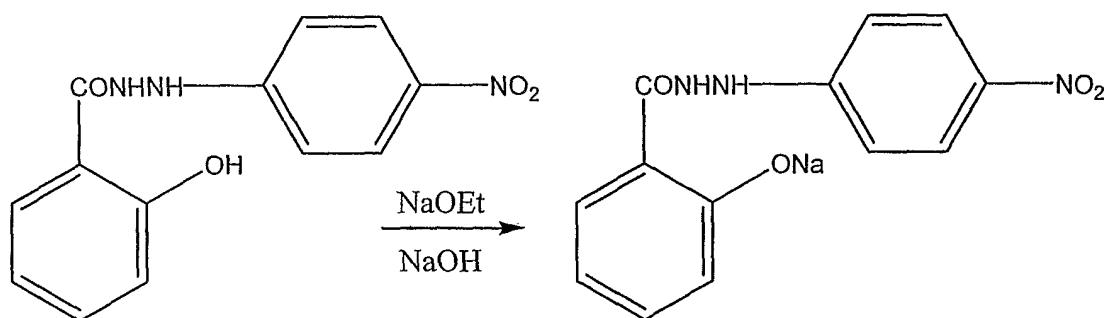


EXAMPLE 5**Synthesis of hydrazide**

A mixture of ethyl salicylate (0.1M), 4-nitrophenylhydrazine (0.1M) in ethanol (150mL) was stirred at room temperature for 2 hours. The separated yellow solid was filtered, washed with ethanol and dried. Recrystallization from ethanol furnished pure hydrazide in 89% yield.

**EXAMPLE 6****Synthesis of sodium salt of hydrazide**

A mixture of hydrazide (0.1M) in ethanol (25mL) was stirred followed by addition of sodium ethoxide (0.1M) in ethanol (25mL). The reaction mixture was stirred and refluxed at for 4 hours, cooled to room temperature. The solvent was evaporated on rotary evaporator, isolated the crude yellow product and dried. Recrystallization from ethanol furnished pure sodium salt in 84% yield.

**Colored to colorless paint composition:****EXAMPLE 1**

Chemical Component	Weight in grams
Methocel A4M (2% solution in water)	90
Phenolphthalein (Na salt)	0.4
Colonial SLS	1.6
Deionized water	7.8
Liquid Germall Plus	0.2

Methocel A4M, phenolphthalein, Colonial SLS, deionized water were stirred and heated at 50°C for 15 minutes, cooled to room temperature, followed by addition of and liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 2

Chemical Component	Weight in grams
Methocel A4M (2% solution in water)	90
o-Cresolphthalein (Na salt)	0.4
Colonial SLS	1.6
Deionized water	7.8
Liquid Germall Plus	0.2

Methocel A4M, o-cresolphthalein, Colonial SLS, deionized water were stirred and heated at 50°C for 15 minutes, cooled to room temperature, followed by addition of and liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 3

Chemical Component	Weight in grams
Methocel A4M (2% solution in water)	90
Thymolphthalein (Na salt)	0.4
Colonial SLS	1.6
Deionized water	7.8
Liquid Germall Plus	0.2

Methocel A4M, thymolphthalein, Colonial SLS, deionized water were stirred and heated at 50°C for 15 minutes, cooled to room temperature, followed by addition of and liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 4

Chemical Component	Weight in grams
Methocel A4M (2% solution in water)	90
Disodium salt of 3,3-Bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone	0.4
Colonial SLS	1.6
Deionized water	7.8
Liquid Germall Plus	0.2

Methocel A4M, disodium salt of 3,3-Bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone, Colonial SLS, deionized water were stirred and heated at 50°C for 15 minutes, cooled to room temperature, followed by addition of and liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 5

Chemical Component	Weight in grams
Methocel A4M (2% solution in water)	90
Disodium salt of 3,3-Bis-(4-hydroxy-3,5-diisopropylphenyl)-1-(3H)-isobenzofuranone	0.4
Colonial SLS	1.6
Deionized water	7.8
Liquid Germall Plus	0.2

Methocel A4M, disodium salt of 3,3-Bis-(4-hydroxy-3,5-diisopropylphenyl)-1-(3H)-isobenzofuranone, Colonial SLS, deionized water were stirred and heated at 50°C for 15 minutes, cooled to room temperature, followed by addition of and liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 6

Chemical Component	Weight in grams
Methocel A4M (2% solution in water)	90
Disodium salt of 3,3-Bis-(4-hydroxy-2-nitrophenyl)-1-(3H)-isobenzofuranone	0.4
Colonial SLS	1.6
Deionized water	7.8
Liquid Germall Plus	0.2

Methocel A4M, disodium salt of 3,3-Bis-(4-hydroxy-2-nitrophenyl)-1-(3H)-isobenzofuranone, Colonial SLS, deionized water were stirred and heated at 50°C for 15 minutes, cooled to room temperature, followed by addition of and liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 7

Chemical Component	Weight in grams
Methocel A4M (2% solution in water)	90
Disodium salt of 3,3-Bis-(4-hydroxy-3-nitrophenyl)-1-(3H)-isobenzofuranone	0.4
Colonial SLS	1.6
Deionized water	7.8
Liquid Germall Plus	0.2

Methocel A4M, disodium salt of 3,3-Bis-(4-hydroxy-3-nitrophenyl)-1-(3H)-isobenzofuranone, Colonial SLS, deionized water were stirred and heated at 50°C for 15 minutes, cooled to room temperature, followed by addition of and liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 8

Chemical Component	Weight in grams
Methocel A4M (2% solution in water)	90
5-Methyl-2-nitrophenol (Na salt)	0.4
Colonial SLS	1.6
Deionized water	7.8
Liquid Germall Plus	0.2

Methocel A4M, 5-methyl-2-nitrophenol (Na salt), Colonial SLS, deionized water were stirred and heated at 50°C for 15 minutes, cooled to room temperature, followed by addition of and liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 9

Chemical Component	Weight in grams
Methocel A4M (2% solution in water)	90
Hydrazide (Na salt) (Example 4)	0.4
Colonial SLS	1.6
Deionized water	7.8
Liquid Germall Plus	0.2

Methocel A4M, hydrazide (Na salt), Colonial SLS, deionized water were stirred and heated at 50°C for 15 minutes, cooled to room temperature, followed by addition of and liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 10

Chemical Component	Weight in grams
Methocel A4M (2% solution in water)	90
Hydrazide (Na salt) (Example 6)	0.4
Colonial SLS	1.6

Deionized water	7.8
Liquid Germall Plus	0.2

Methocel A4M, hydrazide (Na salt), Colonial SLS, deionized water were stirred and heated at 50°C for 15 minutes, cooled to room temperature, followed by addition of and liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature

Table 1 shows the color change observed in paint compositions in Examples 1 through 10 as given below:

Table 1: Color change in colored to colorless paint composition

Example #	Color change observed
Example 1	Pink to Colorless
Example 2	Red to Colorless
Example 3	Blue to Colorless
Example 4	Bright purple-red to colorless
Example 5	Violet to colorless
Example 6	Orange to colorless
Example 7	Yellow to colorless
Example 8	Golden yellow to colorless
Example 9	Yellow to colorless
Example 10	Yellow to colorless

The following examples were prepared as follows:

Total 100g color solution was made using 0.1g dye, equivalent sodium hydroxide, 16g Colonial SLS and remaining DI water to make total volume 100g.

EXAMPLE 1

Chemical Component	Weight in grams
Methocel A4M (1% solution)	5.00

Carbowax 4000	5.00
Color solution (Thymolphthalein)	10.00

In a plastic bottle, a mixture of Methocel A4M, Carbowax 4000, and color solution of thymolphthalein, sodium hydroxide and Colonial SLS was stirred for 3 hours at room temperature.

Color of the solution: Blue

Color change: Blue to colorless

EXAMPLE 2

Chemical Component	Weight in grams
Methocel A4M (1% solution)	5.00
Carbowax 4000	5.00
Color solution (o-Cresolphthalein)	10.00

In a plastic bottle, a mixture of Methocel A4M, Carbowax 4000, and color solution of o-cresolphthalein, sodium hydroxide and Colonial SLS was stirred for 3 hours at room temperature.

Color of the solution: Magenta

Color change: Magenta to colorless

EXAMPLE 3

Chemical Component	Weight in grams
Methocel A4M (1% solution)	5.00
Carbowax 4000	5.00
Color solution	10.00
(3,3-bis-(4-hydroxy-3-phenylphenyl)-1-(3H)-isobenzofuranone)	

In a plastic bottle, a mixture of Methocel A4M, Carbowax 4000, and color solution of 3,3-bis-(4-hydroxy-3-phenylphenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Colonial SLS was stirred for 3 hours at room temperature.

