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(54) ELECTROPHORETIC MEDIUM FOR ELECTRO-OPTIC DISPLAYS

ELEKTROPHORETISCHES MEDIUM FÜR ELEKTRO-OPTISCHE BILDSCHIRME

MILIEU ÉLECTROPHORÉTIQUE POUR DES ECRANS PHOTO-OPTIQUES

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Description

[0001] The present invention relates to an electro-optic medium for use in electro-optic displays and to materials for use therein. More specifically, this invention relates to binders having controlled volume resistivity, and to electro-optic displays incorporating such materials. The present invention is especially intended for use in displays containing encapsulated electrophoretic media. Certain materials provided by the present invention may be useful in applications other than electro-optic displays.

[0002] Electro-optic displays comprise a layer of electro-optic material, a term which is used herein in its conventional meaning in the imaging art to refer to a material having first and second display states differing in at least one optical property, the material being changed from its first to its second display state by application of an electric field to the material. Although the optical property is typically color perceptible to the human eye, it may be another optical property, such as optical transmission, reflectance, luminescence or, in the case of displays intended for machine reading, pseudo-color in the sense of a change in reflectance of electromagnetic wavelengths outside the visible range.

[0003] In the present invention, the electro-optic medium will typically be a solid (such displays may hereinafter for convenience be referred to as "solid electro-optic displays"), in the sense that the electro-optic medium has solid external surfaces, although the medium may, and often does, have internal liquid- or gas-filled spaces. Thus, the term "solid electro-optic displays" includes encapsulated electrophoretic displays, encapsulated liquid crystal displays, and other types of displays discussed below.

[0004] The terms "bistable" and "bistability" are used herein in their conventional meaning in the art to refer to displays comprising display elements having first and second display states differing in at least one optical property, and such that after any given element has been driven, by means of an addressing pulse of finite duration, to assume either its first or second display state, after the addressing pulse has terminated, that state will persist for at least several times, for example at least four times, the minimum duration of the addressing pulse required to change the state of the display element. It is shown in published U.S. Patent Application No. 2002/0180687 that some particle-based electrophoretic displays capable of gray scale are stable not only in their extreme black and white states but also in their intermediate gray states, and the same is true of some other types of electro-optic displays. This type of display is properly called "multi-stable" rather than bistable, although for convenience the term "bistable" may be used herein to cover both bistable and multi-stable displays.

[0005] Several types of electro-optic displays are known. One type of electro-optic display is a rotating bichromal member type as described, for example, in U.S. Patents Nos. 5,808,783; 5,777,782; 5,760,761; 6,054,071 6,055,091; 6,097,531; 6,128,124; 6,137,467; and 6,147,791 (although this type of display is often referred to as a "rotating bichromal ball" display, the term "rotating bichromal member" is preferred as more accurate since in some of the patents mentioned above the rotating members are not spherical). Such a display uses a large number of small bodies (typically spherical or cylindrical) which have two or more sections with differing optical characteristics, and an internal dipole. These bodies are suspended within liquid-filled vacuoles within a matrix, the vacuoles being filled with liquid so that the bodies are free to rotate. The appearance of the display is changed to applying an electric field thereto, thus rotating the bodies to various positions and varying which of the sections of the bodies is seen through a viewing surface. This type of electro-optic medium is typically bistable.

[0006] Another type of electro-optic display uses an electrochromic medium, for example an electrochromic medium in the form of a nanochromic film comprising an electrode formed at least in part from a semi-conducting metal oxide and a plurality of dye molecules capable of reversible color change attached to the electrode; see, for example O'Regan, B., et al., Nature 1991, 353, 737; and Wood, D., Information Display, 18(3), 24 (March 2002). See also Bach, U., et al., Adv. Mater., 2002, 14(11), 845. Nanochromic films of this type are also described, for example, in U.S. Patent No. 6,301,038, International Application Publication No. WO 01/27690, and in U.S. Patent Application 2003/0214695. This type of medium is also typically bistable.

