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(54) Title: ERADICABLE BALL-PEN INKS

(57) Abstract: Improved combination eradicable ball-pen and re-write inks are disclosed. The combination eradicable and re-write ball-pen inks disclosed include water, glycerol, one or more acids and an eradicable dye. Glycerol is present in an amount greater than the water content, which is relatively low and the eradicable dye is provided in substantial amounts so that the glycerol and eradicable dye provide the requisite viscosity for a ball-pen ink. The combination of the high dye content and acid content also enables the eradicable ball-pen ink to be used as the re-write ink.

ERADICABLE BALL-PEN INKS

Technical Field

A series of improved eradicable ball-pen inks are disclosed. Some of the disclosed eradicable ball-pen inks can be used as an initially applied ink that can be eradicated with an eradicating fluid and further that can also be used as the re-write ink which eliminates the need for a third fluid for use as the re-write ink.

Background of the Related Art

Correction fluids for correcting errors on typewritten and handwritten materials are known in the art. Typically, such correction fluids are opaque material, often white in color but various tinted formulations are available for use on non-white paper. Currently available correction fluids provide an opaque coating over the error and provide a surface for writing or printing the correction. One problem associated with currently available correction fluids is that the color of the correction fluid rarely matches the color of the paper exactly, thereby further drawing attention to the corrected mistake and diminishing the appearance of the finished written product. Further, use of correction fluids changes the texture of the paper and can draw the readers attention to the corrected mistake. Also, if the user begins to write or print over the correction fluid before it is sufficiently dried, the smoothness of the correction fluid surface will be destroyed thereby making the correction sloppy and unprofessional looking.

To eliminate these problems associated with the use of conventional correction fluids, ink eradicators have been developed. An ink eradicator is a liquid material that reacts with the dye of an eradicable ink to change the color of the dye in the eradicatable ink from a colored state to a clear or colorless state. In other words, an eradicating fluid can "erase" the inked error.

Typical eradicator fluids are near Newtonian, water-based fluids and are applied by way of a porous tip in fluid communication with a reservoir containing the eradicator fluid. Typically, eradicator fluids are provided in felt tip marker type instruments and the user rubs the felt tip against the incorrect written material until the incorrect written material disappears on the page. Then, after waiting a sufficient amount of time for the eradicator fluid to dry, the user can make the correction with a re-write ink.

Typically, the re-write ink is different than the original eradicable ink because it is resistant to chemical reaction with the dried eradicator fluid. Specifically, the re-write ink does not contain a dye that has the ability to be decolorized by the eradicator or eradicating fluid.

Thus, in current systems utilizing an eradicating fluid as opposed to a correction fluid, three different materials are required: the eradicable ink, the eradicating fluid and the re-write ink. As a result, three different writing instruments may be required: one for the eradicating fluid, one for the eradicable ink and one for the re-write ink. In current systems, it is very easy for the consumer to confuse the eradicable ink, which should be used for the original marking, and the re-write ink, which must be used for the correction because it will not react with the dried eradicating fluid.

To simplify the use of eradicating fluids and eradicable inks, there is a need for an improved eradicable ball-pen ink system which permits the eradicable ball-pen ink to also be used for making the corrections.

In addressing this problem, most ball-pen inks are organic non-polar solvent based. However, most eradicable inks are not soluble in organic solvents. To make eradicable inks soluble in non-polar organic solvents, U.S. Patent No. 6,221,432, commonly assigned with this application, teaches the use of various salts for use as counter ions to provide a hydrophobic property to the eradicable dye thereby rendering it soluble in organic solvents. However, this requires additional process steps thereby adding to the cost of such an eradicable ball-pen ink system.

Accordingly, because eradicable ball-pen inks are typically hydrophilic, a water-based system would be preferable, or a system that does not depend upon the use of polar organic solvents. Therefore, there is a need for an improved water-based ball-pen ink that is eradicable and can also be used as a re-write ink.

SUMMARY OF THE DISCLOSURE

In satisfaction of the aforenoted needs, a plurality of water-based, organic solvent-free ball-pen inks that may be also be used as re-write inks.

In an embodiment, an improved eradicable ball-pen ink comprises water, one or more polyols, one or more acids, an eradicable dye and the ink is free of organic solvents and has a ratio of polyol to water that is greater than 1. Polyols, at

room temperature, are not considered to be an organic solvent due to their high melting and boiling points and polarities.

In a refinement, the one of more polyols are selected from the group consisting of glycerol, one or more glycols, one or more glymes or glycol diethers, glycol ethers, glycol acetates and mixtures thereof.

Preferably, the polyol is glycerol with or without one or more glycols.

In a refinement, the disclosed ink is also free of resins as viscosity required for a ball-pen ink is provided by the glycerol content and the high content of the eradicable dye. While polymer coating additives such as poly vinyl pyrollidone (PVP) may be used, these types of additives are not considered to be resins.

In another refinement, the eradicable dye is present in an amount greater than 20 wt%.

In yet another refinement, one or more glycols may be added with glycerol. It has been found that glycols in combination with a non-resinous thickener, such as a gum (e.g., xanthan gum) enhance the performance characteristics of the ball-pen ink and help to prevent leakage of the ink through a ball-pen tip when the pen is not in use.

In another refinement, the ratio of polyol to water is greater than 2:1.

In another refinement, the eradicable dye is selected from the group consisting of Auramine O, Basic Yellow 2, Basic Yellow 11, Basic Yellow 13, Basic Yellow 21, Basic Yellow 28, Basic Yellow 29, Basic Yellow 40, Basic Yellow 49, Acid Blue 22, Acid Blue 83, Acid Blue 93, Acid Fuchsin, Acid Green 3, Acid Green 5, Acid Green 9, Acid Magenta, Acid Roseine, Acid Rubin, Acid Violet 17, Acid Violet 19, Acid Violet 49, Alizarol Cyanin R, Aluminon, Aniline Blue Ws, Basic Blue 8, Basic Blue 15, Basic Blue 20, Basic Blue 26, Basic Fuchsin, Basic Green 4, Basic Red 9, Basic Red 14, Basic Red 15, Basic Red 29, Basic Red 46, Basic Violet 2, Basic Violet 3, Basic Violet 4, Basic Violet 14, Chrome Violet Cg, Chromoxane Cyanin R, Cotton Blue, Crystal Violet, Dahlia, Diamond Green B, Eriochrome Cyanin R, Ethyl Green, Ethyl Violet, Fast Green Fcf, Food Green 3, Gentian Violet, Helvetia Blue, Hoffman's Violet, Light Green, Lissamine Green Sf, Magenta 0, Magenta I, Magenta Ii, Magenta Iii, Malachite Green, Methyl Blue, Methyl Green, Methyl Violet, Methyl Violet 2b, Methyl Violet 10b, Mordant Blue 3, Mordant Violet 39, New Fuchsin, Night Blue, Acid Orange 10, Acid Orange 21, Pararosanilin,

Primula, Rosanilin, Solochrome Cyanin R, Victoria Blue 4r, Victoria Blue B, Victoria Green B, Water Blue I, and combinations thereof.