Color of the solution: Purple

Color change: Purple to colorless

EXAMPLE 4

Chemical Component	Weight in grams
Methocel A4M (1% solution)	5.00
Carbowax 4000	5.00
Color solution	10.00
(3,3-bis-(4-hydroxy-3,5-diisopropylphenyl)-1-(3H)-isobenzofuranone)	

In a plastic bottle, a mixture of Methocel A4M, Carbowax 4000, and color solution of 3,3-bis-(4-hydroxy-3,5-diisopropylphenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Colonial SLS was stirred for 3 hours at room temperature.

Color of the solution: Violet

Color change: Violet to colorless

EXAMPLE 5

Chemical Component	Weight in grams
Methocel A4M (1% solution)	5.00
Carbowax 4000	5.00
Color solution	10.00
(3,3-bis-(4-hydroxy-3,5-dimethoxyphenyl)-1-(3H)-isobenzofuranone)	

In a plastic bottle, a mixture of Methocel A4M, Carbowax 4000, and color solution of 3,3-bis-(4-hydroxy-3,5-dimethoxyphenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Colonial SLS was stirred for 3 hours at room temperature.

Color of the solution: Teal

Color change: Teal to colorless

EXAMPLE 6

Chemical Component	Weight in grams
Methocel A4M (1% solution)	5.00
Carbowax 4000	5.00
Color solution	10.00
(3,3-bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone)	

In a plastic bottle, a mixture of Methocel A4M, Carbowax 4000, and color solution of 3,3-bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Colonial SLS was stirred for 3 hours at room temperature.

Color of the solution: Pink

Color change: Pink to colorless

EXAMPLE 7

Chemical Component	Weight in grams
Methocel A4M (1% solution)	5.00
Carbowax 4000	5.00
Color solution	10.00
(3,3-bis-(4-hydroxy-3-nitrophenyl)-1-(3H)-isobenzofuranone)	

In a plastic bottle, a mixture of Methocel A4M, Carbowax 4000, and color solution of 3,3-bis-(4-hydroxy-3-nitrophenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Colonial SLS was stirred for 3 hours at room temperature.

Color of the solution: Yellow

Color change: Yellow to colorless

EXAMPLE 8

Chemical Component	Weight in grams
Methocel A4M (1% solution)	5.00
Carbowax 4000	5.00

Color solution 10.00
(m-Nitrophenol)

In a plastic bottle, a mixture of Methocel A4M, Carbowax 4000, and color solution of m-nitrophenol, sodium hydroxide and Colonial SLS was stirred for 3 hours at room temperature.

Color of the solution: Golden yellow

Color change: Golden yellow to colorless

One color to another color paint composition:

EXAMPLE 1

Chemical Component	Weight in grams
Methocel A4M (2% solution in water)	90
Phenol red (Na salt)	0.4
Colonial SLS	1.6
Deionized water	7.8
Liquid Germall Plus	0.2

Methocel A4M, phenol red, Colonial SLS, deionized water were stirred and heated at 50°C for 15 minutes, cooled to room temperature, followed by addition of and liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 2

Chemical Component	Weight in grams
Methocel A4M (2% solution in water)	90
Thymol blue (Na salt)	0.4
Colonial SLS	1.6

Deionized water	7.8
Liquid Germall Plus	0.2

Methocel A4M, thymol blue, Colonial SLS, deionized water were stirred and heated at 50°C for 15 minutes, cooled to room temperature, followed by addition of and liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 3

Chemical Component	Weight in grams
Methocel A4M (2% solution in water)	90
o-Cresol red (Na salt)	0.4
Colonial SLS	1.6
Deionized water	7.8
Liquid Germall Plus	0.2

Methocel A4M, o-cresol red, Colonial SLS, deionized water were stirred and heated at 50°C for 15 minutes, cooled to room temperature, followed by addition of and liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 4

Chemical Component	Weight in grams
Methocel A4M (2% solution in water)	90
m-cresol purple (Na salt)	0.4
Colonial SLS	1.6
Deionized water	7.8
Liquid Germall Plus	0.2

Methocel A4M, m-cresol purple, Colonial SLS, deionized water were stirred and heated at 50°C for 15 minutes, cooled to room temperature, followed

by addition of and liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

Table 1 shows the color change observed in paint formulation in various Examples 1 through 4 as given below:

Table 1: Color change in one colored to another colored in paint composition

Example #	Color change observed
Example 1	Red to Yellow
Example 2	Blue to Yellow
Example 3	Red to Yellow
Example 4	Purple to Yellow

Finger Paints Application Examples:

Color Solution:

Total 100g color solution was made using 0.1g dye, equivalent sodium hydroxide, 16g Colonial SLS and remaining DI water to make total volume 100g.

EXAMPLE 1

Chemical Component	Weight in grams
Methocel A4M (1% solution)	10.00
Carbowax 4000	9.00
Color solution (Thymolphthalein)	1.00

In a plastic bottle, a mixture of Methocel A4M, Carbowax 4000, and color solution of thymolphthalein, sodium hydroxide and Colonial SLS was stirred for 3 hours at room temperature.

Color of the solution: Blue

Color change: Blue to colorless

EXAMPLE 2

Chemical Component	Weight in grams
Methocel A4M (1% solution)	10.00
Carbowax 4000	9.00
Color solution (o-Cresolphthalein)	1.00

In a plastic bottle, a mixture of Methocel A4M, Carbowax 4000, and color solution of o-cresolphthalein, sodium hydroxide and Colonial SLS was stirred for 3 hours at room temperature.

Color of the solution: Magenta

Color change: Magenta to colorless

EXAMPLE 3

Chemical Component	Weight in grams
Methocel A4M (1% solution)	10.00
Carbowax 4000	9.00

Color solution 1.00
(3,3-bis-(4-hydroxy-3-phenylphenyl)-1-(3H)-isobenzofuranone)

In a plastic bottle, a mixture of Methocel A4M, Carbowax 4000, and color solution of 3,3-bis-(4-hydroxy-3-phenylphenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Colonial SLS was stirred for 3 hours at room temperature.

Color of the solution: Purple

Color change: Purple to colorless

EXAMPLE 4

Chemical Component	Weight in grams
Methocel A4M (1% solution)	10.00
Carbowax 4000	9.00
Color solution	1.00
(3,3-bis-(4-hydroxy-3,5-diisopropylphenyl)-1-(3H)-isobenzofuranone)	

In a plastic bottle, a mixture of Methocel A4M, Carbowax 4000, and color solution of 3,3-bis-(4-hydroxy-3,5-diisopropylphenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Colonial SLS was stirred for 3 hours at room temperature.

Color of the solution: Violet

Color change: Violet to colorless

EXAMPLE 5

Chemical Component	Weight in grams
Methocel A4M (1% solution)	10.00
Carbowax 4000	9.00
Color solution	1.00
(3,3-bis-(4-hydroxy-3,5-dimethoxyphenyl)-1-(3H)-isobenzofuranone)	

In a plastic bottle, a mixture of Methocel A4M, Carbowax 4000, and color solution of 3,3-bis-(4-hydroxy-3,5-dimethoxyphenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Colonial SLS was stirred for 3 hours at room temperature.

Color of the solution: Teal

Color change: Teal to colorless

EXAMPLE 6

Chemical Component	Weight in grams
Methocel A4M (1% solution)	10.00
Carbowax 4000	9.00
Color solution	1.00
(3,3-bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone)	

In a plastic bottle, a mixture of Methocel A4M, Carbowax 4000, and color solution of 3,3-bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Colonial SLS was stirred for 3 hours at room temperature.

Color of the solution: Pink

Color change: Pink to colorless

EXAMPLE 7

Chemical Component	Weight in grams
Methocel A4M (1% solution)	10.00
Carbowax 4000	9.00
Color solution	1.00
(3,3-bis-(4-hydroxy-3-nitrophenyl)-1-(3H)-isobenzofuranone)	

In a plastic bottle, a mixture of Methocel A4M, Carbowax 4000, and color solution of 3,3-bis-(4-hydroxy-3-nitrophenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Colonial SLS was stirred for 3 hours at room temperature.

Color of the solution: Yellow

Color change: Yellow to colorless

EXAMPLE 8

Chemical Component	Weight in grams
Methocel A4M (1% solution)	10.00
Carbowax 4000	9.00
Color solution	1.00
(m-Nitrophenol)	

In a plastic bottle, a mixture of Methocel A4M, Carbowax 4000, and color solution of m-nitrophenol, sodium hydroxide and Colonial SLS was stirred for 3 hours at room temperature.

Color of the solution: Golden yellow

Color change: Golden yellow to colorless

Marker Examples:

EXAMPLE 1

Chemical Component	Weight in grams
Triton X100	0.5
Methocel A4M (1% solution)	20.00
Thymolphthalein	0.5
Sodium hydroxide	0.09
Deionized water	78.91

In a plastic bottle, a mixture of deionized water, Triton X100, thymolphthalein, sodium hydroxide and Methocel A4M was stirred for 2 hours at room temperature.