[0007] Another type of electro-optic display, which has been the subject of intense research and development for a number of years, is the particle-based electrophoretic display, in which a plurality of charged particles move through a suspending fluid under the influence of an electric field. Electrophoretic displays can have attributes of good brightness and contrast, wide viewing angles, state bistability, and low power consumption when compared with liquid crystal displays. Nevertheless, problems with the long-term image quality of these displays have prevented their widespread usage. For example, particles that make up electrophoretic displays tend to settle, resulting in inadequate service-life for these displays.

[0008] As noted above, electrophoretic media require the presence of a suspending fluid. In most prior art electrophoretic media, this suspending fluid is a liquid, but electrophoretic media can be produced using gaseous suspending fluids; see, for example, Kitamura, T., et al., "Electrical toner movement for electronic paper-like display", IDW Japan, 2001, Paper HCS1-1, and Yamaguchi, Y., et al., "Toner display using insulative particles charged triboelectrically", IDW Japan, 2001, Paper AMD4-4). See also European Patent Applications 1,429,178; 1,462,847; 1,482,354; and 1,484,625; and International Applications WO 2004/090626; WO 2004/079442; WO 2004/077140; WO 2004/059379; WO

2004/055586; WO 2004/008239; WO 2004/006006; WO 2004/001498; WO 03/091799; and WO 03/088495. Such gas-based electrophoretic media appear to be susceptible to the same types of problems due to particle settling as liquid-based electrophoretic media, when the media are used in an orientation which permits such settling, for example in a sign where the medium is disposed in a vertical plane. Indeed, particle settling appears to be a more serious problem in gas-based electrophoretic media than in liquid-based ones, since the lower viscosity of gaseous suspending fluids as compared with liquid ones allows more rapid settling of the electrophoretic particles.

[0009] Numerous patents and applications assigned to or in the names of the Massachusetts Institute of Technology (MIT) and E Ink Corporation have recently been published describing encapsulated electrophoretic media. Such encapsulated media comprise numerous small capsules, each of which itself comprises an internal phase containing electrophoretically-mobile particles suspended in a liquid suspending medium, and a capsule wall surrounding the internal phase. Typically, the capsules are themselves held within a polymeric binder to form a coherent layer positioned between two electrodes. Encapsulated media of this type are described, for example, in U.S. Patents Nos. 5,930,026; 5,961,804; 6,017,584; 6,067,185; 6,118,426; 6,120,588; 6,120,839; 6,124,851; 6,130,773; 6,130,774; 6,172,798; 6,177,921; 6,232,950; 6,249,721; 6,252,564; 6,262,706; 6,262,833; 6,300,932; 6,312,304; 6,312,971; 6,323,989; 6,327,072; 6,376,828; 6,377,387; 6,392,785; 6,392,786; 6,413,790; 6,422,687; 6,445,374; 6,445,489; 6,459,418; 6,473,072; 6,480,182; 6,498,114; 6,504,524; 6,506,438; 6,512,354; 6,515,649; 6,518,949; 6,521,489; 6,531,997; 6,535,197; 6,538,801; 6,545,291; 6,580,545; 6,639,578; 6,652,075; 6,657,772; 6,664,944; 6,680,725; 6,683,333; 6,704,133; 6,710,540; 6,721,083; 6,727,881; 6,738,050; 6,750,473; and 6,753,999; and U.S. Patent Applications Publication Nos. 2002/0019081; 2002/0021270; 2002/0060321; 2002/0060321; 2002/0063661; 2002/0090980; 2002/0113770; 2002/0130832; 2002/0131147; 2002/0171910; 2002/0180687; 2002/0180688; 2002/0185378; 2003/0011560; 2003/0020844; 2003/0025855; 2003/0038755; 2003/0053189; 2003/0102858; 2003/0132908; 2003/0137521; 2003/0137717; 2003/0151702; 2003/0214695; 2003/0214697; 2003/0222315; 2004/0008398; 2004/0012839; 2004/0014265; 2004/0027327; 2004/0075634; 2004/0094422; 2004/0105036; 2004/0112750; and 2004/0119681; and International Applications Publication Nos. WO 99/67678; WO 00/05704; WO 00/38000; WO 00/38001; WO00/36560; WO 00/67110; WO 00/67327; WO 01/07961; WO 01/08241; WO 03/107,315; WO 2004/023195; and WO 2004/049045.