In another refinement, the acid is present in an amount less than 20 wt%.

In a further refinement of this concept, the acid is selected from the group consisting of citric acid, phosphoric acid, benzoic acid, lactic acid, acetic acid, propanoic acid, acetoacetic acid, crotonic acid, formic acid, glycerlic acid, glycollic acid, glyoxylic acid, lactic acid, pyruvic acid, trans-aconitic acid, fumaric acid, maleic acid, malic acid, tartaric acid, acetylenedicarboxylic acid, tetrahydrophthalic acid, mesaconic acid, phthalic acid, isophthalic acid, terephthalic acid, itaconic acid, trans-ethyleneoxidedicarboxylic acid, succinic acid, adipic acid, pimellic acid, suberic acid, azelic acid, substituted phosphoric acid, citric acid, hemimellitic acid, trimellitic, trimesic acid, 2-carboxyethyliminodiacetic acid, nitrilotriacetic acid, phosphonic acid, mellophanic acid, prehnitic acid, pyromellitic acid, 2-phosphonoethyliminodiacetic acid, diethylenetetraacetic acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, hydrofluoric acid, nitric acid, sulfuric acid, carbonic acid, chromic acid, phosphorous acid, phosphonic acid and combinations thereof.

In another refinement, the disclosed ink is free of resins. The disclosed ink can be free of resins or substantial amounts of thickeners due to the high polyol content and high eradicable dye content. For example, glycerol, in addition to providing the high viscosity required for suitable ball-pen ink, also provides a carrier for the high amounts of eradicable dyes present in the formulation.

In another refinement, the disclosed inks have a pH of less than 3 thereby enabling the disclosed eradicable bell-pen inks to also be used as re-write inks.

Further, in an improved combination eradicable and re-write ink in a viscosity suitable for use in ball-point pens is disclosed which comprises an acid in the form of citric acid, a low water content, an eradicable dye and an acid that helps to increase the viscosity and limit or eliminate the need for a resin to increase the viscosity.

In a refinement, the eradicable dye of the combination eradicable and re-write ball-pen ink described above is selected from the group consisting of acid

blue 93, basic green 4, acid violet 19, basic red 14 and mixtures thereof. Other eradicable dyes are available, some of which are listed below.

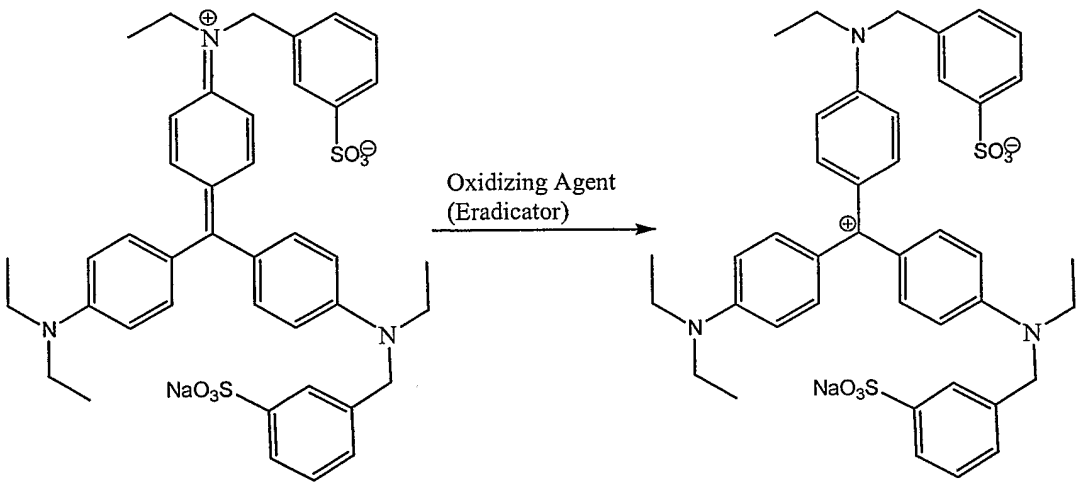
In a further refinement, the combination eradicable and re-write ball-pen ink has a pH of less than 3.

As the disclosed inks are used for a ball pen, the viscosity ranges from about 1 to about 6 Kcp and has a pH ranging from about 2 to about 3 as well. The moderate pH ink will avoid corrosion of ball point pen tips and porous tips as described above.

Additionally, the eradicable inks and eradicators disclosed herein have applications to other technologies where a color changing liquid is needed.

DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS

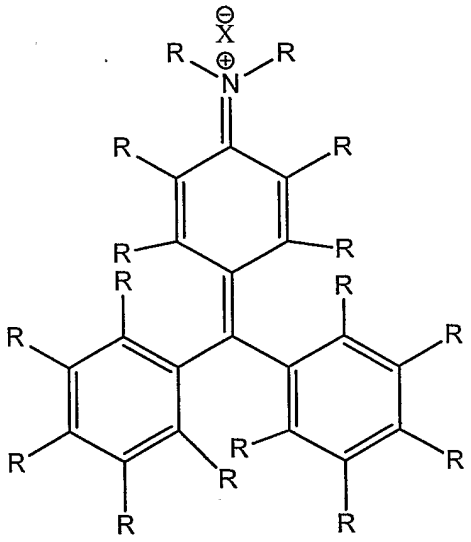
A typical formulation for an eradicable ink includes a solvent (*e.g.*, water) to dissolve a dye that is capable of such being eradicated (*e.g.*, a triarylmethane dye). The eradication solution includes an eradicator that, by a chemical process, converts an otherwise colored dye into a substantially colorless compound or a color that matches that of the substrate (*e.g.*, white for white paper). Such compounds include oxidizing agents, reducing agents, acid-base reactants, and chemicals that can sublime under the influence of heat. Without intending to be limited to any particular method of eradication, it is believed that for triarylmethane dyes, the active colored dye is able to reflect color in the visible range (between 380 nm to 780 nm) because of the conjugation of the aromatic rings in the molecule; however, once an oxidizing agent is applied to the triarylmethane dye, it destroys the conjugation and the dye becomes at least substantially colorless. This proposed process is shown below for Acid Violet 17:



Violet **Colorless**

The eradication solution preferably includes water or an organic solvent as the primary solvent, an eradicator such as, for example, a sulfite, bisulfite, or an amine (*e.g.*, sodium glycinate) that can cause certain dyes to lose their colors (*e.g.*, triarylmethane dyes) or to change color, and a film-forming polymer. A suitable eradicator solution for the inks disclosed herein is a commercially available eradicator solution that includes both a sulfite and an amine as active eradicating agents (*e.g.*, oxidizers) (available from Sanford Reynolds of Valence, France). See also the eradicating fluids disclosed in commonly assigned U.S. Patent Application No. 10/619,706.