Color of the solution: Blue

Color change: Blue to colorless

EXAMPLE 2

Chemical Component	Weight in grams
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Triton X100	0.5
Methocel A4M (1% solution)	20.00
o-Cresolphthalein	0.5
Sodium hydroxide	0.11
Deionized water	78.89

In a plastic bottle, a mixture of deionized water, Triton X100, o-cresolphthalein, sodium hydroxide and Methocel A4M was stirred for 2 hours at room temperature.

Color of the solution: Magenta

Color change: Magenta to colorless

EXAMPLE 3

Chemical Component	Weight in grams
Triton X100	0.5
Methocel A4M (1% solution)	20.00
3,3-bis-(4-hydroxy-3-phenylphenyl)- 1-(3H)-isobenzofuranone	0.5
Sodium hydroxide	0.08
Deionized water	78.92

In a plastic bottle, a mixture of deionized water, Triton X100, 3,3-bis-(4-hydroxy-3-phenylphenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Methocel A4M was stirred for 2 hours at room temperature.

Color of the solution: Purple

Color change: Purple to colorless

EXAMPLE 4

Chemical Component	Weight in grams
Triton X100	0.5
Methocel A4M (1% solution)	20.00
3,3-bis-(4-hydroxy-3,5-diisopropylphenyl)- 1-(3H)-isobenzofuranone	0.5
Sodium hydroxide	0.08
Deionized water	78.92

In a plastic bottle, a mixture of deionized water, Triton X100, 3,3-bis-(4-hydroxy-3,5-diisopropylphenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Methocel A4M was stirred for 2 hours at room temperature.

Color of the solution: Violet

Color change: Violet to colorless

EXAMPLE 5

Chemical Component	Weight in grams
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Triton X100	0.5
Methocel A4M (1% solution)	20.00
3,3-bis-(4-hydroxy-3,5-dimethoxyphenyl)- 1-(3H)-isobenzofuranone	0.5
Sodium hydroxide	0.09
Deionized water	78.91

In a plastic bottle, a mixture of deionized water, Triton X100, 3,3-bis-(4-hydroxy-3,5-dimethoxyphenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Methocel A4M was stirred for 2 hours at room temperature.

Color of the solution: Teal

Color change: Teal to colorless

EXAMPLE 6

Chemical Component	Weight in grams
Triton X100	0.5
Methocel A4M (1% solution)	20.00
3,3-bis-(4-hydroxy-3-isopropylphenyl)- 1-(3H)-isobenzofuranone	0.5
Sodium hydroxide	0.09
Deionized water	78.91

In a plastic bottle, a mixture of deionized water, Triton X100, 3,3-bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Methocel A4M was stirred for 2 hours at room temperature.

Color of the solution: Pink

Color change: Pink to colorless

EXAMPLE 7

Chemical Component	Weight in grams
Triton X100	0.5
Methocel A4M (1% solution)	20.00
3,3-bis-(4-hydroxy-3-nitrophenyl)- 1-(3H)-isobenzofuranone	0.5
Sodium hydroxide	0.08
Deionized water	78.92

In a plastic bottle, a mixture of deionized water, Triton X100, 3,3-bis-(4-hydroxy-3-nitrophenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Methocel A4M was stirred for 2 hours at room temperature.

Color of the solution: Yellow

Color change: Yellow to colorless

EXAMPLE 8

Chemical Component	Weight in grams
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Triton X100	0.5
Methocel A4M (1% solution)	20.00
m-Nitrophenol	0.5
Sodium hydroxide	0.08
Deionized water	78.92

In a plastic bottle, a mixture of deionized water, Triton X100, m-nitrophenol, sodium hydroxide and Methocel A4M was stirred for 2 hours at room temperature.

Color of the solution: Golden yellow

Color change: Golden yellow to colorless

EXAMPLE 9

Chemical Component	Weight in grams
Dow Corning 190	0.5
Methocel A4M (1% solution)	20.00
Thymolphthalein	0.5
Sodium hydroxide	0.09
Deionized water	78.91

In a plastic bottle, a mixture of deionized water, Dow Corning 190, thymolphthalein, sodium hydroxide and Methocel A4M was stirred for 2 hours at room temperature.

Color of the solution: Blue

Color change: Blue to colorless

EXAMPLE 10

Chemical Component	Weight in grams
Dow Corning 190	0.5
Methocel A4M (1% solution)	20.00
o-Cresolphthalein	0.5
Sodium hydroxide	0.11
Deionized water	78.89

In a plastic bottle, a mixture of deionized water, Dow Corning 190, o-cresolphthalein, sodium hydroxide and Methocel A4M was stirred for 2 hours at room temperature.

Color of the solution: Magenta

Color change: Magenta to colorless

EXAMPLE 11

Chemical Component	Weight in grams
Dow Corning 190	0.5
Methocel A4M (1% solution)	20.00
3,3-bis-(4-hydroxy-3-phenylphenyl)- 1-(3H)-isobenzofuranone	0.5

Sodium hydroxide	0.08
Deionized water	78.92

In a plastic bottle, a mixture of deionized water, Dow Corning 190, 3,3-bis-(4-hydroxy-3-phenylphenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Methocel A4M was stirred for 2 hours at room temperature.

Color of the solution: Purple

Color change: Purple to colorless

EXAMPLE 12

Chemical Component	Weight in grams
Dow Corning 190	0.5
Methocel A4M (1% solution)	20.00
3,3-bis-(4-hydroxy-3,5-diisopropylphenyl)- 1-(3H)-isobenzofuranone	0.5
Sodium hydroxide	0.08
Deionized water	78.92

In a plastic bottle, a mixture of deionized water, Dow Corning 190, 3,3-bis-(4-hydroxy-3,5-diisopropylphenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Methocel A4M was stirred for 2 hours at room temperature.

Color of the solution: Violet

Color change: Violet to colorless

EXAMPLE 13

Chemical Component	Weight in grams
Dow Corning 190	0.5
Methocel A4M (1% solution)	20.00
3,3-bis-(4-hydroxy-3,5-dimethoxyphenyl)- 1-(3H)-isobenzofuranone	0.5
Sodium hydroxide	0.09
Deionized water	78.91

In a plastic bottle, a mixture of deionized water, Dow Corning 190, 3,3-bis-(4-hydroxy-3,5-dimethoxyphenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Methocel A4M was stirred for 2 hours at room temperature.

Color of the solution: Teal

Color change: Teal to colorless

EXAMPLE 14

Chemical Component	Weight in grams
Dow Corning 190	0.5
Methocel A4M (1% solution)	20.00
3,3-bis-(4-hydroxy-3-isopropylphenyl)- 1-(3H)-isobenzofuranone	0.5
Sodium hydroxide	0.09

Deionized water 78.91

In a plastic bottle, a mixture of deionized water, Dow Corning 190, 3,3-bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Methocel A4M was stirred for 2 hours at room temperature.

Color of the solution: Pink

Color change: Pink to colorless

EXAMPLE 15

Chemical Component	Weight in grams
Dow Corning 190	0.5
Methocel A4M (1% solution)	20.00
3,3-bis-(4-hydroxy-3-nitrophenyl)- 1-(3H)-isobenzofuranone	0.5
Sodium hydroxide	0.08
Deionized water	78.92

In a plastic bottle, a mixture of deionized water, Dow Corning 190, 3,3-bis-(4-hydroxy-3-nitrophenyl)-1-(3H)-isobenzofuranone, sodium hydroxide and Methocel A4M was stirred for 2 hours at room temperature.

Color of the solution: Yellow

Color change: Yellow to colorless

EXAMPLE 16

Chemical Component	Weight in grams
Dow Corning 190	0.5
Methocel A4M (1% solution)	20.00
m-Nitrophenol	0.5
Sodium hydroxide	0.08
Deionized water	78.92

In a plastic bottle, a mixture of deionized water, Dow Corning 190, m-nitrophenol, sodium hydroxide and Methocel A4M was stirred for 2 hours at room temperature.

