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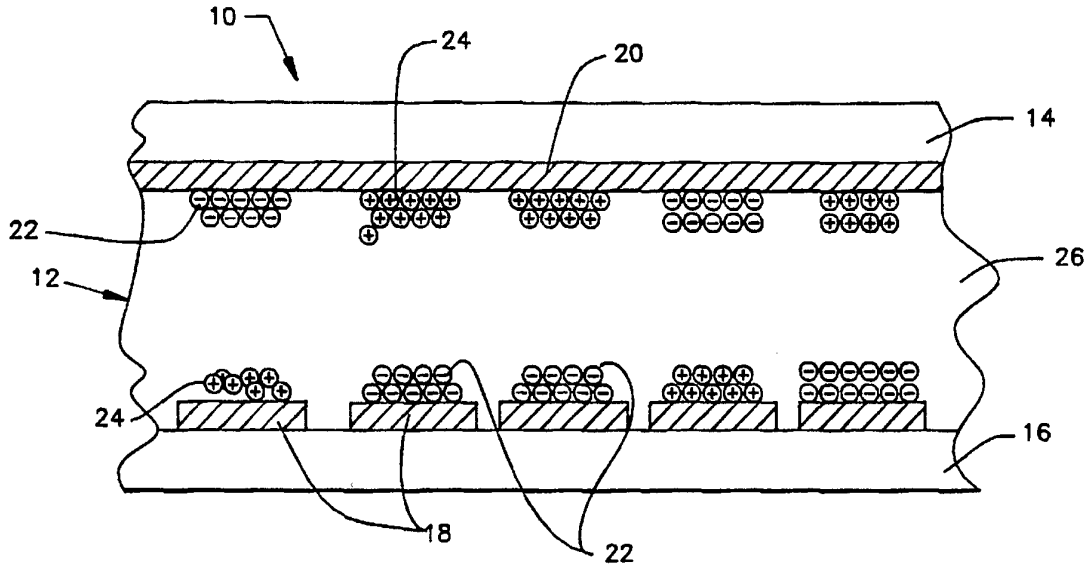

(57) Abstract

A dielectric dispersion (12) for use in an electrophoretic display (10) includes a dielectric fluid (26), a first plurality of particles of a first color (22) having a surface charge of a selected polarity dispersed within the dielectric fluid and a second plurality of particles of a second color (24) having a surface charge of opposite polarity to that of the first plurality and a steric repulsion thereto preventing coagulation of the first and second pluralities. In one embodiment, the first and second plurality of particles are each formed by separate two stage dispersion polymerization reactions. Each set of particles is formed with unique secondary and functional monomers. Corresponding charge control agents are added to the dispersion to establish opposite polarities on the respective particles.

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METHODS OF PREPARING ELECTROPHORETIC DISPERSIONS CONTAINING TWO TYPES OF PARTICLES WITH DIFFERENT COLORS AND OPPOSITE CHARGES

TECHNICAL FIELD OF THE INVENTION

The present invention relates to dielectric particles and electrophoretic dispersions containing them for use in electrophoretic image displays, electrostatic printing or the like, and a corresponding method of producing same. More particularly, the present invention relates to the formation of stable electrophoretic dispersions which contain two types of particles having different colors and opposite charges.

BACKGROUND ART

The electrophoretic effect is well known and the prior art is replete with a number of patents and articles which describe the effect. As will be recognized by a person skilled in the art, the electrophoretic effect operates on the principle that certain particles, when suspended in a medium, can be electrically charged and thereby to migrate through the medium to an electrode of opposite charge. Electrostatic printing and electrophoretic image displays (EPID) utilize the electrophoretic effect to produce desired images.

In prior art EPIDs, colored dielectric particles are suspended in a fluid medium of an optically contrasting color as compared to the dielectric particles. The colored electrophoretic particles are then selectively caused to migrate to, and impinge upon, a transparent screen, thereby displacing the fluid medium from the screen surface and creating the desired image. EPIDs commonly use readily manufactured light colored electrophoretic particles suspended in media which contains dark color dyes. Such EPIDs are exemplified in U.S. Patent Nos: 4,655,897 to DiSanto et al., 4,093,534 to Carter et al., 4,298,448 to Muller et al., and 4,285,801 to Chaing. The dark medium can not be completely displaced by the suspended particles because there is always some

dark liquid left on the screen or around the particle surface. The resulting images therefore suffer some loss of contrast.

An alternative way of creating contrasting images is to have a dispersion that contains both black and white dielectric particles having opposite charges. When an electric field is applied, the black and white particles are caused to migrate in opposite directions due to their opposite polarity. This creates the desired image with black and white contrast. Since the black and white dielectric particles have opposite charges, they will completely separate and migrate in opposite directions under the applied electric field, without leaving any black particles on the white image or any white particles on the black image. This produces highly contrasted black and white images. Ideally, the black and white dielectric particles must have optimum electrophoretic mobilities and be thermodynamically stable in the same medium in order to have reasonable imaging speed and to prevent flocculation due to the electrostatic attraction between the oppositely-charged particles.

In nature, as well as in industry, aggregation of oppositely-charged particles in dispersion has been shown in a large variety of fields such as soil conditioning, water purification, filtration and adhesion or aggregation of biological cells. Good examples are given in Colloids and Surface, 6, 83(1983); 6, 101(1983) and in Journal of Chemical Society Faraday, 76, 665(1980), in which the particles adsorption isotherms of small positively-charged polystyrene particles onto large negatively-charged polystyrene particles have been reported. In the prior art, it has proven difficult to produce an electrophoretic dispersion containing oppositely-charged particles without flocculation, particularly in non-aqueous systems. Theoretically, with the addition of a proper polymeric stabilizer, it is possible to stabilize two oppositely-charged particles in the same medium if the steric repulsion provided from the absorbed polymer layer can overcome the electrostatic attraction between the two oppositely-charged particles. However, very few surfactants have been found to be able to produce enough

steric repulsion to stabilize oppositely-charged particles without trading off their electrophoretic mobility. Accordingly, there is no known electrophoretic image display, which gives a highly contrasted black and white image.