The eradicable nature of the ink is derived from the ability to convert the dye (chromophore) from a colored compound to at least substantially colorless, or alternatively, to another color (*e.g.*, the color of the paper used). As discussed above, this can be achieved with the combination of a dye that is sensitive to oxidation. Dyes which are capable of performing this change in color include diarylmethane derivative dyes, triarylmethane derivative dyes, and methine derivative dyes. Diaryl dyes for use with the inks disclosed herein include Auramine O (Chemical Index No. 41000), and Basic Yellow 2 (Chemical Index No. 41000). In the colored state, the bi- and triarylmethane, and methine dyes often contain one or more cationic imine groups. The generic structure of a triarylmethane dye is shown below in formula (II):



(II)

wherein each R group is the same or different and preferably is selected from C_1 to C_{10} alkyl groups. A non-exhaustive list of triarylmethane dyes for use in inks disclosed herein are listed below in Table I.

Table I[1]

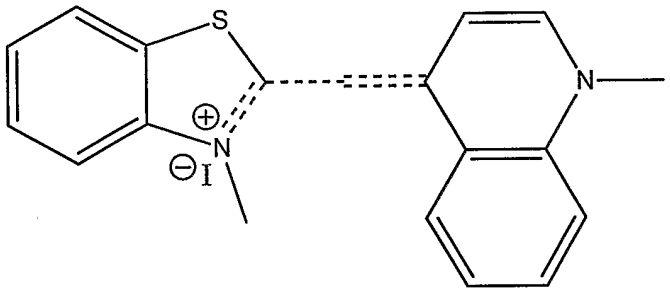
Color Index Name	Color Index No.	Common/Commercial Name
Acid Blue 22	42755	Water Blue I
Acid Blue 93	42780	Methyl Blue
Acid Fuchsin	42685	Acid Fuchsin
Acid Green 3	42095	Light Green Sf Yellowish
Acid Green 5	42095	Light Green Sf Yellowish
Acid Magenta	42685	Acid Fuchsin
Acid Roseine	42685	Acid Fuchsin
Acid Rubin	42685	Acid Fuchsin
Acid Violet 17	42650	Acid Violet 4BN
Acid Violet 19	42685	Acid Fuchsin
Alizarol Cyanin R	43820	Eriochrome Cyanin R
Aluminon	43810	Triphenylmethane Chrome Violet Cg
Aniline Blue Ws		Aniline Blue Ws
Basic Blue 8	42563	Victoria Blue 4r
Basic Blue 15	44085	Night Blue
Basic Blue 20	42585	Methyl Green
Basic Blue 26	44045	Victoria Blue B
Basic Fuchsin		Basic Fuchsin
Basic Green 4	42000	Malachite Green
Basic Red 9	42500	Pararosanilin
Basic Red 14	48016	Cationic Brilliant Red 5GN
Basic Violet 2	42520	New Fuchsin
Basic Violet 3	42555	Crystal Violet

[1] *See*, R.D. Lillie, Conn's Biological Stains (8th ed., 1969), Williams and Wilkins Company, Baltimore, Maryland; Susan Budavari (Ed.), The Merck Index, (12th ed., 1996), Merck & Co., Whitehouse Station, N.J; *see also*, P. A. Lewis (Ed.), Pigment Handbook Vol. I, Properties and Economics, sections I(D)f(1) and I(D)g, John Wiley & Sons, (2nd ed., 1988); H. Zollinger, Color Chemistry: Syntheses, Properties, and Applications of Organic Dyes And Pigments, Chapter 4, VCH Publishers (1987); D. R. Waring and G. Hallas (Eds.), The Chemistry and Application of Dyes, Chapter 2, Section IX, Plenum Press (1990); and M. Okawara, T. Kitao, T. Hirashima, and M. Matsuoka, Organic Colorants: A Handbook of Data of Selected Dyes for Electro-Optical Applications, Section VI, Elsevier (1988).

Basic Violet 4	42600	Ethyl Violet
Basic Violet 14	42510	Rosanilin
Chrome Violet Cg	43810	Triphenylmethane Chrome Violet Cg
Chromoxane Cyanin R	4382	Eriochrome Cyanin R
Cotton Blue	42780	Methyl Blue
Crystal Violet	42555	Crystal Violet
Dahlia	42530	Hoffman's Violet
Diamond Green B	42000	Malachite Green
Eriochrome Cyanin R	43820	Eriochrome Cyanin R
Ethyl Green	42590	Ethyl Green
Ethyl Violet	42600	Ethyl Violet
Fast Green Fcf	42053	Fast Green Fcf
Food 3	42053	Fast Green Fcf
Gentian Violet		Methyl Violet 2b
Helvetia Blue	42780	Methyl Blue
Hoffman's Violet	42530	Hoffman's Violet
Light Green	42095	Light Green Sf Yellowish
Lissamine Green Sf	42095	Light Green Sf Yellowish
Magenta 0	42500	Pararosanilin
Magenta I	42510	Rosanilin
Magenta Ii		Magenta Ii
Magenta Iii	42520	New Fuchsin
Malachite Green	42000	Malachite Green
Methyl Blue	42780	Methyl Blue
Methyl Green	42585	Methyl Green
Methyl Violet	42535	Methyl Violet 2b
Methyl Violet 2b	42535	Methyl Violet 2b
Methyl Violet 10b	42555	Crystal Violet
Mordant Blue 3	43820	Eriochrome Cyanin R
Mordant Violet 39	43810	Triphenylmethane Chrome Violet Cg
New Fuchsin	4252	New Fuchsin
Night Blue	44085	Night Blue
Pararosanilin	42500	Pararosanilin