Color of the solution: Golden yellow

Color change: Golden yellow to colorless

**[0352] 1.0 Color Disappearing/Color Changing Bubbles and
Compositions**

**[0353] 1.1 Color Disappearing Bubbles with Acid-Base Indicator
and Base**

EXAMPLE 1

Chemical Component	Weight in grams
Glycerin	10
Phenolphthalein (Na salt)	2
Methocel A4M (2% solution in water)	6
Colonial SLS	14

Deionized water	67
Triethanolamine	0.8
Liquid Germall Plus	0.2

Glycerin, phenolphthalein are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, triethanolamine & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 2

Chemical Component	Weight in grams
Glycerin	10
o-Cresolphthalein (Na salt)	2
Methocel A4M (2% solution in water)	6
Colonial SLS	14
Deionized water	67
Triethanolamine	0.8
Liquid Germall Plus	0.2

Glycerin, o-cresolphthalein are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, Methocel A4M, Colonial SLS, triethanolamine & Liquid Germall Plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 3

Chemical Component	Weight in grams
Glycerin	10
Thymolphthalein (Na salt)	2
Methocel A4M (2% solution in water)	6
Colonial SLS	14
Deionized water	67

Triethanolamine	0.8
Liquid Germall Plus	0.2

Glycerin, thymolphthalein are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, Methocel A4M, Colonial SLS, triethanolamine & Liquid Germall Plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 4

Chemical Component	Weight in grams
Glycerin	5
Phenolphthalein (Na salt)	2
Colamid C	4
Miracare BC-27	7
Deionized water	81
Triethanolamine	0.8
Liquid Germall Plus	0.2

Glycerin, phenolphthalein, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, triethanolamine & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 5

Chemical Component	Weight in grams
Glycerin	5
o-Cresolphthalein (Na salt)	2
Colamid C	4
Miracare BC-27	7
Deionized water	81
Triethanolamine	0.8

Liquid Germall Plus

0.2

Glycerin, o-cresolphthalein, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, triethanolamine & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 6

Chemical Component	Weight in grams
Glycerin	5
Thymolphthalein (Na salt)	2
Colamid C	4
Miracare BC-27	7
Deionized water	81
Triethanolamine	0.8
Liquid Germall Plus	0.2

Glycerin, thymolphthalein, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, triethanolamine & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

Table 1 shows the color change observed in colored bubble solution in various Examples 1 through 6 as given below:

Table 1: Color change in colored bubble solution

Example #	Color change observed
Example 1	Pink to Colorless
Example 2	Red to Colorless
Example 3	Blue to Colorless
Example 4	Pink to Colorless

Example 5 Red to Colorless

Example 6 Blue to Colorless

[0354] 1.2 Color Changing Bubbles with Acid-Base Indicator Base

EXAMPLE 1

Chemical Component	Weight in grams
Glycerin	10
Phenol red (Na salt)	2
Methocel A4M (2% solution in water)	6
Colonial SLS	14
Deionized water	67
Triethanolamine	0.8
Liquid Germall Plus	0.2

Glycerin, phenol red are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, triethanolamine & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 2

Chemical Component	Weight in grams
Glycerin	10
Thymol blue (Na salt)	2
Methocel A4M (2% solution in water)	6
Colonial SLS	14
Deionized water	67
Triethanolamine	0.8
Liquid Germall Plus	0.2

Glycerin, thymol blue are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, Methocel A4M, Colonial SLS, triethanolamine & Liquid Germall Plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 3

Chemical Component	Weight in grams
Glycerin	10
m-Cresol red (Na salt)	2
Methocel A4M (2% solution in water)	6
Colonial SLS	14
Deionized water	67
Triethanolamine	0.8
Liquid Germall Plus	0.2

Glycerin, m-cresol red are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, Methocel A4M, Colonial SLS, triethanolamine & Liquid Germall Plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 4

Chemical Component	Weight in grams
Glycerin	10
m-Cresol purple (Na salt)	2
Methocel A4M (2% solution in water)	6
Colonial SLS	14
Deionized water	67
Triethanolamine	0.8
Liquid Germall Plus	0.2

Glycerin, m-cresol purple are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, triethanolamine & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 5

Chemical Component	Weight in grams
Glycerin	5
Phenol red (Na salt)	2
Colamid C	4
Miracare BC-27	7
Deionized water	81
Triethanolamine	0.8
Liquid Germall Plus	0.2

Glycerin, phenol red, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, triethanolamine & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 6

Chemical Component	Weight in grams
Glycerin	5
Thymol blue (Na salt)	2
Colamid C	4
Miracare BC-27	7
Deionized water	81
Triethanolamine	0.8
Liquid Germall Plus	0.2

Glycerin, thymol blue, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, triethanolamine & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 7

Chemical Component	Weight in grams
Glycerin	5
m-Cresol red (Na salt)	2
Colamid C	4
Miracare BC-27	7
Deionized water	81
Triethanolamine	0.8
Liquid Germall Plus	0.2

Glycerin, m-cresol red, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, triethanolamine & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 8

Chemical Component	Weight in grams
Glycerin	5
m-Cresol purple (Na salt)	2
Colamid C	4
Miracare BC-27	7
Deionized water	81
Triethanolamine	0.8
Liquid Germall Plus	0.2

Glycerin, m-cresol purple, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, triethanolamine & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

Table 1 shows the color change observed in colored bubble solution in various Examples 1 through 8 as given below:

Table 1: Color change in colored bubble solution

Example #	Color change observed
Example 1	Red to Yellow
Example 2	Blue to Yellow
Example 3	Red to Yellow
Example 4	Purple to Yellow
Example 5	Red to Yellow
Example 6	Blue to Yellow
Example 7	Red to Yellow
Example 8	Purple to Yellow

[0355] 2.0 Film Formed Colored Bubbles/ Disappearing Colored Bubbles/Changing Color Bubbles and Compositions

[0356] 2.1 Film Formed Colored Bubbles with FD&C Dye

EXAMPLE 1

Chemical Component	Weight in grams
Glycerin	10
FD & C Red 3	5
Methocel A4M (2% solution in water)	6
Colonial SLS	14
Deionized water	56.8
Elvanol 71-30	8

Liquid Germall Plus

0.2

Elvanol 71-30 slowly added to DI water with stirring and heated at 90°C for 30 minutes, cooled to room temperature, followed by addition of glycerin, FD & C Red 3, deionized water, methocel A4M, colonial SLS, & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 2

Chemical Component	Weight in grams
Glycerin	10
FD & C Blue 1	5
Methocel A4M (2% solution in water)	6
Colonial SLS	14
Deionized water	56.8
Elvanol 71-30	8
Liquid Germall Plus	0.2

Elvanol 71-30 slowly added to DI water with stirring and heated at 90°C for 30 minutes, cooled to room temperature, followed by addition of glycerin, FD & C Blue 1, deionized water, methocel A4M, colonial SLS, & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 3

Chemical Component	Weight in grams
Glycerin	10
Vitasyn Tetrazine X 90	5
Methocel A4M (2% solution in water)	6
Colonial SLS	14
Deionized water	56.8
Elvanol 71-30	8
Liquid Germall Plus	0.2

Elvanol 71-30 slowly added to DI water with stirring and heated at 90°C for 30 minutes, cooled to room temperature, followed by addition of glycerin, Vitasyn Tetrazine X 90, deionized water, methocel A4M, colonial SLS, & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 4

Chemical Component	Weight in grams
Glycerin	10
Vitasyn Orange RGL 90	5
Methocel A4M (2% solution in water)	6
Colonial SLS	14
Deionized water	56.8
Elvanol 71-30	8
Liquid Germall Plus	0.2

Elvanol 71-30 slowly added to DI water with stirring and heated at 90°C for 30 minutes, cooled to room temperature, followed by addition of glycerin, Vitasyn Orange RGL 90, deionized water, methocel A4M, colonial SLS, & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 5

Chemical Component	Weight in grams
Glycerin	10
Emerald Fast Green	5
Methocel A4M (2% solution in water)	6
Colonial SLS	14
Deionized water	56.8
Elvanol 71-30	8

Liquid Germall Plus 0.2

Elvanol 71-30 slowly added to DI water with stirring and heated at 90°C for 30 minutes, cooled to room temperature, followed by addition of glycerin, Emerald Fast Green, deionized water, methocel A4M, colonial SLS, & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

[0357] 2.2 Film Formed Colored Bubbles with Fluorescent Dyes

EXAMPLE 1

Chemical Component	Weight in grams
Glycerin	5
Fluorescein (Na salt)	5
Colamid C	4
Miracare BC-27	7
Deionized water	78.8
Liquid Germall Plus	0.2

Glycerin, fluorescein, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 2

Chemical Component	Weight in grams
Glycerin	5
Rhodamine B	5
Colamid C	4
Miracare BC-27	7
Deionized water	78.8

Liquid Germall Plus 0.2

Glycerin, rhodamine B, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 3

Chemical Component	Weight in grams
Glycerin	5
Rhodamine 6G	5
Colamid C	4
Miracare BC-27	7
Deionized water	78.8
Liquid Germall Plus	0.2

Glycerin, rhodamine 6G, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 4

Chemical Component	Weight in grams
Glycerin	5
Rhodamine 123	5
Colamid C	4
Miracare BC-27	7
Deionized water	78.8
Liquid Germall Plus	0.2

Glycerin, rhodamine 123, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

[0358] 2.3 Film Formed Colored Bubbles with Polymeric Dyes

EXAMPLE 1

Chemical Component	Weight in grams
Glycerin	10
Palmer Blue B232	25
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 508 (20% Solution)	20
Deionized water	39.8
Liquid Germall Plus	0.2

Glycerin, Palmer Blue B232 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 2