[0010] Many of the aforementioned patents and applications recognize that the walls surrounding the discrete microcapsules in an encapsulated electrophoretic medium could be replaced by a continuous phase, thus producing a so-called polymer-dispersed electrophoretic display, in which the electrophoretic medium comprises a plurality of discrete droplets of an electrophoretic fluid and a continuous phase of a polymeric material, and that the discrete droplets of electrophoretic fluid within such a polymer-dispersed electrophoretic display may be regarded as capsules or microcapsules even though no discrete capsule membrane is associated with each individual droplet; see for example, the aforementioned 2002/0131147. Accordingly, for purposes of the present application, such polymer-dispersed electrophoretic media are regarded as subspecies of encapsulated electrophoretic media.

[0011] A related type of electrophoretic display is a so-called "microcell electrophoretic display". In a microcell electrophoretic display, the charged particles and the suspending fluid are not encapsulated within microcapsules but instead are retained within a plurality of cavities formed within a carrier medium, typically a polymeric film. See, for example, International Application Publication No. WO 02/01281, and published US Application No. 2002/0075556, both assigned to Sipix Imaging, Inc.

[0012] Although electrophoretic media are often opaque (since, for example, in many electrophoretic media, the particles substantially block transmission of visible light through the display) and operate in a reflective mode, many electrophoretic displays can be made to operate in a so-called "shutter mode" in which one display state is substantially opaque and one is light-transmissive. See, for example, the aforementioned U.S. Patents Nos. 6,130,774 and 6,172,798, and U.S. Patents Nos. 5,872,552; 6,144,361; 6,271,823; 6,225,971; and 6,184,856. Dielectrophoretic displays, which are similar to electrophoretic displays but rely upon variations in electric field strength, can operate in a similar mode; see U.S. Patent No. 4,418,346.

[0013] An encapsulated or microcell electrophoretic display typically does not suffer from the clustering and settling failure mode of traditional electrophoretic devices and provides further advantages, such as the ability to print or coat the display on a wide variety of flexible and rigid substrates. (Use of the word "printing" is intended to include all forms of printing and coating, including, but without limitation: pre-metered coatings such as patch die coating, slot or extrusion coating, slide or cascade coating, curtain coating; roll coating such as knife over roll coating, forward and reverse roll coating; gravure coating; dip coating; spray coating; meniscus coating; spin coating; brush coating; air knife coating; silk screen printing processes; electrostatic printing processes; thermal printing processes; ink jet printing processes; and other similar techniques.) Thus, the resulting display can be flexible. Further, because the display medium can be printed (using a variety of methods), the display itself can be made inexpensively.

[0014] In addition to the layer of electro-optic material, an electro-optic display normally comprises at least two other layers disposed on opposed sides of the electro-optic material, one of these two layers being an electrode layer. In most such displays both the layers are electrode layers, and one or both of the electrode layers are patterned to define the pixels of the display. For example, one electrode layer may be patterned into elongate row electrodes and the other into elongate column electrodes running at right angles to the row electrodes, the pixels being defined by the intersections of the row and column electrodes. Alternatively, and more commonly, one electrode layer has the form of a single continuous electrode and the other electrode layer is patterned into a matrix of pixel electrodes, each of which defines one pixel of the display. In another type of electro-optic display, which is intended for use with a stylus, print head or similar movable electrode separate from the display, only one of the layers adjacent the electro-optic layer comprises an electrode, the layer on the opposed side of the electro-optic layer typically being a protective layer intended to prevent the movable electrode damaging the electro-optic layer.