Primula	42530	Hoffman's Violet
Rosanilin	42510	Rosanilin
Solochrome Cyanin R	43820	Eriochrome Cyanin R
Victoria Blue 4r	42563	Victoria Blue 4r
Victoria Blue B	44045	Victoria Blue B
Victoria Green B	42000	Malachite Green
Water Blue I	42755	Water Blue I

Another type of dye that can be used in an ink are the methine class of dyes. The methine dyes generally relate to dyes that contain a chromophore that consists of one or more of a methine group (—CH==C—), also called methylidyne or methine group. When the methine dye only contains one methine group the dye is sometimes referred to as a cyanine dye, with three methine groups the dye is sometime referred to as a carbocyanine dye, and with more than three methine groups the dye is often referred to as a polymethine dye. An example of a methine dye is Thiazole Orange, shown below:



wherein the bonds that make up the methine groups are shown above as dashed lines. Other examples of methine dyes include Basic Red 15, Basic Yellow 11, and Basic Yellow 13. For a comprehensive listing of methine dyes, see F. M. Hamer, The Chemistry of Heterocyclic Compounds, A. Weissberger (Ed.), The Cyanine Dyes and Related Compounds, Wiley Interscience, New York (1964).

In spectroscopic terms, the color white is represented as having the property of reflecting light at of substantially all visible wavelengths without a substantial loss. If one considers the color white as a theoretical spectral starting point, once a wavelength of visible light is absorbed by the white material, that material is colored. For example, if a material is white and is made to absorb visible light at 470 nm, then that material would appear blue instead of white. Likewise, the color black, in

spectroscopic terms, is represented as having the property of absorbing light at of substantially all visible wavelengths without a substantial loss.

When formulating an eradicable ball-pen ink of a particular color, whether by the addition of one dye or a mixture of dyes, the rate of eradication of a dye (once applied to a substrate) is a consideration when selecting a dye. Without intending to be limited to a particular mechanism, it is believed that the rate of eradication of diarylmethane, triarylmethane, and methine dyes is proportional to the concentration of the dye in the ink. The ink described herein includes one or more dyes selected from the group consisting of diarylmethane dyes, triarylmethane dye, methine dyes, and combinations thereof. The dye preferably is present in an amount in a range of about 20% to about 40% by weight of the total weight of the composition, more preferably about 261% to about 32% by weight. The high content of the dye also helps to provide the viscosity needed for a ball-pen ink.

In selecting particular dyes for use in the ink, there are a number of dyes to choose from, and as a result, these dyes of different colors can be mixed to create an ink of almost any color. An eradicable ink disclosed herein can include two or more dyes that, when combined, provide an eradicable ink from a variety of colors. The dyes may be combined to provide a black eradicable ball-pen ink. Two competing considerations when formulating a black eradicable ink are the rate of eradication and the intensity of the black color. An increase in the concentration of the dyes used to create the black color will increase the intensity of the color, however, as discussed above, an increase in the dye concentration also increases the amount of time needed to eradicate the dye. It has been found that for the ball-pen ink disclosed herein the dye concentration in the range of about 20% to about 40% by weight based on the total weight of the composition is a preferred concentration to balance these considerations.

The color of the ink disclosed herein will primarily be determined by the dyes which cause the inks to reflect a particular wavelength of visible light. Mixing two dyes to form an ink of a particular color can be done with the use of two complementary colors, or combinations that contain all three primary colors (red, yellow, and blue). When two complementary colors are mixed, the resultant mixture is gray, with black being the completely saturated form of gray. The complement color of red is green, the complement color of orange is blue, and the complement color of yellow is violet. When using complementary colors, these pairs of

complementary colors actually reflect all three primary colors. For example, when red and green dyes are mixed as complementary colors, it is the equivalent of mixing red with yellow and blue, because green is composed of a mixture of the two primary colors yellow and blue. In another example, the mixture of the two complementary colors yellow and violet is the equivalent of mixing yellow with red and blue, because violet is composed of two primary colors, red and blue.

In the inks described herein, the color black can be achieved by the mixing of dyes of either two complementary colors (*e.g.*, green-red, or yellow-magenta) or by dyes with the combination of all three primary colors (red, yellow, and blue). Also, in the inks described herein, a black ink is preferably formed from the combination of a green dye with a dye selected from the group consisting of a red dye, a violet dye, and combinations thereof. One preferred combination of red and green is the combination of Basic Red 14 and Basic Green 4.

When combining two or more colors to form an ink of a desired color, it is understood that the desired color (*e.g.*, black), may be reached even though an undertone of another color (*e.g.*, a bluish-black color) might be perceptible. For example, it is understood that an ink that is colored black can have a red or a blue undertone, and yet still be considered a black ink.

When mixing dyes that are capable of eradication (*e.g.*, di-, triarylmethane and methine dyes) into an ink, it is extremely difficult to prepare a black eradicable ink. Quite surprisingly, it has been found that the combination of a green eradicable dye and a violet and/or a red dye is able to mix to form a black eradicable ink. One embodiment of an ink disclosed herein is a black eradicable ink, including a mixture of two or more dyes selected from the group consisting of diarylmethane derivatives, triarylmethane derivatives, methine dyes, and combinations thereof, wherein the mixture of dyes appears black in color.

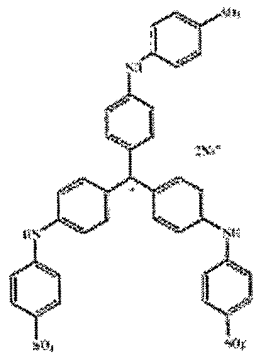
The black eradicable inks described herein are considered black even though they may have a red or blue undertone. Control of undertone of the black color can be achieved by altering the weight ratio of the red and green dyes used to mix to form the black color, for example. An increase in the red dye concentration will lead to a red undertone to the black ink, and an increase in the concentration of the green dye (a mixture of the two primary colors yellow and blue) will lead to a blue undertone. When a black ink is formed from the combination of a red dye and a green dye, the preferred weight ratio of the red dye to the green dye is in the range of about 10:1

about 1:10, more preferably about 4:1 to about 1:4. When a black ink is formed from the combination of a violet dye and a green dye, the preferred weight ratio of the violet dye to the green dye is in the range of about 10:1 about 1:10, more preferably about 4:1 to about 1:4.