Chemical Component	Weight in grams
Glycerin	10
Palmer Yellow R	25
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 508 (20% Solution)	20
Deionized water	39.8
Liquid Germall Plus	0.2

Glycerin, Palmer Yellow R are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 3

Chemical Component	Weight in grams
Glycerin	10
Palmer Scarlett	25
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 508 (20% Solution)	20
Deionized water	39.8
Liquid Germall Plus	0.2

Glycerin, Palmer Scarlett are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 4

Chemical Component	Weight in grams
Glycerin	10
Palmer Orange B113	25
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 508 (20% Solution)	20
Deionized water	39.8
Liquid Germall Plus	0.2

Glycerin, Palmer Orange B113 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 5

Chemical Component	Weight in grams
Glycerin	10
Palmer Magenta	25
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 508 (20% Solution)	20
Deionized water	39.8
Liquid Germall Plus	0.2

Glycerin, Palmer Magenta are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 6

Chemical Component	Weight in grams
Glycerin	10
Palmer FL Red	25
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 508 (20% Solution)	20
Deionized water	39.8
Liquid Germall Plus	0.2

Glycerin, Palmer FL Red are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 7

Chemical Component	Weight in grams
Glycerin	10
Palmer Black B57	25
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 508 (20% Solution)	20
Deionized water	39.8
Liquid Germall Plus	0.2

Glycerin, Palmer Black B57 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 8

Chemical Component	Weight in grams
Glycerin	10
Palmer Patent Blue	25
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 508 (20% Solution)	20
Deionized water	39.8
Liquid Germall Plus	0.2

Glycerin, Palmer Patent Blue are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 9

Chemical Component	Weight in grams
Glycerin	10
LiquiTone Magenta 418	25
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 508 (20% Solution)	20
Deionized water	39.8
Liquid Germall Plus	0.2

Glycerin, Palmer LiquiTone Magenta 418 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

[0359] 2.4 Film Formed Color Disappearing Bubbles with Acid-Base Indicator and Base

EXAMPLE 1

Chemical Component	Weight in grams
Triethanolamine	10
Phenolphthalein (Na salt)	5
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 508 (20% Solution)	60
Deionized water	19.8

Liquid Germall Plus 0.2

Triethanolamine, phenolphthalein are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 2

Chemical Component	Weight in grams
Triethanolamine	10
o-Cresolphthalein (Na salt)	5
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 508 (20% Solution)	60
Deionized water	19.8
Liquid Germall Plus	0.2

Triethanolamine, o-cresolphthalein are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 3

Chemical Component	Weight in grams
Triethanolamine	10
Thymolphthalein (Na salt)	5
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 508 (20% Solution)	60
Deionized water	19.8
Liquid Germall Plus	0.2

Triethanolamine, thymolphthalein are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 4

Chemical Component	Weight in grams
Triethanolamine	10
Phenolphthalein (Na salt)	5
Colamid C	1.5
Miracare BC-27	3.5
Celvol 508 (20% Solution)	60
Deionized water	19.8
Liquid Germall Plus	0.2

Triethanolamine, phenolphthalein, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 5

Chemical Component	Weight in grams
Triethanolamine	10
o-Cresolphthalein (Na salt)	5
Colamid C	1.5
Miracare BC-27	3.5
Celvol 508 (20% Solution)	60
Deionized water	19.8
Liquid Germall Plus	0.2

Triethanolamine, o-cresolphthalein, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 6

Chemical Component	Weight in grams
Triethanolamine	10
Thymolphthalein (Na salt)	5
Colamid C	1.5
Miracare BC-27	3.5
Celvol 508 (20% Solution)	60
Deionized water	19.8
Liquid Germall Plus	0.2

Triethanolamine, thymolphthalein, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

Table 1 shows the color change observed in colored bubble solution in various Examples 1 through 6 as given below:

Table 1: Color change in colored bubble solution

Example #	Color change observed
Example 1	Pink to Colorless
Example 2	Red to Colorless
Example 3	Blue to Colorless
Example 4	Pink to Colorless
Example 5	Red to Colorless

Example 6 Blue to Colorless

[0360] 2.5 Film Formed Color Changing Bubbles with Acid-Base Indicator and Base

EXAMPLE 1

Chemical Component	Weight in grams
Triethanolamine	10
Phenol red (Na salt)	5
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 508 (20% Solution)	60
Deionized water	19.8
Liquid Germall Plus	0.2

Triethanolamine, phenol red are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 2

Chemical Component	Weight in grams
Triethanolamine	10
Thymol blue (Na salt)	5
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 508 (20% Solution)	60
Deionized water	19.8
Liquid Germall Plus	0.2

Triethanolamine, thymol blue are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 3

Chemical Component	Weight in grams
Triethanolamine	10
o-Cresol red (Na salt)	5
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 508 (20% Solution)	60
Deionized water	19.8
Liquid Germall Plus	0.2

Triethanolamine, o-cresol red are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 4

Chemical Component	Weight in grams
Triethanolamine	10
m-Cresol purple (Na salt)	5
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 508 (20% Solution)	60
Deionized water	19.8
Liquid Germall Plus	0.2

Triethanolamine, m-cresol purple are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, methocel A4M, colonial SLS, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 5

Chemical Component	Weight in grams
Triethanolamine	10
Phenol red (Na salt)	5
Colamid C	1.5
Miracare BC-27	3.5
Celvol 508 (20% Solution)	60
Deionized water	19.8
Liquid Germall Plus	0.2

Triethanolamine, phenol red, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 6

Chemical Component	Weight in grams
Triethanolamine	10
Thymol blue (Na salt)	5
Colamid C	1.5
Miracare BC-27	3.5
Celvol 508 (20% Solution)	60
Deionized water	19.8
Liquid Germall Plus	0.2

Triethanolamine, thymol blue, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 7

Chemical Component	Weight in grams
Triethanolamine	10
o-Cresol red (Na salt)	5
Colamid C	1.5
Miracare BC-27	3.5
Celvol 508 (20% Solution)	60
Deionized water	19.8
Liquid Germall Plus	0.2

Triethanolamine, o-cresol red, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 8

Chemical Component	Weight in grams
Triethanolamine	10
m-Cresol purple (Na salt)	5
Colamid C	1.5
Miracare BC-27	3.5
Celvol 508 (20% Solution)	60
Deionized water	19.8
Liquid Germall Plus	0.2

Triethanolamine, m-cresol purple, Colamid C, Miracare BC-27 are stirred and heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of deionized water, celvol 508 & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

Table 1 shows the color change observed in colored bubble solution in various Examples 1 through 6 as given below:

Table 1: Color change in colored bubble solution

Example #	Color change observed
Example 1	Red to Yellow
Example 2	Blue to Yellow
Example 3	Red to Yellow
Example 4	Purple to Yellow
Example 5	Red to Yellow
Example 6	Blue to Yellow
Example 7	Red to Yellow
Example 8	Purple to Yellow

[0361] 3.0 Film Formed Colorless Bubbles and Compositions

EXAMPLE 1

Chemical Component	Weight in grams
Glycerin	1
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 508	20
Deionized water	73.8
Liquid Germall Plus	0.2

Celvol 508 was slowly added to stirring deionized water and heated at 85°C for 30 minutes, cooled to room temperature, followed by addition of

methocel A4M, colonial SLS, glycerin & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 2

Chemical Component	Weight in grams
Glycerin	1
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 350	7
Deionized water	86.8
Liquid Germall Plus	0.2

Celvol 350 was slowly added to stirring deionized water and heated at 93°C for 30 minutes, cooled to room temperature, followed by addition of methocel A4M, colonial SLS, glycerin & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 3

Chemical Component	Weight in grams
Glycerin	1
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 125	10
Deionized water	83.8
Liquid Germall Plus	0.2

Celvol 125 was slowly added to stirring deionized water and heated at 96°C for 30 minutes, cooled to room temperature, followed by addition of methocel A4M, colonial SLS, glycerin & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 4

Chemical Component	Weight in grams
Glycerin	1
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Celvol 165	7
Deionized water	86..8
Liquid Germall Plus	0.2

Celvol 165 was slowly added to stirring deionized water and heated at 96°C for 30 minutes, cooled to room temperature, followed by addition of methocel A4M, colonial SLS, glycerin & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 5

Chemical Component	Weight in grams
Glycerin	1
Methocel A4M (4% solution in water)	2.5
Colonial SLS	2.5
Elvanol 71-30	10
Deionized water	83.8
Liquid Germall Plus	0.2

Elvanol 71-30 was slowly added to stirring deionized water and heated at 96°C for 30 minutes, cooled to room temperature, followed by addition of methocel A4M, colonial SLS, glycerin & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 6

Chemical Component	Weight in grams
Glycerin	20

Methocel A4M (2% solution in water)	15
Colonial SLS	15
PVP K-90	4
Deionized water	45..8
Liquid Germall Plus	0.2