DISCLOSURE OF THE INVENTION

The problems and disadvantages associated with conventional dielectric dispersions are overcome by the present invention which includes a dielectric fluid, a first plurality of particles of a first color having a surface charge of a selected polarity dispersed within the dielectric fluid and a second plurality of particles of a second color having a surface charge of opposite polarity to that of the first plurality and a steric repulsion thereto preventing coagulation of the first and second pluralities. A method in accordance with the present invention for making a dielectric dispersion includes providing a dielectric fluid; preparing a first plurality of particles of a first color and having a surface charge of a selected polarity; preparing a second plurality of particles of a second color having a surface charge of opposite polarity to that of the first plurality and a steric repulsion thereto preventing coagulation of said first and second pluralities; and dispersing the first plurality of particles and second plurality of particles in the dielectric fluid. A charge control agent is added to the dielectric fluid.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1, the sole figure, is a diagrammatic, cross-sectional view of an EPID having particles in accordance with a first embodiment of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

In the present invention, electrophoretic dispersions containing two types of particles having different colors e.g., black and white, and opposite

charges, which are thermodynamically stable, are produced by properly selecting certain surfactants which selectively charge the different types of particles positively and negatively, and also provide enough steric repulsion to prevent the flocculation of the oppositely-charged particles without trading off their electrophoretic mobilities.

Products in accordance with this invention can also be used in electrostatic printing for color images. In the prior art, conventional electrostatic printing produces color images by a multi-step printing process in which each step of printing only forms one color. Combinations of different color images from each single printing process, thereby, produce a desired color image. Since the formation of each color image needs to go through every single printing cycle, it usually takes a long time to produce a multi-colored image. In this invention, electrophoretic dispersions containing two different color particles with opposite charges are capable of producing two color images in one printing cycle resulting in energy and time saved.

Although the present invention's electrophoretic dispersions can be used in many different applications where dispersions containing different color particles with opposite charges are desired, such as paint, ink and electrostatic toner, it is especially suitable for use in connection with electrophoretic image displays (EPIDs). Accordingly, the present invention will be described in connection with a typical EPID.

Referring to Fig. 1, there is shown a cross sectional view of a segment of a simple electrophoretic image display 10 magnified to show a single pixel. As will be recognized by a person skilled in the art, an EPID may contain a volume of an electrophoretic dispersion 12 disposed between an anode 14 and a cathode 16. The anode 14 and cathode 16 are deposited upon glass plates 18, 20 in the form of a thin layer of indium-tin-oxide (ITO) or a like compound. The ITO layer is deposited in such a manner as to be substantially transparent when viewed through the glass plates 20, 18.

In accordance with an embodiment of the present invention, the electrophoretic dispersion 12 is comprised of white dielectric electrophoretic particles 22 suspended in a dark color medium 24. The electrophoretic particles 22 have a density substantially equivalent to that of the fluid medium 24 so as to remain randomly disperse.

Referring again to FIG. 1, in the embodiment shown, the electrophoretic dispersion 12 is comprised of black dielectric particles 22 and white dielectric particles 24 suspended in a clear medium 26. When a selected electrical bias is applied between a cathode line 14 and an anode line 16, the black dielectric particles 22 and white dielectric particles 24 separate and migrate in opposite directions to the cathode line 14 and anode line 16 due to the opposite polarity of the black and white particles, thereby creating an image with optical contrast between the black electrophoretic particles 22 and the white electrophoretic particles 24. The vertical dashed arrows 28 show the direction of motion.

As indicated above, the production of an electrophoretic dispersion containing two types of particles with different colors and opposite charges is highly desirable to produce black and white contrasting images. However, a major problem associated therewith is creating a thermodynamically stable electrophoretic dispersion with oppositely-charged particles. The present invention white electrophoretic particles 22 and black electrophoretic particles 24 may be formed from crosslinked polymer particles using a two stage dispersion polymerization technique with and without staining with a metal oxide, respectively. Since the surface functionalities of the electrophoretic particles can be well controlled during the polymerization, the black and white particles can be made with acidic and basic (or basic and acidic) surface characteristics, respectively and can be charged negatively and positively (or positively and negatively). In general, the polymeric materials are dielectric and have densities close to 1 g/cm^3, therefore the final electrophoretic particles are non-conductive

and can easily match the specific gravity of many suspension fluids. In addition, the electrophoretic particles are highly crosslinked polymer particles, which have excellent heat and solvent resistance. As a result, they can be used in a wide range of organic solvents and at high temperatures during cell sampling. In addition to the synthetic black and white polymeric particles, other light color inorganic or organic pigments such as titanium dioxide, zinc oxide, silica, Dairylide Yellow, perinone orange, Ultramarine Blue and the like, can also be used to form contrast images with the black synthetic polymer particles.

To form electrophoretic dispersions containing two types of particles with different colors and opposite charges, surfactants are selected to charge the two different types of particles positively and negatively and to provide a strong steric repulsion between the two oppositely-charged particles to form a thermodynamically stable dispersion. As will be recognized by a person skilled in the art, surface charging for a non-aqueous dispersion is dependent upon the surface functionality of the particles and the charge control agent selected. The surface functionality of particles can be controlled during the formation of particles or be modified after the formation of particles by chemical or physical means.

PROCESS ONE

In an exemplary embodiment of the present invention, the electrophoretic dispersion is made to contain both positively-charged black particles and negatively-charged white particles (or negatively-charged black particles and positively-charged white particles) in a dielectric medium. The black and white dielectric particles are each separately prepared by a two-stage dispersion polymerization technique. The polymerization recipes for producing the positively-charged and negatively-charged polymer particles are listed in Table I and Table II, respectively.

Table I

Materials	Weight (g)
Methanol	100
divinylbenzene	5
styrene	5
2,2'-azobisisobutyronitrile	0.5
poly(vinyl pyrrolidone)	2
Acrylamide	0.5

Table II

Materials	Weight (g)
Methanol	100
divinylbenzene	5
styrene	5
2,2'-azobisisobutyronitrile	0.5
poly(acrylic acid)	2
methacrylic acid	0.5

Although prepared separately, the oppositely charged dielectric particles are formed by essentially the same overall process. Namely, prior to use, the inhibitors of the monomer styrene and the crosslinker divinylbenzene are removed by washing with 10% NaOH aqueous solution several times, drying with calcium carbonate overnight at 0°C and then passing through a column containing an appropriate inhibitor remover. The inhibitor-free monomers and crosslinker are stored in a freezer for later use. In this, and subsequent processes, the styrene is of the type commercially available from Fisher Scientific, Inc. and the divinylbenzene is of the type commercially produced by Aldrich Chemical Co.

The initiator, 2,2-azobisisobutyronitrile (AIBN), is made by Kodak Co. and the stabilizers, poly(vinyl pyrrolidone) (PVP) and poly(acrylic acid), are made by GAF Co. and Aldrich Co. respectively. The second stage monomers, acrylamide and methacrylic acid, and the dispersion medium, methanol, are of the types commercially available from Fisher Scientific, Inc.