A black eradicable ink can be formed by the combination of a green dye and a dye selected from the group consisting of red dyes, violet dyes, and combinations thereof. Preferably, the dye is formed from the combination of a green dye in an amount in a range of about 25% to about 98% by weight with a red dye in an amount in a range of about 2% to about 75% by weight, and/or with a violet dye in an amount in a range of about 2% to about 75% by weight, each based on the total weight of the dye portion of the ink. More preferably, the dye is formed from the combination a green dye in an amount in the range of about 25% to about 98% with a red dye present in an amount in the range of about 1% to about 30%, and/or with a violet dye present in an amount in the range of about 1% to about 30%, each by weight based on the total weight of the dye portion of the ink.

A green dye preferably is selected from the group consisting of Acid Green 3, Acid Green 5, Basic Green 4, Diamond Green B, Ethyl Green, Fast Green Fcf, Food Green 3, Light Green, Lissamine Green Sf, Malachite Green, Methyl Green, Victoria Green B, and combinations thereof. Preferably, a red dye is selected from the group consisting of Basic Red 9, Basic Red 14, Basic Red 15, Basic Red 29, Basic Red 46, and combinations thereof. Preferably, a violet dye is selected from the group consisting of Acid Violet 17, Acid Violet 19, Basic Violet 2, Basic Violet 3, Basic Violet 4, Basic Violet 14, Basic Yellow 49, Chrome Violet Cg, Crystal Violet, Ethyl Violet, Gentian Violet, Hoffman's Violet, Methyl Violet, Methyl Violet 2b, Methyl Violet 10b, Mordant Violet 39, and combinations thereof. To form a yellow ink, a yellow dye is preferably selected from the group consisting of Basic Yellow 11, Basic Yellow 13, Basic Yellow 21, Basic Yellow 28, Basic Yellow 29, Basic Yellow 40, and combinations thereof.

For blue inks, Acid Blue 93 is the preferred eradicable dye. Acid Blue 93 as the following structure:



It will be noted that the combination of dyes and eradicating fluids disclosed herein may be useful in applications other than writing instruments where a color change to a liquid is desired such as diagnostic tests or other types of indicators where a visual signal is needed to indicate that a chemical reaction has occurred.

EXAMPLES

With the above concepts in mind, disclosed inks will be described below by the way of the following examples which are not intended to be limiting but are intended for the purposes of illustration.

In Table II below, four exemplary high viscosity, moderate pH ball-pen inks are disclosed. The viscosities for the inks of Examples 1-4 are also sufficiently high so as to enable them to be used in ball-pens as their viscosities exceed 2 Kcp.

TABLE II

	Ex. 1	Ex. 2	Ex. 3	Ex. 4
Component				
Water (carrier/solvent)	15	15	15	15
Glycerol (carrier/solvent)	39.5	39.2	47.2	36.2
Dow 65 (defoamer)	0.5	0.5	0.5	0.5
75% Phosphoric Acid	0	0	7	3
Acid Blue 93 (dye)	30	30	30	30
Benzotriazole (corrosion inhibitor)	0	0.3	0.3	0.
Totals	100	100	100	100
Physical Properties				
CarrieMed visc. (2 cm/.25° plate)				
shear rate/ viscosity (cp)	132/5800	155/5500	140/1000	200/3600
" "	980/2485	1000/2400	1000/750	1000/2400
" "	4000/2050	4000/1950	4000/590	4000/2000
pH	2.63	2.54	2.01	2.03

The following Table III discloses ball-pen ink Examples 5-9.

TABLE III

	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
Component					
Water	19.2	0	18.5	14	15
Glycerol	45	0	42.7	35.2	44.2
Dow 65	0.5	0	0.5	0.5	0.5
75% Phosphoric Acid	5	0	4.75	5	0
Citric Acid	0	5	4.75	15	10
Example 5	0	95	0	0	0
Acid Blue 93 Dye	30	0	28.5	30	30
Benzotriazole	0.3	0	0.3	0.3	0.3
Totals	100	100	100	100	100
Physical Properties					
CarrieMed visc (2 cm/0.25° plate)					
shear rate/ viscosity (cp)	400/400	480/800	412/260	426/2752	267/1070
" "	900/315	1068/535	1014/262	1028/2642	1027/833
" "	4000/245	4071/464	2790/225	4023/2182	1881/806

Referring to Tables II and III, it will be noted that all Examples have a relatively low water content, preferably ranging from about 10 to about 20%. The low water content reduces the cost of the disclosed inks as an additional resin thickener for viscosity purposes is not required. Substantial viscosity is provided by the relatively high glycerol content which is preferably provided in an amount at least as great as the water content and, more preferably, in a ratio of glycerol:water ranging from about 1:1 to 3:1 or greater than 3:1. A glycerol:water ratio substantially exceeding a ratio of 3:1 and approaching 4:1 would provide a viscosity in excess of that required (ball-pen inks generally require a viscosity ranging from about 2 Kcp to about 5 Kcp) and would limit the solubility of the eradicable dye.

The eradicable dye can be present in an amount greater than 20% with about 30 wt% being the preferred eradicable dye content. All of the eradicable dye is not "in solution" in these disclosed inks. Rather, a portion of the eradicable dye is in solution and the remaining portions of the eradicable dye are "in suspension." The high dye content also contributes to the relatively high viscosity required for such ball pen inks.

While the Examples disclose the use of citric acid and phosphoric acid, a number of different acids can be utilized. Specifically, both organic or mineral acids, are applicable in this application. The acids can be monobasic, di-basic, tri-basic, tetra-basic, and so on. The primary acid can also contain substituents as well as unsaturation in the substituents.

Examples of monobasic organic acids include, but are not limited to, benzoic acid, lactic acid, acetic acid, propanoic acid, acetoacetic acid, crotonic acid, formic acid, glycerlic acid, glycollic acid, glyoxylic acid, lactic acid, pyruvic acid, and so on. Examples of dibasic organic acids include, but are not limited to, trans-aconitic acid, fumaric acid, maleic acid, malic acid, tartaric acid, acetylenedicarboxylic acid, tetrahydrophthalic acid, mesaconic acid, phthalic acid, isophthalic acid, terephthalic acid, Itaconic acid, trans-ethyleneoxidedicarboxylic acid, succinic acid, adipic acid, pimellic acid, suberic acid and azelic acid.

Examples of tribasic organic acids include, but are not limited to, substituted phosphoric acid, substituted phosphorous, citric acid, hemimellitic acid, trimellitic, trimesic acid, 2-carboxyethyliminodiacetic acid and nitrilotriacetic acid.

Examples of tetra-basic organic acids include, but are not limited to, phosphonic acid and its various substituted forms, mellophanic acid, prehnitic acid, pyromellitic acid, 2-phosphonoethyliminodiacetic acid, diethylenetetraacetic acids and its other forms.