PVP K-90, glycerin was heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of methocel A4M, colonial SLS, deionized water & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 7

Chemical Component	Weight in grams
Glycerin	20
Methocel A4M (2% solution in water)	15
Colonial SLS	15
PVP K-30	4
Deionized water	45..8
Liquid Germall Plus	0.2

PVP K-30, glycerin was heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of methocel A4M, colonial SLS, deionized water & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 8

Chemical Component	Weight in grams
Glycerin	20
Methocel A4M (2% solution in water)	15
Colonial SLS	15
PVP K-15	4

Deionized water	45..8
Liquid Germall Plus	0.2

PVP K-15, glycerin was heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of methocel A4M, colonial SLS, deionized water & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 9

Chemical Component	Weight in grams
Glycerin	10
Methocel A4M (2% solution in water)	10
Colonial SLS	10
Polyox N10	5
Deionized water	64..8
Liquid Germall Plus	0.2

Polyox N10, glycerin was heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of methocel A4M, colonial SLS, deionized water & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 10

Chemical Component	Weight in grams
Glycerin	10
Methocel A4M (2% solution in water)	10
Colonial SLS	10
Polyox N750	5
Deionized water	64..8
Liquid Germall Plus	0.2

Polyox N750, glycerin was heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of methocel A4M, colonial SLS, deionized water & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 11

Chemical Component	Weight in grams
Glycerin	10
Methocel A4M (2% solution in water)	10
Colonial SLS	10
Polyox N3000	5
Deionized water	64..8
Liquid Germall Plus	0.2

Polyox N3000, glycerin was heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of methocel A4M, colonial SLS, deionized water & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 12

Chemical Component	Weight in grams
Glycerin	10
Methocel A4M (2% solution in water)	10
Colonial SLS	10
Polyox 205	5
Deionized water	64..8
Liquid Germall Plus	0.2

Polyox 205, glycerin was heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of methocel A4M, colonial SLS, deionized

water & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 13

Chemical Component	Weight in grams
Glycerin	10
Methocel A4M (2% solution in water)	10
Colonial SLS	10
K-4844	20
Deionized water	49.8
Liquid Germall Plus	0.2

K-4844, glycerin was heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of methocel A4M, colonial SLS, deionized water & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 14

Chemical Component	Weight in grams
Glycerin	20
Methocel A4M (2% solution in water)	15
Colonial SLS	15
Gum arabic	1
Deionized water	48.8
Liquid Germall Plus	0.2

Gum arabic, glycerin was heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of methocel A4M, colonial SLS, deionized water & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 15

Chemical Component	Weight in grams
Glycerin	20
Methocel A4M (2% solution in water)	15
Colonial SLS	15
Starch	1
Deionized water	48..8
Liquid Germall Plus	0.2

Starch, glycerin was heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of methocel A4M, colonial SLS, deionized water & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

EXAMPLE 16

Chemical Component	Weight in grams
Glycerin	20
Methocel A4M (2% solution in water)	15
Colonial SLS	15
Gelatin	1
Deionized water	48..8
Liquid Germall Plus	0.2

Gelatin, glycerin was heated at 50°C for 30 minutes, cooled to room temperature, followed by addition of methocel A4M, colonial SLS, deionized water & liquid germall plus. The reaction mixture was further stirred for 2 hours at room temperature.

[0362] Temporary Cosmetic Coloration

[0363] EXAMPLE 1

[0364] A composition could be prepared with 0.5 g of the disodium salt of 3,3-Bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone, 0.5 g of vinyl pyrrolidone/vinyl acetate copolymer, (60/40), 0.4 g Gafquat 734 quaternized polyvinyl pyrrolidone, 0.2 g alkyl dimethylhydroxy ethyl ammonium bromide wherein the alkyl is the residue of tallow, 50 ml of ethanol and 100 cc of water (pH approximately 8-9, to form a deep purple-red color). Samples of permanent gray hair would be immersed in the dye solution, using 7 cc of solution per gram of hair. The sample would then be permitted to remain in contact with the dye solution for a period of 5 minutes at ambient temperature. The samples would then be drained and dried.

[0365] Their color would be determined in accordance with the Munsell system.

[0366] The dried hair can be washed with shampoo to easily remove the color.

[0367] In conclusion, the acid-base indicator in accordance with the present invention imparts to hair an intense semipermanent color which can be easily removed on washing, whereas the colored polymer of the prior art imparts to hair a less intense color which is resistant to washing.

[0368] EXAMPLE 2

[0369] A lipstick having the following composition can be prepared with 2 g of the disodium salt of 3,3-Bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone, Castor oil 65 g, Lanolin 10 g, Isopropyl myristate 5 g, beeswax 6 g, Carnauba wax 3 g, Candellila wax 3 g, Ozokerite 3 g. The oils and fatty substances would be heated to about 60-65°C., and at this temperature the acid-base indicator would be dispersed with vigorous stirring. After cooling, a magenta-colored stick would be obtained.

[0370] The lipstick can be applied and the magenta color would slowly disappear.

[0371] EXAMPLE 3

[0372] A make-up foundation having the following composition could be prepared with disodium salt of 3,3-Bis-(4-hydroxy-3-isopropylphenyl)-1-(3H)-isobenzofuranone 2g, Lanolin fatty alcohols oxyethyleneated with 20 mol of ethylene oxide 7 g, triglycerides of coconut fatty acids 30 g, glycerol monostearate 2 g, silicone oil 1.5 g, cetyl alcohol 1.5 g and water is 100 g. The acid-base indicator would be dissolved in water containing the emulsifiers (oxyethyleneated lanolin fatty alcohols and glycerol monostearate).

[0373] The aqueous phase would be heated to about 80°C.; the fatty phase, previously heated to 80°C., would be added with vigorous stirring. The mixture would be allowed to return to room temperature with moderate stirring.

[0374] A make-up foundation is obtained which can be applied readily and uniformly to the skin where the purple-red color would disappear with time.

[0375] Although the present invention has been described with reference to preferred embodiments, persons skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.

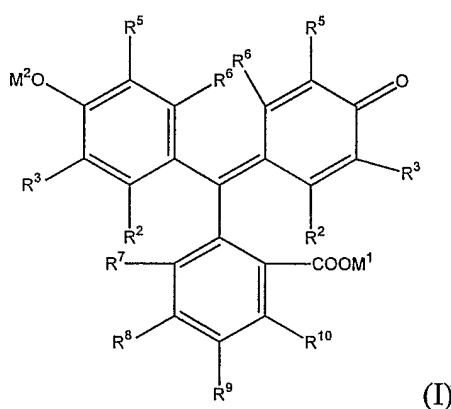
[0376] Those skilled in the art will recognize, or be able to ascertain, using no more than routine experimentation, many equivalents to specific embodiments of the invention described specifically herein. Such equivalents are intended to be encompassed in the scope of the following claims.

[0377]

CLAIMS

I claim:

1. A paint composition comprising:
an aqueous solution;
a film forming agent comprising between about 2 % and about 99% by weight of the total weight of the composition; and
an acid-base indicator comprising:



wherein

R^2 is selected from the group consisting of hydrogen, nitro, amino and alkyl;

R^3 is selected from the group consisting of hydrogen, aryl, alkyl, nitro, acetamido and alkoxide;

R^5 is selected from the group consisting of hydrogen, halo, alkoxide and alkyl;

R^6 is selected from the group consisting of hydrogen and alkyl;

R^7 , R^8 , R^9 and R^{10} are all hydrogen;

optionally, one of the carbons connected to R^2 , R^3 , R^5 or R^6 can be substituted with a nitrogen atom; and

M^1 and M^2 are each independently a hydrogen atom, a metal ion or an ammonium ion, provided that at least one of M^1 or M^2 is a metal ion or an

ammonium ion, and provided that R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are not all hydrogen atoms.

2. The paint composition of claim 1, wherein R^2 is selected from the group consisting of hydrogen and methyl; R^3 is selected from the group consisting of hydrogen, phenyl, isopropyl, methyl, ethyl, sec-butyl, nitro and methoxy; R^5 is selected from the group consisting of hydrogen, bromo, methoxy, isopropyl and methyl; and R^6 is selected from the group consisting of hydrogen and methyl.

3. The paint composition of claim 1, wherein R^2 is hydrogen, R^3 is Me, and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are hydrogen atoms, or R^2 is Me, R^3 is a hydrogen atom, R^5 is an iso-propyl group, R^6 , R^7 , R^8 , R^9 and R^{10} are hydrogen atoms or R^2 is H, R^3 is Me, R^5 is Br and R^6 , R^7 , R^8 , R^9 and R^{10} are hydrogen atoms or R^2 is Me, R^3 is Br, R^5 is an isopropyl and R^6 , R^7 , R^8 , R^9 and R^{10} are hydrogen atoms.