The styrene and divinylbenzene are mixed with methanol and charged to a closed container containing the initiator and stabilizer which are carefully weighed. The closed container is purged with nitrogen by bubbling through the solution for a certain time. The container is then warmed and agitated for a desired reaction time. In one preferred embodiment, the mixture is tumbled at thirty revolutions per minute for eight hours at sixty degrees celsius. After eight hours of tumbling, the second stage monomer, either methacrylic acid or acrylamide, is injected into the container which continues to tumble at the same reaction condition for another desired reaction time. The final product made by the two stage dispersion polymerization process is highly crosslinked poly(styrene-co-divinylbenzene) particles with polyacrylamide grafted on the surface in the case of acrylamide as the second stage monomer or, in this case of methacrylic acid, poly(methacrylic acid) is grafted on the surface. The final particles are uniform in size and vary from 0.2 to 2 μm depending upon the reaction media used, i.e. mixtures of methanol and xylene produce larger particles. The particle size being dependent upon the ratio of the mixed solvents. The final particles are dielectric with good whiteness and have densities close to 1 g/cm^3.

To form dark particles, one or the other of the polymer particles produced from the preceding process are separated from the dispersion medium by centrifuging and decanting the dispersion medium. They are then mixed and tumbled with a two weight percent osmium tetroxide aqueous solution at room temperature for a desired reaction time. The osmium tetroxide reacts with, and stains, the residual double bonds of the poly(styrene-co-divinylbenzene) particles, thereby resulting in highly crosslinked polymer particles having a desired degree of blackness, that can be used as the present invention black dielectric particles 22. It should be understood that in place and stead of the osmium tetroxide, ruthenium tetroxide or other metal oxides may also be used.

By varying the polymerization recipe of Table I and Table II and by varying other reaction parameters of the method of manufacture, the surface characteristics of the white and black particles produced can be selectively altered for particle charging. The surface functionality of the final particles can be varied by introducing different basic functional monomers, such as vinyl acetate, methyl methacrylate, acrylonitrile, N-(iso-butoxymethyl) acrylamide, dimethylaminopropylmethacrylamide, and the like, at the second stage polymerization to produce poly(styrene-co-divinylbenzene) particles with basic surface characteristics which are suitable for positive charging in dielectric media. Alternatively, by introducing different acidic functional monomers, such as acrylic acid, sodium styrene sulfonate, maleic acid, chlorostyrene, vinyl alcohol, and the like, at the second stage polymerization, poly(styrene-co-divinylbenzene) particles with acidic surface characteristics which are suitable for developing negatively-charged particles in dielectric media may be produced.

As will be recognized by a person skilled in the art, the other ingredients, such as the stabilizer, initiator, monomer, crosslinker, and the ratio of the monomer and the crosslinker in Table I and Table II can also be varied to effect other properties of the final particles, such as molecular weight and glass transition temperature for different applications.

As will be recognized by a person skilled in the art, highly crosslinked polymer particles having surfaces with controlled acidic moieties or basic moieties, made by emulsion polymerization, miniemulsion polymerization, microemulsion polymerization, suspension polymerization, precipitation, seeded emulsion polymerization or seeded dispersion polymerization, could be used as the white or as the black (after being stained with the metal oxide) electrophoretic particles.

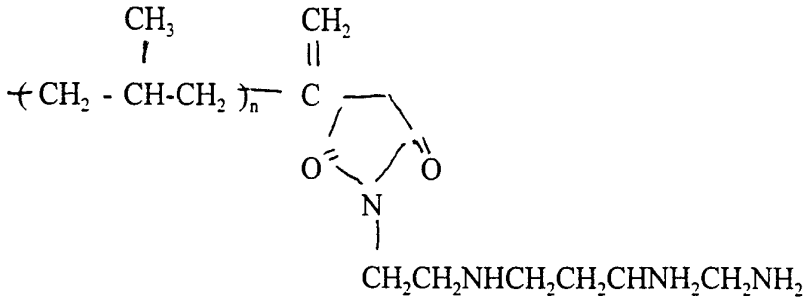
After the polymerization process, each of the final polymer particle products are transferred from their respective dispersion mediums to a desired dielectric medium by a washing process. This involves mixing the final product

with a solvent which is mutually soluble in both the dispersion medium and the desired dielectric medium, centrifuging the mixture to separate the particles and the liquids and decanting the supernatant to receive the concentrated particles. The washing process is repeated several times until the dispersion medium (methanol) is completely removed. The solvent washed particles are then redispersed in a dielectric medium with the addition of a desired charge control agent. The particles made from the Recipe I (Table I) exhibiting basic surface functionality, which can be charged positively by a positive charge control agent, can be used either as white positively-charged particles if not stained with a metal oxide, or as black positively-charged particles after being stained with a metal oxide. Similarly, the particles made from Recipe II (Table II) exhibiting acidic surface functionality, which can be charged negatively by a negative charge control agent, can be used as white negatively-charged particles if not stained with a metal oxide or as black negatively-charged particles after being stained with a metal oxide.

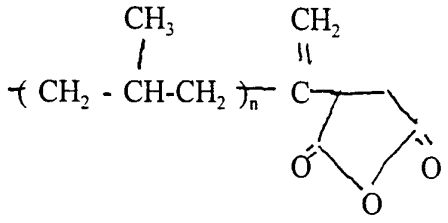
The preferred dielectric media for the final dispersion are non-polar solvents such as tetrachloroethylene, carbon tetrachloride, pentane, octane, decane, cyclohexane, benzene, xylene, sec-butylbenzene, Isopars, and the like, or a mixture of these liquids. The solvents used for washing the particles should be mutually soluble in both the dispersion medium and the dielectric medium. Examples are ethanol, propanol, butanol, acetone, tetrahydrofuran, ketones, ethers, esters, and the like.

The preferred surfactants in the present invention are functionalized polymeric (or oligomeric) compounds which not only function as charge control agents for particle charging but also function as steric stabilizers to prevent coagulation. In accordance with the present invention, the molecular weight of the surfactants ranges from a few thousand to hundreds of thousands. Simultaneously using two different surfactants having similar molecular weight and chemical structure but different end groups, is preferred. The surfactants

used for negative charging preferably have basic end groups; with the surfactants used for positive charging preferably having acidic end groups. Examples for negative and positive charging are polyisobutylene succinimide and polyisobutylene succinic anhydride, respectively. The chemical structure of these two surfactants are given below:



Polyisobutylene Succinimide



Polyisobutylene Succinic Anhydride

Alternatively, mixtures of charge control agents and steric stabilizers are also useful in producing a thermodynamically stable dispersion containing positively-charged and negatively-charged particles. The desirable charge control agents for positive charging are surfactants with acidic character such as cupric naphthenate, zirconium octoate, zinc octoate, calcium octoate, polyvinyl alcohol, polyacrylic acid, polymethacrylic acid, polyvinyl chloride, and the like. The desirable negative charge control agents, however, are surfactants with a basic character

such as barium petronate, barium sulfonate, barium dinolynphthalenesulfonate, metal oxides, polyvinyl pyridine, pyridine, lecithin, polyvinyl acetate, polyethylene oxide, polymethyl methacrylate, polyacrylamide, polyesters, polyethers, and the like. The preferred stabilizers or co-stabilizers used with the charge control agents are typically high molecular weight compounds including homopolymers, copolymers, graft polymers, block copolymer, natural high molecular weight compounds, and the like. Specific examples of suitable stabilizers are poly(12-hydroxystearic acid)-graft-poly(methyl methacrylate-methacrylic acid), polystyrene-co-poly(vinyl pyridine), poly(vinyl alcohol)-co-polyethylene, polyisobutylene-co-polyacrylic acid, polyisobutylene-co-polyamide, and the like.