Acids with higher basicity (five and beyond) are theoretically feasible for this application, but their effectiveness will be greatly dependent on solubility.

Mineral acids can also be used. Monobasic mineral acids include, but are not limited to, hydrochloric acid, hydrobromic acid, hydroiodic acid, hydrofluoric acid, nitric acid, and so on. Dibasic mineral acids include, but are not limited to, sulfuric acid, carbonic acid, chromic acid and so on. Tribasic mineral acids include, but are not limited to, phosphoric acid, phosphorous acid and so on. Tetrabasic mineral acids include, but are not limited to, phosphonic acid.

Benzotriazole is a corrosion inhibitor which is preferably used to protect the ball-pen tip using the disclosed inks even though their acidity is moderate (pH ranging from 2 to 3). Dow 65 is a defoamer commonly used in the ink industry.

The viscosity measurements set forth in Tables II and III are carried out on a CarrieMed Rheometer utilizing a 2 cm 0.25° plate. The viscosities where measured at varying shear rates ranging from 132 to a maximum of 4,000. The measured viscosity

at the differing shear rates shown range from greater than 0.2 Kcp to almost 6 Kcp. Examples 1, 2, 4 and 8 are preferred embodiments due to their satisfactory viscosities as shown in Tables II and III.

Additional components include one or more glycols such as ethylene glycol and/or propylene glycol and a non-resinous thickener such as a gum (e.g. xanthan gum or PVP as a thickening or coating additive).

Thus, applicant has surprisingly found that an organic solvent-free, resin-free ball-pen ink can be produced that is both eradicable and that can be used as a re-write ink. The moderate pH enables a minimal amount of corrosion inhibiting materials to be used without damaging the structure of a ball-pen dispensing tip. Manipulation of the eradicable dye is not required and therefore the inks are easy to prepare using conventional batch mixing equipment.

The foregoing description is given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, as modifications within the scope of the invention may be apparent to those having ordinary skill in the art. Throughout the specification, where compositions are described as including components or materials, it is contemplated that the compositions can also consist essentially of, or consists of, any combination of the recited components or materials, unless stated otherwise.

What is Claimed is:

1. An eradicable ball pen ink comprising:

water,

a polyol,

an acid,

an eradicable dye,

wherein the ink is free of non-polar organic solvents and has a ratio of polyol to water that is greater than 1.

2. The ink of claim 1 wherein the polyol is selected from the group consisting of glycerol, one or more glycols, one or more glymes or glycol diethers, glycol ethers, glycol acetates and mixtures thereof.

3. The ink of claim 1 wherein the polyol is glycerol.

4. The ink of claim 1 wherein the polyol is a mixture of glycerol and one or more glycols.

5. The ink of claim 1 wherein the ink has a pH of less than 3.

6. The ink of claim 1 wherein the ink has a viscosity of greater than 2 Kcp and a pH of than about 3.

7. The ink of claim 1 wherein the ink has a viscosity ranging from about 2 Kcp to about 6 Kcp and a pH ranging from about 2 to about 3.

8. The ink of claim 1 wherein the eradicable dye is selected from the group consisting of Auramine O, Basic Yellow 2, Basic Yellow 11, Basic Yellow 13, Basic Yellow 21, Basic Yellow 28, Basic Yellow 29, Basic Yellow 40, Basic Yellow 49, Acid Blue 22, Acid Blue 83, Acid Blue 93, Acid Fuchsin, Acid Green 3, Acid Green 5, Acid Green 9, Acid Magenta, Acid Orange 10, Acid Roseine, Acid Rubin, Acid Violet 17, Acid Violet 19, Acid Violet 49, Alizarol Cyanin R, Aluminon, Aniline Blue Ws, Basic Blue 8, Basic Blue 15, Basic Blue 20, Basic Blue 26, Basic Fuchsin, Basic Green 4, Basic Orange 21, Basic Red 9, Basic Red 14, Basic Red 15,

Basic Red 29, Basic Red 46, Basic Violet 2, Basic Violet 3, Basic Violet 4, Basic Violet 14, Chrome Violet Cg, Chromoxane Cyanin R, Cotton Blue, Crystal Violet, Dahlia, Diamond Green B, Eriochrome Cyanin R, Ethyl Green, Ethyl Violet, Fast Green Fcf, Food Green 3, Gentian Violet, Helvetia Blue, Hoffman's Violet, Light Green, Lissamine Green Sf, Magenta 0, Magenta I, Magenta Ii, Magenta Iii, Malachite Green, Methyl Blue, Methyl Green, Methyl Violet, Methyl Violet 2b, Methyl Violet 10b, Mordant Blue 3, Mordant Violet 39, New Fuchsin, Night Blue, Pararosanilin, Primula, Rosanilin, Solochrome Cyanin R, Victoria Blue 4r, Victoria Blue B, Victoria Green B, Water Blue I, and combinations thereof.

9. The ink of claim 1 wherein the eradicable dye is present in an amount greater than 20 wt%.

10. The ink of claim 1 wherein the acid is selected from the group consisting of citric acid, phosphoric acid, benzoic acid, lactic acid, acetic acid, propanoic acid, acetoacetic acid, crotonic acid, formic acid, glycerlic acid, glycollic acid, glyoxylic acid, lactic acid, pyruvic acid, trans-aconitic acid, fumaric acid, maleic acid, malic acid, tartaric acid, acetylenedicarboxylic acid, tetrahydrophthalic acid, mesaconic acid, phthalic acid, isophthalic acid, terephthalic acid, itaconic acid, trans-ethyleneoxidedicarboxylic acid, succinic acid, adipic acid, pimellic acid, suberic acid, azelic acid, substituted phosphoric acid, citric acid, hemimellitic acid, trimellitic, trimesic acid, 2-carboxyethyliminodiacetic acid, nitrilotriacetic acid, phosphonic acid, mellophanic acid, prehnitic acid, pyromellitic acid, 2-phosphonoethyliminodiacetic acid, diethylenetetraacetic acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, hydrofluoric acid, nitric acid, sulfuric acid, carbonic acid, chromic acid, phosphorous acid, phosphonic acid and combinations thereof.

11. The ink of claim 1 wherein water is present in an amount ranging from about 10 to about 20 wt% and the glyercol is present in an amount ranging from about 30 to about 50 wt%.

12. The ink of claim 1 wherein a ratio of polyol to water is greater than 2:1.

13. The ink of claim 1 wherein the acid is present in an amount of less than 20 wt%.

14. The ink of claim 1 wherein the ink is free of resin.

15. The ink of claim 1 further comprising ethylene glycol or propylene glycol or a mixture of ethylene and propylene glycols.