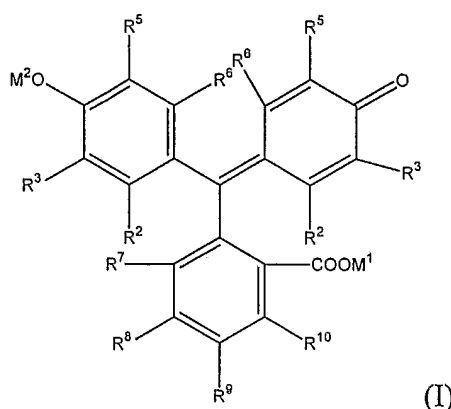
4. The paint composition of claim 1, wherein R^2 is H, R^3 is phenyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 and R^5 are isopropyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is methyl, R^5 is H, R^6 is methyl, R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 and R^5 are methoxy and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 and R^5 are methyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is ethyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is isopropyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is methoxide and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms or R^2 , R^3 and R^5 are all methyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} are all hydrogen atoms and R^3 is sec-butyl, or R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} are all hydrogen atoms and R^3 is nitro.

5. The paint composition of claim 1, further comprising a base.

6. The paint composition of claim 5, wherein the base is a metal hydroxide.

7. A substantially uniformly colored bubble composition comprising:
a surfactant;
water; and

an acid-base indicator comprising:



wherein

R^2 is selected from the group consisting of hydrogen, nitro, amino and alkyl;

R^3 is selected from the group consisting of hydrogen, aryl, alkyl, nitro, acetamido and alkoxide;

R^5 is selected from the group consisting of hydrogen, halo, alkoxide and alkyl;

R^6 is selected from the group consisting of hydrogen and alkyl;

R^7 , R^8 , R^9 and R^{10} are all hydrogen;

optionally, one of the carbons connected to R^2 , R^3 , R^5 or R^6 can be substituted with a nitrogen atom; and

M^1 and M^2 are each independently a hydrogen atom, a metal ion or an ammonium ion, provided that at least one of M^1 or M^2 is a metal ion or an ammonium ion.

8. The substantially uniformly colored bubble composition of claim 7, wherein R^2 is selected from the group consisting of hydrogen and methyl; R^3 is selected from the group consisting of hydrogen, phenyl, isopropyl, methyl, ethyl, sec-butyl, nitro and methoxy; R^5 is selected from the group consisting of hydrogen, bromo, methoxy, isopropyl and methyl; and R^6 is selected from the group consisting of hydrogen and methyl.

9. The substantially uniformly colored bubble composition of claim 7, wherein R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is hydrogen, R^3 is Me, and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are hydrogen atoms, or R^2 is Me, R^3 is a hydrogen atom, R^5 is an iso-propyl group, R^6 , R^7 , R^8 , R^9 and R^{10} are hydrogen atoms or R^2 is H, R^3 is Me, R^5 is Br and R^6 , R^7 , R^8 , R^9 and R^{10} are hydrogen atoms or R^2 is Me, R^3 is Br, R^5 is an isopropyl and R^6 , R^7 , R^8 , R^9 and R^{10} are hydrogen atoms.

10. The substantially uniformly colored bubble composition of claim 7, wherein R^2 is H, R^3 is phenyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 and R^5 are isopropyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is methyl, R^5 is H, R^6 is methyl, R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 and R^5 are methoxy and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 and R^5 are methyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is ethyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is isopropyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is methoxide and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms or R^2 , R^3 and R^5 are all methyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} are all hydrogen atoms and R^3 is sec-butyl, or R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} are all hydrogen atoms and R^3 is nitro.

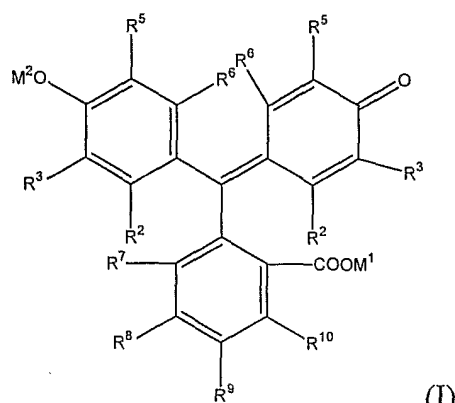
11. The substantially uniformly colored bubble composition of claim 7, further comprising a base.

12. The substantially uniformly colored bubble composition of claim 11, wherein the base is a metal hydroxide.

13. The substantially uniformly colored bubble composition of claim 1, wherein the surfactant is a cellulosic ether.

14. The substantially uniformly colored bubble composition of claim 1, wherein the surfactant is a combination of lauryl sulfate, C10-C16 alkyl alcohols, sodium salts and C10-C16 alcohols.

15. An applicator embedded with a compound comprising an acid-base indicator having the formula:



wherein

R^2 is selected from the group consisting of hydrogen, nitro, amino and alkyl;

R^3 is selected from the group consisting of hydrogen, aryl, alkyl, nitro, acetamido and alkoxide;

R^5 is selected from the group consisting of hydrogen, halo, alkoxide and alkyl;

R^6 is selected from the group consisting of hydrogen and alkyl;

R^7 , R^8 , R^9 and R^{10} are all hydrogen;

optionally, one of the carbons connected to R^2 , R^3 , R^5 or R^6 can be substituted with a nitrogen atom; and

M^1 and M^2 are each independently a hydrogen atom, a metal ion or an ammonium ion, provided that at least one of M^1 or M^2 is a metal ion or an ammonium ion, provided that R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are not all hydrogen atoms; and

a carrier.

16. The applicator of claim 15, wherein R^2 is selected from the group consisting of hydrogen and methyl; R^3 is selected from the group consisting of hydrogen, phenyl, isopropyl, methyl, ethyl, sec-butyl, nitro and methoxy; R^5 is selected from the group consisting of hydrogen, bromo, methoxy, isopropyl and methyl; and R^6 is selected from the group consisting of hydrogen and methyl.

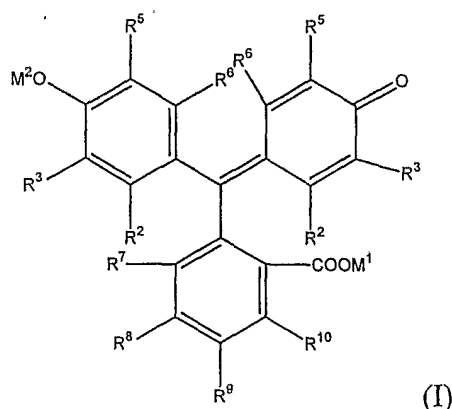
17. The applicator of claim 15, wherein R^2 is hydrogen, R^3 is Me, and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are hydrogen atoms, or R^2 is Me, R^3 is a hydrogen atom, R^5 is an iso-propyl group, R^6 , R^7 , R^8 , R^9 and R^{10} are hydrogen atoms or R^2 is H, R^3 is Me, R^5 is Br and R^6 , R^7 , R^8 , R^9 and R^{10} are hydrogen atoms or R^2 is Me, R^3 is Br, R^5 is an isopropyl and R^6 , R^7 , R^8 , R^9 and R^{10} are hydrogen atoms.

18. The applicator of claim 15, wherein R^2 is H, R^3 is phenyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 and R^5 are isopropyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is methyl, R^5 is H, R^6 is methyl, R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 and R^5 are methoxy and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 and R^5 are methyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is ethyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is isopropyl and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is methoxide and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms or R^2 , R^3 and R^5 are all methyl and R^6 , R^7 , R^8 , R^9 and R^{10} are all hydrogen atoms, or R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} are all hydrogen atoms and R^3 is sec-butyl, or R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} are all hydrogen atoms and R^3 is nitro.

19. The applicator of claim 15, wherein M^1 and M^2 are both hydrogen atoms.

20. The applicator of claim 15, further comprising a base.

21. A temporary hair colorant composition comprising:
a polyvinylpyrrolidone/vinyl acetate copolymer;
a surfactant;
water;
a pH sensitive acid-base indicator having the formula:



wherein

R^2 is selected from the group consisting of hydrogen, nitro, amino and alkyl;

R^3 is selected from the group consisting of hydrogen, aryl, alkyl, nitro, acetamido and alkoxide;

R^5 is selected from the group consisting of hydrogen, halo, alkoxide and alkyl;

R^6 is selected from the group consisting of hydrogen and alkyl;

R^7 , R^8 , R^9 and R^{10} are all hydrogen;

optionally, one of the carbons connected to R^2 , R^3 , R^5 or R^6 can be substituted with a nitrogen atom; and

M^1 and M^2 are each independently a hydrogen atom, a metal ion or an ammonium ion, provided that at least one of M^1 or M^2 is a metal ion or an ammonium ion, provided that R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are not all hydrogen atoms;

22. The temporary hair colorant composition of claim 21, wherein R^2 is selected from the group consisting of hydrogen and methyl; R^3 is selected from the group consisting of hydrogen, phenyl, isopropyl, methyl, ethyl, sec-butyl, nitro and methoxy; R^5 is selected from the group consisting of hydrogen, bromo, methoxy, isopropyl and methyl; and R^6 is selected from the group consisting of hydrogen and methyl.