After preparing the black and white electrophoretic dispersions individually, the positively-charged white dispersion is then mixed with the negatively-charged black dispersion or the positively-charged black dispersion is mixed with the negatively-charged white dispersion to form a thermodynamically stable electrophoretic dispersion containing both black and white dielectric particles with opposite charges. The mixed dispersion is gray in color, however, it forms a black and white contrasting image after applying an electric field in an electrophoretic image display.

As will be recognized by a person skilled in the art, the ratio of the black and white electrophoretic dispersions can be varied to produce a desired degree of black and white contrast in EPIDs.

PROCESS TWO

In the following description of alternative embodiments in Processes Two through Seven, the preferred dielectric media, solvents for washing the particles, surfactants, stabilizers, charge control agents, and co-stabilizers are the same as those described in Process One above unless otherwise

noted. In a second, alternative embodiment of the present invention, the black electrophoretic dispersions with positively-charged or negatively-charged particles made by Process One are mixed with a negatively-charged or positively-charged titanium dioxide dispersion to form an electrophoretic dispersion which is able to produce black and white contrasting images.

The titanium dioxide particles are either pre-treated with alumina to form a basic surface or pre-treated with silica to form an acidic surface, which can be positively charged with a positive charge control agent or be negatively charged with a negative charge control agent respectively, and mixed with the negatively-charged or positively-charged black dispersion to produce black and white contrasting images in EPIDs.

PROCESS THREE

In a third alternative embodiment of the present invention, electrophoretic dispersions containing positively-charged black particles and negatively-charged white particles or negatively-charged black particles and positively-charged white particles are made to produce black and white contrasting images in EPIDs.

The black electrophoretic dispersions with positively-charged or negatively-charged particles are made by Process One and the white electrophoretic dispersions are mixtures of the white electrophoretic dispersions made by Process One and titanium dioxide dispersions.

As in Process Two, the titanium dioxide particles are either pre-treated with alumina to form a basic surface or pre-treated with silica to form an acidic surface, which can be positively charged with a positive charge control agent or be negatively charged with a negative charge control agent respectively. The particles are then mixed with the positively or negatively-charged white dispersion made by the Process One yielding a fluid which produces black and white contrasting images in EPIDs.

PROCESS FOUR

In a fourth alternative embodiment of the present invention, the black electrophoretic dispersions with positively-charged or negatively-charged particles made by Process One are mixed with a yellow electrophoretic dispersion to form an electrophoretic dispersion which is able to produce black and yellow contrasting images.

The yellow particles are either organic or inorganic pigments such as Dairylide Yellow, Hansa Yellow, Benzidine Yellow and the like. The yellow pigments can be modified to produce a basic or acidic surface, which can be positively charged with a positive charge control agent or be negatively charged with a negative charge control agent respectively, and mixed with the negatively-charged or positively charged black dispersion to produce black and yellow contrasting images in EPIDs.

PROCESS FIVE

In a fifth alternative embodiment of the present invention, the black electrophoretic dispersions with positively-charged or negatively-charged particles made by Process One are mixed with a light-color electrophoretic dispersion to form an electrophoretic dispersion which is able to produce black and light color contrasting images.

The light-color particles are either organic or inorganic pigments such as titanium dioxide, zinc oxide, silica, zinc sulfide, calcium silicate, alumina hydrate, Dairylide Yellow, Arylide Yellow, Diarylide Orange, Perinone Orange, Ultramarine Blue and the like. The light color pigments are further modified to produce a basic surface or acidic surface, which can be positively charged with a positive charge control agent or be negatively charged with a negative charge control agent respectively, and mixed with the negatively-charged or positively charged black dispersion to produce black and yellow contrasting images in EPIDs.

As will be recognized by a person skilled in the art, the ratio of the black and light-colored electrophoretic dispersions can be varied to produce a desired degree of black and light-color contrast in EPIDs.

PROCESS SIX

In a sixth alternative embodiment of the present invention, the black electrophoretic dispersions with positively-charged or negatively-charged particles made by Process One are mixed with a mixture of light-color electrophoretic dispersions to form an electrophoretic dispersion which is able to produce black and a desired color contrasting images.

The light-color particles are either organic or inorganic pigments such as the white polymeric particles made the Process One, Titanium dioxide, zinc oxide, silica, zinc sulfide, calcium silicate, alumina hydrate, Dairylide Yellow, Arylide Yellow, Diarylide Orange, Perinone Orange, Ultramarine Blue and the like. The light color pigments are be further modified to same surface characters and mixed together, which can be positively charged with a positive charge control agent or be negatively charged with a negative charge control agent respectively, and mixed with the negatively-charged or positively-charged black dispersion to produce black and a desired color contrasting images in EPIDs.

PROCESS SEVEN

In a seventh alternative embodiment of the present invention, a dark color electrophoretic dispersion with positively-charged or negatively-charged particles is mixed with a mixture of light-color electrophoretic dispersion to form an electrophoretic dispersion which is able to produce dark and desired color contrasting images.

The dark-color particles are either organic or inorganic pigments such as carbon black, iron oxide black, lamp black, Zn Fe Cr brown Spinel,

Magnesium Ferrite, Chreen Spinel, Cr oxide Green, Indanthrone Blue, Ultramarine Blue Dioxazine Violet, Quinacridone Violet, Anthraquinoid Red, Perylene Red and the like. The light-colored particles are either organic or inorganic pigments such as the white polymeric particles made by Process One, titanium dioxide, zinc oxide, silica, zinc sulfide, calcium silicate, alumina hydrate, Dairylide Yellow, Arylide Yellow, Diarylide Orange, Perinone Orange and the like. The light-color pigments are further modified to same surface characters and mixed together, which can be positively charged with a positive charge control agent or be negatively charged with a negative charge control agent respectively, and mixed with the negatively-charged or positively charged dark-color dispersion to produce a desired color contrasting images in EPIDs.