16. The ink of claim 15 further comprising xanthan gum.

17. An eradicable ball pen ink comprising:
water,
a polyol,
an acid,
an eradicable dye,
wherein the ink is free of organic solvents and free of resins.

18. The ink of claim 17 wherein the polyol is are selected from the group consisting of glycerol, one or more glycols, one or more glymes or glycol diethers, glycol ethers, glycol acetates and mixtures thereof.

19. The ink of claim 17 wherein the polyol is glycerol.

20. The ink of claim 17 wherein the polyol is a mixture of glycerol and one or more glycols.

21. The ink of claim 17 wherein the glycerol is present in an amount greater than water.

22. The ink of claim 17 wherein the ink has a pH of less than 3.

23. The ink of claim 17 wherein the ink has a viscosity of greater than 2 Kcp and a pH of than about 3.

24. The ink of claim 17 wherein the ink has a viscosity ranging from about 2 Kcp to about 3 Kcp and a pH ranging from about 2 to about 3.

25. The ink of claim 17 wherein the dye is selected from the group consisting of Auramine O, Basic Yellow 2, Basic Yellow 11, Basic Yellow 13, Basic Yellow 21, Basic Yellow 28, Basic Yellow 29, Basic Yellow 40, Basic Yellow 49, Acid Blue 22, Acid Blue 83, Acid Blue 93, Acid Fuchsin, Acid Green 3, Acid Green 5, Acid Green 9, Acid Magenta, Acid Orange 10, Acid Roseine, Acid Rubin, Acid Violet 17, Acid Violet 19, Acid Violet 49, Alizarol Cyanin R, Aluminon, Aniline Blue Ws, Basic Blue 8, Basic Blue 15, Basic Blue 20, Basic Blue 26, Basic Fuchsin, Basic Green 4, Basic Orange 21, Basic Red 9, Basic Red 14, Basic Red 15, Basic Red 29, Basic Red 46, Basic Violet 2, Basic Violet 3, Basic Violet 4, Basic Violet 14, Chrome Violet Cg, Chromoxane Cyanin R, Cotton Blue, Crystal Violet, Dahlia, Diamond Green B, Eriochrome Cyanin R, Ethyl Green, Ethyl Violet, Fast Green Fcf, Food Green 3, Gentian Violet, Helvetia Blue, Hoffman's Violet, Light Green, Lissamine Green Sf, Magenta 0, Magenta I, Magenta Ii, Magenta Iii, Malachite Green, Methyl Blue, Methyl Green, Methyl Violet, Methyl Violet 2b, Methyl Violet 10b, Mordant Blue 3, Mordant Violet 39, New Fuchsin, Night Blue, Pararosanilin, Primula, Rosanilin, Solochrome Cyanin R, Victoria Blue 4r, Victoria Blue B, Victoria Green B, Water Blue I, and combinations thereof.

26. The ink of claim 17 where in the eradicable dye is present in an amount greater than 20 wt%.

27. The ink of claim 17 wherein the acid is selected from the group consisting of citric acid, phosphoric acid, benzoic acid, lactic acid, acetic acid, propanoic acid, acetoacetic acid, crotonic acid, formic acid, glycerlic acid, glycollic acid, glyoxylic acid, lactic acid, pyruvic acid, trans-aconitic acid, fumaric acid, maleic acid, malic acid, tartaric acid, acetylenedicarboxylic acid, tetrahydrophthalic acid, mesaconic acid, phthalic acid, isophthalic acid, terephthalic acid, itaconic acid, trans-ethyleneoxidedicarboxylic acid, succinic acid, adipic acid, pimellic acid, suberic acid, azelic acid, substituted phosphoric acid, citric acid, hemimellitic acid, trimellitic, trimesic acid, 2-carboxyethyliminodiacetic acid, nitrilotriacetic acid, phosphonic acid, mellophanic acid, prehnitic acid, pyromellitic acid, 2-

phosphonoethyliminodiacetic acid, diethylenetetraacetic acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, hydrofluoric acid, nitric acid, sulfuric acid, carbonic acid, chromic acid, phosphorous acid, phosphonic acid and combinations thereof.

28. The ink of claim 17 wherein water is present in an amount ranging from about 10 to about 20 wt% and the glyercol is present in an amount ranging from about 30 to about 50 wt%.

29. The ink of claim 17 wherein a ratio of glycerol to water is greater than 2:1.

30. The ink of claim 17 wherein the acid is present in an amount of less than 20 wt%.

31. The ink of claim 17 wherein the ink is free of resin.

32. The ink of claim 17 further comprising ethylene glycol or propylene glycol or a mixture of ethylene and propylene glycols.

33. The ink of claim 32 further comprising xanthan gum.

34. An eradicable ball pen ink comprising:
water,
a polyol,
an acid,
an eradicable dye in an amount greater than 20 wt%,
wherein the ink is free of organic solvents, is resin free and has a ratio of glycerol to water is greater than 2:1.

35. The ink of claim 34 wherein the ink has a pH of less than 3.

36. The ink of claim 34 wherein the ink has a viscosity of greater than 2 Kcp and a pH of than about 3.

37. The ink of claim 34 wherein the ink has a viscosity ranging from about 2 Kcp to about 6 Kcp and a pH ranging from about 2 to about 3.

38. The ink of claim 34 wherein the dye is selected from the group consisting of Auramine O, Basic Yellow 2, Basic Yellow 11, Basic Yellow 13, Basic Yellow 21, Basic Yellow 28, Basic Yellow 29, Basic Yellow 40, Basic Yellow 49, Acid Blue 22, Acid Blue 83, Acid Blue 93, Acid Fuchsin, Acid Green 3, Acid Green 5, Acid Green 9, Acid Magenta, Acid Orange 10, Acid Roseine, Acid Rubin, Acid Violet 17, Acid Violet 19, Acid Violet 49, Alizarol Cyanin R, Aluminon, Aniline Blue Ws, Basic Blue 8, Basic Blue 15, Basic Blue 20, Basic Blue 26, Basic Fuchsin, Basic Green 4, Basic Orange 21, Basic Red 9, Basic Red 14, Basic Red 15, Basic Red 29, Basic Red 46, Basic Violet 2, Basic Violet 3, Basic Violet 4, Basic Violet 14, Chrome Violet Cg, Chromoxane Cyanin R, Cotton Blue, Crystal Violet, Dahlia, Diamond Green B, Eriochrome Cyanin R, Ethyl Green, Ethyl Violet, Fast Green Fcf, Food Green 3, Gentian Violet, Helvetia Blue, Hoffman's Violet, Light Green, Lissamine Green Sf, Magenta 0, Magenta I, Magenta Ii, Magenta Iii, Malachite Green, Methyl Blue, Methyl Green, Methyl Violet, Methyl Violet 2b, Methyl Violet 10b, Mordant Blue 3, Mordant Violet 39, New Fuchsin, Night Blue, Pararosanilin, Primula, Rosanilin, Solochrome Cyanin R, Victoria Blue 4r, Victoria Blue B, Victoria Green B, Water Blue I, and combinations thereof.