23. The temporary hair colorant composition of claim 21, wherein R^2 is hydrogen, R^3 is Me, and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are hydrogen atoms, or R^2 is

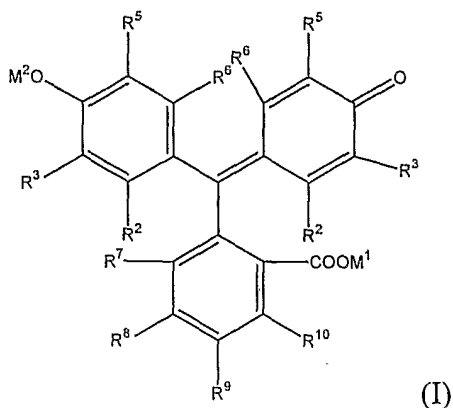
Me, R³ is a hydrogen atom, R⁵ is an iso-propyl group, R⁶, R⁷, R⁸, R⁹ and R¹⁰ are hydrogen atoms or R² is H, R³ is Me, R⁵ is Br and R⁶, R⁷, R⁸, R⁹ and R¹⁰ are hydrogen atoms or R² is Me, R³ is Br, R⁵ is an isopropyl and R⁶, R⁷, R⁸, R⁹ and R¹⁰ are hydrogen atoms.

24. The temporary hair colorant composition of claim 21, wherein R² is H, R³ is phenyl and R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms, or R² is H, R³ and R⁵ are isopropyl and R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms, or R² is H, R³ is methyl, R⁵ is H, R⁶ is methyl, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms, or R² is H, R³ and R⁵ are methoxy and R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms, or R² is H, R³ and R⁵ are methyl and R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms, or R² is H, R³ is ethyl and R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms, or R² is H, R³ is isopropyl and R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms, or R² is H, R³ is methoxide and R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms or R², R³ and R⁵ are all methyl and R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms, or R², R³, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰ are all hydrogen atoms and R³ is sec-butyl, or R², R³, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰ are all hydrogen atoms and R³ is nitro.

25. The temporary hair colorant composition of claim 21, further comprising a base.

26. The temporary hair colorant composition of claim 25, wherein the base is a metal hydroxide.

27. A temporary lipstick composition comprising:
an oil carrier;
a wax;
a pH sensitive acid-base indicator having the formula:



wherein

R^2 is selected from the group consisting of hydrogen, nitro, amino and alkyl;

R^3 is selected from the group consisting of hydrogen, aryl, alkyl, nitro, acetamido and alkoxide;

R^5 is selected from the group consisting of hydrogen, halo, alkoxide, nitro and alkyl;

R^6 is selected from the group consisting of hydrogen and alkyl;

R^7 , R^8 , R^9 and R^{10} are all hydrogen;

optionally, one of the carbons connected to R^2 , R^3 , R^5 or R^6 can be substituted with a nitrogen atom; and

M^1 and M^2 are each independently a hydrogen atom, a metal ion or an ammonium ion, provided that at least one of M^1 or M^2 is a metal ion or an ammonium ion, provided that R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are not all hydrogen atoms;

28. The temporary lipstick composition of claim 27, wherein R^2 is selected from the group consisting of hydrogen and methyl; R^3 is selected from the group consisting of hydrogen, phenyl, isopropyl, methyl, ethyl, sec-butyl, nitro and methoxy; R^5 is selected from the group consisting of hydrogen, bromo, methoxy, isopropyl and methyl; and R^6 is selected from the group consisting of hydrogen and methyl.

29. The temporary lipstick composition of claim 27, wherein R^2 is hydrogen, R^3 is Me, and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are hydrogen atoms, or R^2 is

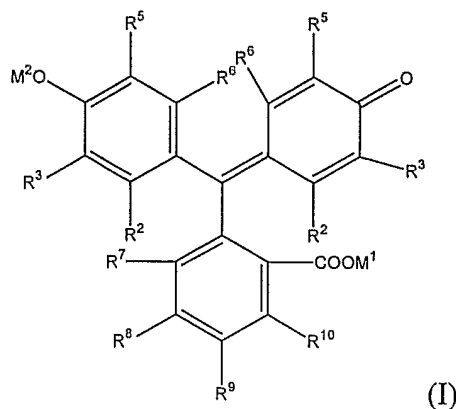
Me, R³ is a hydrogen atom, R⁵ is an iso-propyl group, R⁶, R⁷, R⁸, R⁹ and R¹⁰ are hydrogen atoms or R² is H, R³ is Me, R⁵ is Br and R⁶, R⁷, R⁸, R⁹ and R¹⁰ are hydrogen atoms or R² is Me, R³ is Br, R⁵ is an isopropyl and R⁶, R⁷, R⁸, R⁹ and R¹⁰ are hydrogen atoms.

30. The temporary lipstick composition of claim 27, wherein R² is H, R³ is phenyl and R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms, or R² is H, R³ and R⁵ are isopropyl and R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms, or R² is H, R³ is methyl, R⁵ is H, R⁶ is methyl, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms, or R² is H, R³ and R⁵ are methoxy and R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms, or R² is H, R³ and R⁵ are methyl and R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms, or R² is H, R³ is ethyl and R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms, or R² is H, R³ is isopropyl and R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms, or R² is H, R³ is methoxide and R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms or R², R³ and R⁵ are all methyl and R⁶, R⁷, R⁸, R⁹ and R¹⁰ are all hydrogen atoms, or R², R³, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰ are all hydrogen atoms and R³ is sec-butyl, or R², R³, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰ are all hydrogen atoms and R³ is nitro.

31. The temporary lipstick composition of claim 27, further comprising a base.

32. The temporary lipstick composition of claim 31, wherein the base is a metal hydroxide.

33. A temporary make up foundation composition comprising:
a fatty alcohol;
a long chain alcohol;
water;
a pH sensitive acid-base indicator having the formula:



wherein

R^2 is selected from the group consisting of hydrogen, nitro, amino and alkyl;

R^3 is selected from the group consisting of hydrogen, aryl, alkyl, nitro, acetamido and alkoxide;

R^5 is selected from the group consisting of hydrogen, halo, alkoxide, nitro and alkyl;

R^6 is selected from the group consisting of hydrogen and alkyl;

R^7 , R^8 , R^9 and R^{10} are all hydrogen;

optionally, one of the carbons connected to R^2 , R^3 , R^5 or R^6 can be substituted with a nitrogen atom; and

M^1 and M^2 are each independently a hydrogen atom, a metal ion or an ammonium ion, provided that at least one of M^1 or M^2 is a metal ion or an ammonium ion, provided that R^2 , R^3 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are not all hydrogen atoms;.

34. The temporary make up foundation composition of claim 33, wherein R^2 is selected from the group consisting of hydrogen and methyl; R^3 is selected from the group consisting of hydrogen, phenyl, isopropyl, methyl, ethyl, sec-butyl, nitro and methoxy; R^5 is selected from the group consisting of hydrogen, bromo, methoxy, isopropyl and methyl; and R^6 is selected from the group consisting of hydrogen and methyl.

35. The temporary make up foundation composition of claim 33, wherein R^2 is hydrogen, R^3 is Me, and R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are hydrogen

atoms, or R^2 is Me, R^3 is a hydrogen atom, R^5 is an iso-propyl group, R^6, R^7, R^8, R^9 and R^{10} are hydrogen atoms or R^2 is H, R^3 is Me, R^5 is Br and R^6, R^7, R^8, R^9 and R^{10} are hydrogen atoms or R^2 is Me, R^3 is Br, R^5 is an isopropyl and R^6, R^7, R^8, R^9 and R^{10} are hydrogen atoms.

36. The temporary make up foundation composition of claim 33, wherein R^2 is H, R^3 is phenyl and R^5, R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 and R^5 are isopropyl and R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is methyl, R^5 is H, R^6 is methyl, R^7, R^8, R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 and R^5 are methoxy and R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 and R^5 are methyl and R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is ethyl and R^5, R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is isopropyl and R^5, R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms, or R^2 is H, R^3 is methoxide and R^5, R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms or R^2, R^3 and R^5 are all methyl and R^6, R^7, R^8, R^9 and R^{10} are all hydrogen atoms, or $R^2, R^3, R^5, R^6, R^7, R^8, R^9, R^{10}$ are all hydrogen atoms and R^3 is sec-butyl, or $R^2, R^3, R^5, R^6, R^7, R^8, R^9, R^{10}$ are all hydrogen atoms and R^3 is nitro.

37. The temporary make up foundation composition of claim 33, further comprising a base.

38. The temporary make up foundation composition of claim 37, wherein the base is a metal hydroxide.