As will be recognized by a person skilled in the art, the ratio of the dark-color and light-color electrophoretic dispersions can be varied to produce a desired degree of dark-color and light-color contrast in EPIDs.

All equivalents, variations and modifications that can be applied to the described present invention by a person skilled in the art, are intended to be included within the scope of this invention as defined by the appended claims.

CLAIMS:

1. A dielectric dispersion, comprising:

(a) a dielectric fluid;

(b) a first plurality of particles of a first color having a surface charge of a selected polarity dispersed within said dielectric fluid; and

(c) a second plurality of particles of a second color having a surface charge of opposite polarity to that of said first plurality and a steric repulsion thereto preventing coagulation of said first and second pluralities.

2. The dispersion of Claim 1, further including therein a charge control agent functioning as a steric stabilizer to prevent coagulation of said first and second pluralities.

3. The dispersion of Claim 2, wherein said first and second plurality of particles have basic and acidic surface functionalities, respectively.

4. The dispersion of Claim 3, wherein said charge control agent is a mixture of a pair of charge control agents, a first charging one of said two pluralities of particles positive and a second charging the other said plurality of particles negative.

5. The dispersion of Claim 4, wherein said pair of charge control agents are each of comparable molecular weight and structure but have differing end groups.

6. The dispersion of Claim 5, wherein said first charge control agent is selected from the group consisting of polyisobutylene succinimide, barium petronate, barium sulfonate, barium dinonylnaphthalensulfonate, metal oxides, polyvinyl pyridine, pyridine, lecithin, polyvinyl acetate, polyethelene oxide, polymethyl methacrylate, polyacrylamide, polyesters and polyethers.

7. The dispersion of Claim 6, wherein said second charge control agent is selected from the group consisting of polyisobutylene succinic anhydride, cupric napthenate, zirconium octoate, zinc octoate, calcium octoate, polyvinyl alcohol, polyacrylic acid, polymethacrylic acid, and polyvinyl chloride.

8. The dispersion of Claim 7, wherein one of said two pluralities of particles is dark colored, the other said plurality of particles is light colored and said dielectric fluid is clear.

9. The dispersion of Claim 8, wherein at least one of said two pluralities of particles are [poly(styrene-co-divinylbenzene)] polymer particles with an outer layer of a different polymer grafted onto the surface thereof.

10. The dispersion of Claim 9, wherein both said first and second pluralities of particles are [poly(styrene-co-divinylbenzene)] polymer particles with an outer layer of a different polymer grafted onto the surface thereof.

11. The dispersion of Claim 10, wherein one of said two pluralities of particles is dyed black by exposure to a metal oxide.

12. The dispersion of Claim 11, further including a third plurality of titanium dioxide particles.

13. The dispersion of Claim 12, wherein said titanium dioxide particles are pre-treated with alumina to form a basic surface thereon for positive surface charging.

14. The dispersion of Claim 13, wherein said first plurality of polymer particles are poly(styrene-co-divinylbenzene) particles with an outer layer of poly(methacrylic acid) grafted onto the surface thereof, said first plurality of particles being dyed black, and said second plurality of poly(styrene-co-divinylbenzene) particles have an outer layer of polyacrylamide grafted onto the surface thereof.

15. The dispersion of Claim 12, wherein said titanium dioxide particles are pre-treated with silica to form an acidic surface thereon for negative surface charging.

16. The dispersion of Claim 15, wherein said first plurality of poly(styrene-co-divinylbenzene) particles have an outer layer of polyacrylamide grafted onto the surface thereof, said first plurality of particles being dyed black, and said second plurality of poly(styrene-co-divinylbenzene) particles have an outer layer of poly(methacrylic acid) grafted onto the surface thereof.

17. The dispersion of Claim 9, wherein said first plurality of particles are polymer particles with an outer layer of a different polymer grafted onto the surface thereof and dyed by exposure to a metal oxide and said second plurality of particles are titanium dioxide particles.

18. The dispersion of Claim 17, wherein said titanium dioxide particles are pre-treated with alumina to form a basic surface thereon for positive surface charging.

19. The dispersion of Claim 18, wherein said first plurality of particles are poly(styrene-co-divinylbenzene) particles with poly(methacrylic acid) grafted on the surface thereof and are charged negative.

20. The dispersion of Claim 17, wherein said titanium dioxide particles are pre-treated with silica to form an acidic surface thereon for negative surface charging.

21. The dispersion of Claim 20, wherein said first plurality of particles are poly(styrene-co-divinylbenzene) particles with polyacrylamide grafted on the surface thereof and are charged positive.

22. The dispersion of Claim 9, wherein said first plurality of particles are polymer particles with an outer layer of a different polymer grafted onto the surface thereof and dyed by exposure to a metal oxide and said second plurality

of particles are yellow pigments selected from the group consisting of dairylide yellow, hansa yellow and benzidine yellow.

23. The dispersion of Claim 9, wherein said first plurality of particles are polymer particles with an outer layer of a different polymer grafted onto the surface thereof and dyed by exposure to a metal oxide and said second plurality of particles are light colored pigments selected from the group consisting of titanium dioxide, zinc oxide, silica, zinc sulfide, calcium silicate, alumina hydrate, dairylide yellow, arylide yellow, diarylide orange, perinone orange and ultramarine blue.

24. The dispersion of Claim 8, wherein said dark colored particles are selected from the group consisting of carbon black, iron oxide black, lamp black, ZnFeCr brown spinel, magnesium ferrite, chreen spinel, Cr oxide green, indanthrone blue, ultramarine blue, dioxazine violet, quinacridone violet, anthraquinoid red and perylene red and said light colored particles are selected from the group consisting of poly(styrene-co-divinylbenzene)/polyacrylamide, poly(styrene-co-divinylbenzene)/poly(methacrylic acid), titanium dioxide, zinc oxide, silica, zinc sulfide, calcium silicate, alumina hydrate, dairylide yellow, arylide yellow, diarylide orange and perinone orange.

25. The dispersion of Claim 7, wherein said first and second charge control agents are surfactants.

26. The dispersion of Claim 25, wherein said first charge control agent charges said second plurality of particles negative and said second charge control agent charges said first plurality of particles positive.

27. The dispersion of Claim 4, further including a stabilizer selected from the group consisting of homopolymers, copolymers, graft polymers and block copolymers.

28. The dispersion of Claim 4, wherein said dielectric fluid is selected from the group consisting of tetrachloroethylene, carbon tetrachloride, pentane, octane, decane, cyclohexane, benzene, xylene, sec-butylbenzene and Isopars.