39. The ink of claim 34 wherein the acid is selected from the group consisting of citric acid, phosphoric acid, benzoic acid, lactic acid, acetic acid, propanoic acid, acetoacetic acid, crotonic acid, formic acid, glycerlic acid, glycollic acid, glyoxylic acid, lactic acid, pyruvic acid, trans-aconitic acid, fumaric acid, maleic acid, malic acid, tartaric acid, acetylenedicarboxylic acid, tetrahydrophthalic acid, mesaconic acid, phthalic acid, isophthalic acid, terephthalic acid, itaconic acid, trans-ethyleneoxidedicarboxylic acid, succinic acid, adipic acid, pimellic acid, suberic acid, azelic acid, substituted phosphoric acid, citric acid, hemimellitic acid, trimellitic, trimesic acid, 2-carboxyethyliminodiacetic acid, nitrilotriacetic acid, phosphonic acid, mellophanic acid, prehnitic acid, pyromellitic acid, 2-phosphonoethyliminodiacetic acid, diethylenetetraacetic acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, hydrofluoric acid, nitric acid, sulfuric acid,

carbonic acid, chromic acid, phosphorous acid, phosphonic acid and combinations thereof.

40. The ink of claim 34 wherein water is present in an amount ranging from about 10 to about 20 wt% and the glyercol is present in an amount ranging from about 30 to about 50 wt%.

41. The ink of claim 34 wherein a ratio of glycerol to water is greater than 2:1.

42. The ink of claim 34 wherein the acid is present in an amount of less than 20 wt%.

43. The ink of claim 34 further comprising at least one glycol.

44. A tinted fluid comprising:
water,
a polyol,
an acid,
an eradicable dye,
wherein the fluid is free of non-polar organic solvents and has a ratio of polyol to water of greater than 1.

45. The fluid of claim 44 wherein the fluid has a pH of less than 3.

46. The fluid of claim 44 wherein the fluid has a viscosity of greater than 2 kep and a pH of less than 3.

47. The fluid of claim 37 wherein the eradicable dye is selected from the group consisting of Auramine O, Basic Yellow 2, Basic Yellow 11, Basic Yellow 13, Basic Yellow 21, Basic Yellow 28, Basic Yellow 29, Basic Yellow 40, Basic Yellow 49, Acid Blue 22, Acid Blue 83, Acid Blue 93, Acid Fuchsin, Acid Green 3, Acid Green 5, Acid Green 9, Acid Magenta, Acid Orange 10, Acid Roseine, Acid Rubin, Acid Violet 17, Acid Violet 19, Acid Violet 49, Alizarol Cyanin R,

Aluminon, Aniline Blue Ws, Basic Blue 8, Basic Blue 15, Basic Blue 20, Basic Blue 26, Basic Fuchsin, Basic Green 4, Basic Orange 21, Basic Red 9, Basic Red 14, Basic Red 15, Basic Red 29, Basic Red 46, Basic Violet 2, Basic Violet 3, Basic Violet 4, Basic Violet 14, Chrome Violet Cg, Chromoxane Cyanin R, Cotton Blue, Crystal Violet, Dahlia, Diamond Green B, Eriochrome Cyanin R, Ethyl Green, Ethyl Violet, Fast Green Fcf, Food Green 3, Gentian Violet, Helvetia Blue, Hoffman's Violet, Light Green, Lissamine Green Sf, Magenta 0, Magenta I, Magenta Ii, Magenta Iii, Malachite Green, Methyl Blue, Methyl Green, Methyl Violet, Methyl Violet 2b, Methyl Violet 10b, Mordant Blue 3, Mordant Violet 39, New Fuchsin, Night Blue, Pararosanilin, Primula, Rosanilin, Solochrome Cyanin R, Victoria Blue 4r, Victoria Blue B, Victoria Green B, Water Blue I, and combinations thereof.

48. The fluid of claim 44 wherein the acid is selected from the group consisting of citric acid, phosphoric acid, benzoic acid, lactic acid, acetic acid, propanoic acid, acetoacetic acid, crotonic acid, formic acid, glycerlic acid, glycollic acid, glyoxylic acid, lactic acid, pyruvic acid, trans-aconitic acid, fumaric acid, maleic acid, malic acid, tartaric acid, acetylenedicarboxylic acid, tetrahydrophthalic acid, mesaconic acid, phthalic acid, isophthalic acid, terephthalic acid, itaconic acid, trans-ethyleneoxidedicarboxylic acid, succinic acid, adipic acid, pimellic acid, suberic acid, azelic acid, substituted phosphoric acid, citric acid, hemimellitic acid, trimellitic, trimesic acid, 2-carboxyethyliminodiacetic acid, nitrilotriacetic acid, phosphonic acid, mellophanic acid, prehnitic acid, pyromellitic acid, 2-phosphonoethyliminodiacetic acid, diethylenetetraacetic acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, hydrofluoric acid, nitric acid, sulfuric acid, carbonic acid, chromic acid, phosphorous acid, phosphonic acid and combinations thereof.

INTERNATIONAL SEARCH REPORT

Ir tional Application No
PCT/US2005/024482

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D11/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 156 657 A (LIN, AN-CHUNG R) 29 May 1979 (1979-05-29) column 3; claim 9	1-48
X	EP 0 032 653 A (PELIKAN AKTIENGESELLSCHAFT) 29 July 1981 (1981-07-29) examples 2,3	1-48
A	US 5 916 357 A (WANG ET AL) 29 June 1999 (1999-06-29) claims 1-15; examples 1,2	1-48
A	DE 199 03 248 A1 (STS SCHREIBGERAETE TECHNIK SCHWARZWALD GMBH & CO. KG) 10 August 2000 (2000-08-10) page 3, lines 44-46; claims 1-10; example 1	1-48

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 September 2005	06/10/2005

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INTERNATIONAL SEARCH REPORT

nformation on patent family members

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PCT/US2005/024482

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