29. A method for making a dielectric dispersion, comprising:

(a) providing a dielectric fluid;

(b) preparing a first plurality of particles of a first color and having a surface charge of a selected polarity;

(c) preparing a second plurality of particles of a second color having a surface charge of opposite polarity to that of said first plurality and a steric repulsion thereto preventing coagulation of said first and second pluralities;

(d) dispersing said first plurality of particles in said dielectric fluid; and

(e) dispersing said second plurality of particles in said dielectric fluid.

30. The method of Claim 29, further including the step of adding a charge control agent to said dielectric fluid and wherein said step of preparing said first plurality of particles includes

providing a dispersion medium;

admixing a first monomer and a crosslinker with said liquid dispersion medium forming a first mixture;

preparing a second mixture of an initiator and a stabilizer;

adding said first mixture to said second mixture to form a third mixture; and

allowing said first monomer to polymerize within said third mixture to form polymer particles, and

introducing a second monomer to said third mixture, said second monomer at least partially polymerizing and grafting upon said polymer particles; and

(d) introducing a functional monomer when said second monomer is introduced to control the surface functionality of said particles.

31. The method of Claim 30, wherein said first monomer is selected from the group consisting of styrene, methyl methacrylate, vinyl acetate, acrylate, ethyl vinylbenzene, vinylpyridine, and acrylonitrile, wherein said crosslinker is selected from the group consisting of nonconjugated divinyl compounds, diacrylate compounds, triacrylate compounds, dimethacrylate compounds and trimethacrylate compounds, wherein said initiator is selected from the group consisting of 2,2'-azobisisobutyronitrile, 4,4'-azobis(r-cyanopentanic acid), 2,2'-azobis(2-methylbutyronitrile), benzoyl peroxide, lauroyl peroxide and octanoyl peroxide, and wherein said stabilizer is selected from the group consisting of poly(vinyl pyrrolidone), homopolymers, copolymers, graft polymers, block polymers, poly(acrylic acid), poly(vinyl alcohol), poly(methacrylic acid) and sorbitan steric acid monoester.

32. The method of Claim 31, wherein said second monomer is acrylamide.

33. The method of Claim 32, wherein said functional monomer is selected from the group consisting of vinyl acetate, methyl methacrylate, acrylonitrile, N-(iso-utoxymethyl) acrylamide and

dimethylaminopropylmethacrylamide and produce dielectric particles with a basic surface suitable for positive charging.

34. The method of Claim 33, wherein said charge control agent is selected from the group consisting of polyisobutylene succinimide, barium petronate, barium sulfonate, barium dinonylnaphthalensulfonate, metal oxides, polyvinyl pyridine, pyridine, lecithin, polyvinyl acetate, polyethelene oxide, polymethyl methacrylate, polyacrylamide, polyesters and polyethers.

35. The method of Claim 34 wherein said step of preparing said second plurality of particles is by two stage dispersion polymerization yielding poly(styrene-co-divinylbenzene) with a layer of poly(methacrylic acid) grafted onto the surface thereof and modified by a functional monomer selected from the group consisting of acrylic acid, sodium styrene sulfonate, maleic acid, chlorostyrene and vinyl alcohol, producing dielectric particles with an acidic surface suitable for negative charging, wherein said charge control agent is a pair of charge control agents, including one selected from the group consisting of polyisobutylene succinic anhydride, cupric napthenate, zirconium octoate, zinc octoate, calcium octoate, polyvinyl alcohol, polyacrylic acid, polymethacrylic acid and polyvinyl chloride.

36. The method of Claim 35, wherein said first plurality of particles is dyed by exposure to a metal oxide prior to said step of dispersing.

37. The method of Claim 35, wherein said second plurality of particles is dyed by exposure to a metal oxide prior to said step of dispersing.

38. The method of Claim 31, wherein said step of preparing said second plurality of particles includes treating finely comminuted titanium dioxide particles with alumina to form a basic surface functionality thereon for positive charging.

39. The method of Claim 31, wherein said step of preparing said second plurality of particles includes treating finely comminuted titanium dioxide particles with silica to form an acidic surface functionality thereon for negative charging.

40. The method of Claim 31, wherein said step of preparing said second plurality of particles includes selecting a pigment from the group consisting of dairylide yellow, hansa yellow and benzidine yellow, zinc oxide, silica, zinc

sulfide, calcium silicate, alumina hydrate, arylide yellow, diarylide orange, perinone, orange and ultramarine blue.

41. The method of Claim 29, wherein said dielectric dispersion is suitable for use in an electrophoretic display and further including the step of filling the fluid envelope of an electrophoretic display with said dispersion.

AMENDED CLAIMS

[received by the international Bureau on 18 October 1994 (18.10.94);
original claims 1-2 and 29 amended;
remaining claims unchanged (12 pages)]

1. A dielectric dispersion, comprising:

(a) a dielectric fluid;

(b) a first plurality of particles of a first color having a surface charge of a selected polarity dispersed within said dielectric fluid; and

(c) a second plurality of particles of a second color which contrasts substantially with said first color, having a surface charge of opposite polarity to that of said first plurality of particles; and

(d) steric repulsion means for preventing coagulation of said first and second plurality of particles.

2. The dispersion of Claim 1, wherein said steric repulsion means comprises a charge control agent functioning as a steric stabilizer to prevent coagulation of said first and second plurality of particles.

3. The dispersion of Claim 2, wherein said first and second plurality of particles have basic and acidic surface functionalities, respectively.

4. The dispersion of Claim 3, wherein said charge control agent is a mixture of a pair of charge control agents, a first charging one of said two pluralities of particles positive and a second charging the other said plurality of particles negative.

5. The dispersion of Claim 4, wherein said pair of charge control agents are each of comparable molecular weight and structure but have differing end groups.

6. The dispersion of Claim 5, wherein said first charge control agent is selected from the group consisting of polyisobutylene succinimide, barium petronate, barium sulfonate, barium dinonylnaphthalensulfonate, metal oxides, polyvinyl pyridine, pyridine, lecithin, polyvinyl acetate, polyethelene oxide, polymethyl methacrylate, polyacrylamide, polyesters and polyethers.

7. The dispersion of Claim 6, wherein said second charge control agent is selected from the group consisting of polyisobutylene succinic anhydride, cupric napthenate, zirconium octoate, zinc octoate, calcium octoate, polyvinyl alcohol, polyacrylic acid, polymethacrylic acid, and polyvinyl chloride.

8. The dispersion of Claim 7, wherein one of said two pluralities of particles is dark colored, the other said plurality of particles is light colored and said dielectric fluid is clear.

9. The dispersion of Claim 8, wherein at least one of said two pluralities of particles are [poly(styrene-co-divinylbenzene)] polymer particles with an outer layer of a different polymer grafted onto the surface thereof.

10. The dispersion of Claim 9, wherein both said first and second pluralities of particles are [poly(styrene-co-divinylbenzene)] polymer particles with an outer layer of a different polymer grafted onto the surface thereof.

11. The dispersion of Claim 10, wherein one of said two pluralities of particles is dyed black by exposure to a metal oxide.

12. The dispersion of Claim 11, further including a third plurality of titanium dioxide particles.

13. The dispersion of Claim 12, wherein said titanium dioxide particles are pre-treated with alumina to form a basic surface thereon for positive surface charging.

14. The dispersion of Claim 13, wherein said first plurality of polymer particles are poly(styrene-co-divinylbenzene) particles with an outer layer of poly(methacrylic acid) grafted onto the surface thereof, said first plurality of particles being dyed black, and said second plurality of poly(styrene-co-divinylbenzene) particles have an outer layer of polyacrylamide grafted onto the surface thereof.

15. The dispersion of Claim 12, wherein said titanium dioxide particles are pre-treated with silica to form an acidic surface thereon for negative surface charging.

16. The dispersion of Claim 15, wherein said first plurality of poly(styrene-co-divinylbenzene) particles have an outer layer of polyacrylamide grafted onto the surface thereof, said first plurality of particles being dyed black, and said second plurality of poly(styrene-co-divinylbenzene) particles have an outer layer of poly(methacrylic acid) grafted onto the surface thereof.

17. The dispersion of Claim 9, wherein said first plurality of particles are polymer particles with an outer layer of a different polymer grafted onto the surface thereof and dyed by exposure to a metal oxide and said second plurality of particles are titanium dioxide particles.

18. The dispersion of Claim 17, wherein said titanium dioxide particles are pre-treated with alumina to form a basic surface thereon for positive surface charging.

19. The dispersion of Claim 18, wherein said first plurality of particles are poly(styrene-co-divinylbenzene) particles with poly(methacrylic acid) grafted on the surface thereof and are charged negative.

20. The dispersion of Claim 17, wherein said titanium dioxide particles are pre-treated with silica to form an acidic surface thereon for negative surface charging.

21. The dispersion of Claim 20, wherein said first plurality of particles are poly(styrene-co-divinylbenzene) particles with polyacrylamide grafted on the surface thereof and are charged positive.

22. The dispersion of Claim 9, wherein said first plurality of particles are polymer particles with an outer layer of a different polymer grafted onto the surface thereof and dyed by exposure to a metal oxide and said second plurality

of particles are yellow pigments selected from the group consisting of dairylide yellow, hansa yellow and benzidine yellow.

23. The dispersion of Claim 9, wherein said first plurality of particles are polymer particles with an outer layer of a different polymer grafted onto the surface thereof and dyed by exposure to a metal oxide and said second plurality of particles are light colored pigments selected from the group consisting of titanium dioxide, zinc oxide, silica, zinc sulfide, calcium silicate, alumina hydrate, dairylide yellow, arylide yellow, diarylide orange, perinone orange and ultramarine blue.

24. The dispersion of Claim 8, wherein said dark colored particles are selected from the group consisting of carbon black, iron oxide black, lamp black, ZnFeCr brown spinel, magnesium ferrite, chreen spinel, Cr oxide green, indanthrone blue, ultramarine blue, dioxazine violet, quinacridone violet, anthraquinoid red and perylene red and said light colored particles are selected from the group consisting of poly(styrene-co-divinylbenzene)/polyacrylamide, poly(styrene-co-divinylbenzene)/poly(methacrylic acid), titanium dioxide, zinc oxide, silica, zinc sulfide, calcium silicate, alumina hydrate, dairylide yellow, arylide yellow, diarylide orange and perinone orange.

25. The dispersion of Claim 7, wherein said first and second charge control agents are surfactants.

26. The dispersion of Claim 25, wherein said first charge control agent charges said second plurality of particles negative and said second charge control agent charges said first plurality of particles positive.

27. The dispersion of Claim 4, further including a stabilizer selected from the group consisting of homopolymers, copolymers, graft polymers and block copolymers.

28. The dispersion of Claim 4, wherein said dielectric fluid is selected from the group consisting of tetrachloroethylene, carbon tetrachloride, pentane, octane, decane, cyclohexane, benzene, xylene, sec-butylbenzene and Isopars.

29. A method for making a dielectric dispersion, comprising:

(a) providing a dielectric fluid;

(b) preparing a first plurality of particles of a first color and having a surface charge of a selected polarity;

(c) preparing a second plurality of particles of a second color having a surface charge of opposite polarity to that of said first plurality and steric repulsion means for preventing coagulation of said first and second plurality of particles;

(d) dispersing said first plurality of particles in said dielectric fluid; and

(e) dispersing said second plurality of particles in said dielectric fluid.

30. The method of Claim 29, further including the step of adding a charge control agent to said dielectric fluid and wherein said step of preparing said first plurality of particles includes

providing a dispersion medium;

admixing a first monomer and a crosslinker with said liquid dispersion medium forming a first mixture;

preparing a second mixture of an initiator and a stabilizer;

adding said first mixture to said second mixture to form a third mixture; and

allowing said first monomer to polymerize within said third mixture to form polymer particles, and

(d) introducing a functional monomer when said second monomer is introduced to control the surface functionality of said particles.

31. The method of Claim 30, wherein said first monomer is selected from the group consisting of styrene, methyl methacrylate, vinyl acetate, acrylate, ethyl vinylbenzene, vinylpyridine, and acrylonitrile, wherein said crosslinker is selected from the group consisting of nonconjugated divinyl compounds, diacrylate compounds, triacrylate compounds, dimethacrylate compounds and trimethacrylate compounds, wherein said initiator is selected from the group consisting of 2,2'-azobisisobutyronitrile, 4,4'-azobis(r-cyanopentanic acid), 2,2'-azobis(2-methylbutyronitrile), benzoyl peroxide, lauroyl peroxide and octanoyl peroxide, and wherein said stabilizer is selected from the group consisting of poly(vinyl pyrrolidone), homopolymers, copolymers, graft polymers, block polymers, poly(acrylic acid), poly(vinyl alcohol), poly(methacrylic acid) and sorbitan steric acid monoester.

32. The method of Claim 31, wherein said second monomer is acrylamide.

33. The method of Claim 32, wherein said functional monomer is selected from the group consisting of vinyl acetate, methyl methacrylate, acrylonitrile, N-(iso-utoxymethyl) acrylamide and

dimethylaminopropylmethacrylamide and produce dielectric particles with a basic surface suitable for positive charging.

34. The method of Claim 33, wherein said charge control agent is selected from the group consisting of polyisobutylene succinimide, barium petronate, barium sulfonate, barium dinonylnaphthalensulfonate, metal oxides, polyvinyl pyridine, pyridine, lecithin, polyvinyl acetate, polyethelene oxide, polymethyl methacrylate, polyacrylamide, polyesters and polyethers.

35. The method of Claim 34 wherein said step of preparing said second plurality of particles is by two stage dispersion polymerization yielding poly(styrene-co-divinylbenzene) with a layer of poly(methacrylic acid) grafted onto the surface thereof and modified by a functional monomer selected from the group consisting of acrylic acid, sodium styrene sulfonate, maleic acid, chlorostyrene and vinyl alcohol, producing dielectric particles with an acidic surface suitable for negative charging, wherein said charge control agent is a pair of charge control agents, including one selected from the group consisting of polyisobutylene succinic anhydride, cupric napthenate, zirconium octoate, zinc octoate, calcium octoate, polyvinyl alcohol, polyacrylic acid, polymethacrylic acid and polyvinyl chloride.

36. The method of Claim 35, wherein said first plurality of particles is dyed by exposure to a metal oxide prior to said step of dispersing.

37. The method of Claim 35, wherein said second plurality of particles is dyed by exposure to a metal oxide prior to said step of dispersing.

38. The method of Claim 31, wherein said step of preparing said second plurality of particles includes treating finely comminuted titanium dioxide particles with alumina to form a basic surface functionality thereon for positive charging.

39. The method of Claim 31, wherein said step of preparing said second plurality of particles includes treating finely comminuted titanium dioxide particles with silica to form an acidic surface functionality thereon for negative charging.

40. The method of Claim 31, wherein said step of preparing said second plurality of particles includes selecting a pigment from the group consisting of dairylide yellow, hansa yellow and benzidine yellow, zinc oxide, silica, zinc sulfide, calcium silicate, alumina hydrate, arylide yellow, diarylide orange, perinone, orange and ultramarine blue.

41. The method of Claim 29, wherein said dielectric dispersion is suitable for use in an electrophoretic display and further including the step of filling the fluid envelope of an electrophoretic display with said dispersion.

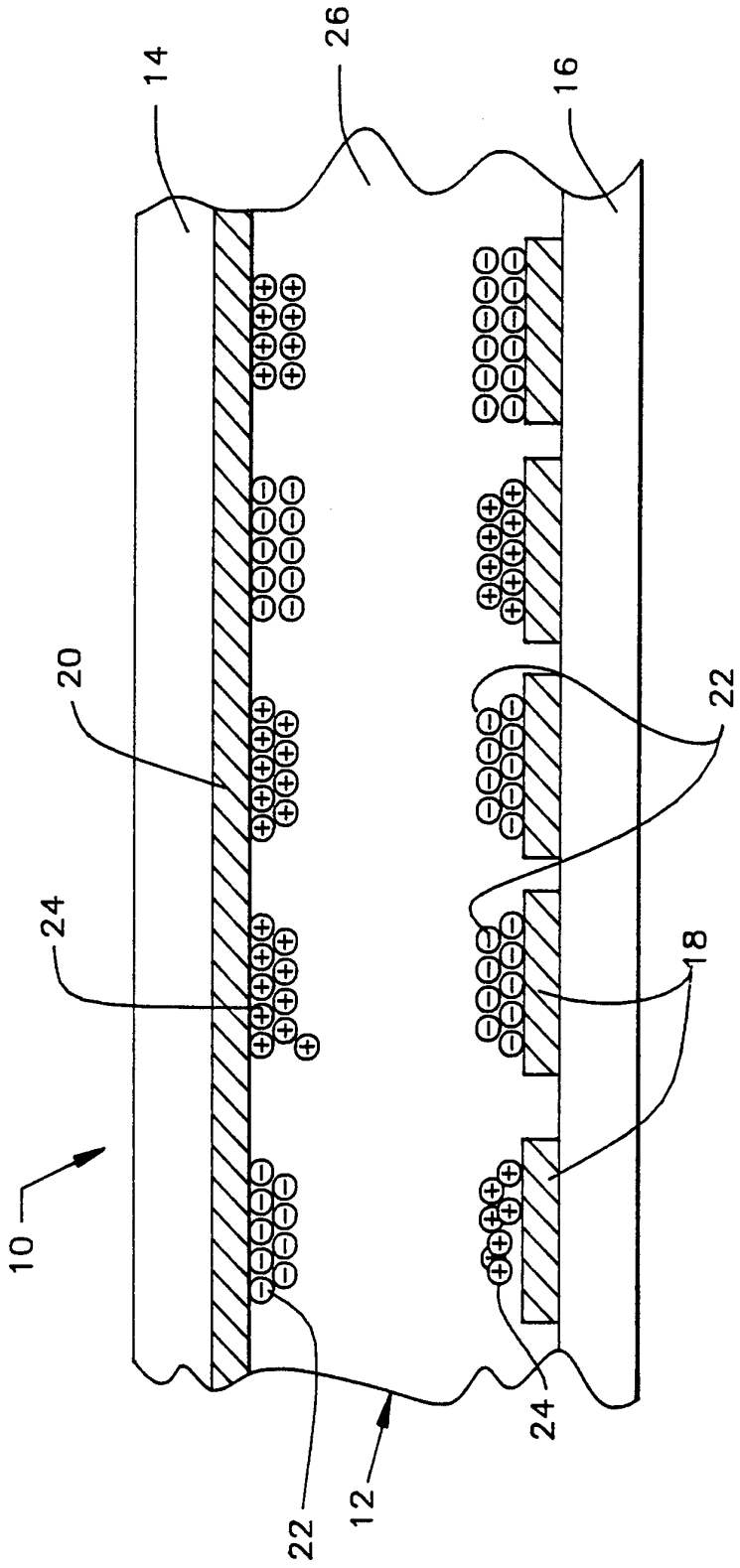


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/05594

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C25D 13/06, 13/08
US CL : 252/73, 77, 79, 572; 204/299R
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/73, 77, 79, 572; 204/299R

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

NONE

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

APC, CAS ONLINE
search terms: electrophoretic, color, colorant, pigment, styrene, divinylbenzene

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,992,192 (AHMED) 12 FEBRUARY 1991, col. 4, line 20 - col. 6, line 11.	1-41
Y	US, A, 3,484,162 (CLARK) 16 DECEMBER 1969, col. 2, lines 3-15.	1-41

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

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier document published on or after the international filing date	"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
"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)	"&"	document member of the same patent family
"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		

Date of the actual completion of the international search	Date of mailing of the international search report
09 AUGUST 1994	14 SEP 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer CHRISTINE SKANE Telephone No. (703) 308-0661

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