[0015] The manufacture of a three-layer electro-optic display normally involves at least one lamination operation. For example, in several of the aforementioned MIT and E Ink patents and applications, there is described a process for manufacturing an encapsulated electrophoretic display in which an encapsulated electrophoretic medium comprising capsules in a binder is coated on to a flexible substrate comprising indium-tin-oxide (ITO) or a similar conductive coating (which acts as an one electrode of the final display) on a plastic film, the capsules/binder coating being dried to form a coherent layer of the electrophoretic medium firmly adhered to the substrate. Separately, a backplane, containing an array of pixel electrodes and an appropriate arrangement of conductors to connect the pixel electrodes to drive circuitry, is prepared. To form the final display, the substrate having the capsule/binder layer thereon is laminated to the backplane using a lamination adhesive. (A very similar process can be used to prepare an electrophoretic display usable with a stylus or similar movable electrode by replacing the backplane with a simple protective layer, such as a plastic film, over which the stylus or other movable electrode can slide.) In one preferred form of such a process, the backplane is itself flexible and is prepared by printing the pixel electrodes and conductors on a plastic film or other flexible substrate. The obvious lamination technique for mass production of displays by this process is roll lamination using a lamination adhesive. Similar manufacturing techniques can be used with other types of electro-optic displays. For example, a microcell electrophoretic medium or a rotating bichromal member medium may be laminated to a backplane in substantially the same manner as an encapsulated electrophoretic medium.

[0016] In the processes described above, the lamination of the substrate carrying the electro-optic layer to the backplane may advantageously be carried out by vacuum lamination. Vacuum lamination is effective in expelling air from between the two materials being laminated, thus avoiding unwanted air bubbles in the final display; such air bubbles may introduce undesirable artifacts in the images produced on the display. However, vacuum lamination of the two parts of an electro-optic display in this manner imposes stringent requirements upon the lamination adhesive used, especially in the case of a display using an encapsulated electrophoretic medium. The lamination adhesive should have sufficient adhesive strength to bind the electro-optic layer to the layer (typically an electrode layer) to which it is to be laminated, and in the case of an encapsulated electrophoretic medium, the adhesive should also have sufficient adhesive strength to mechanically hold the capsules together. If the electro-optic display is to be of a flexible type (and one of the important advantages of rotating bichromal member and encapsulated electrophoretic displays is that they can be made flexible), the adhesive should have sufficient flexibility not to introduce defects into the display when the display is flexed. The lamination adhesive should have adequate flow properties at the lamination temperature to ensure high quality lamination, and in this regard, the demands of laminating encapsulated electrophoretic and some other types of electro-optic media are unusually difficult; the lamination has be conducted at a temperature of not more than about 130°C since the medium cannot be exposed to substantially higher temperatures without damage, but the flow of the adhesive must cope with the relatively uneven surface of the capsule-containing layer, the surface of which is rendered irregular by the underlying capsules. The lamination temperature should indeed be kept as low as possible, and room temperature lamination would be ideal, but no commercial adhesive has been found which permits such room temperature lamination. The lamination adhesive should be chemically compatible with all the other materials in the display.

[0017] As discussed in detail in the aforementioned 2003/0025855, a lamination adhesive used in an electro-optic display should meet certain electrical criteria, and this introduces considerable problems in the selection of the lamination adhesive. Commercial manufacturers of lamination adhesives naturally devote considerable effort to ensuring that properties, such as strength of adhesion and lamination temperatures, of such adhesives are adjusted so that the adhesives perform well in their major applications, which typically involve laminating polymeric and similar films. However, in such applications, the electrical properties of the lamination adhesive are not relevant, and consequently the commercial manufacturers pay no heed to such electrical properties. Indeed, substantial variations (of up to several fold) in certain electrical properties may exist between different batches of the same commercial lamination adhesive, presumably because the manufacturer was attempting to optimize non-electrical properties of the lamination adhesive (for example, resistance to bacterial growth) and was not at all concerned about resulting changes in electrical properties.

[0018] However, in electro-optic displays, in which the lamination adhesive is normally located between the electrodes, which apply the electric field needed to change the electrical state of the electro-optic medium, the electrical properties of the adhesive may become crucial. As will be apparent to electrical engineers, the volume resistivity of the lamination adhesive becomes important, since the voltage drop across the electro-optic medium is essentially equal to the voltage drop across the electrodes, minus the voltage drop across the lamination adhesive. If the resistivity of the adhesive layer is too high, a substantial voltage drop will occur within the adhesive layer, requiring an increase in voltage across the electrodes. Increasing the voltage across the electrodes in this manner is undesirable, since it increases the power consumption of the display, and may require the use of more complex and expensive control circuitry to handle the increased voltage involved. On the other hand, if the adhesive layer, which extends continuously across the display, is in contact with a matrix of electrodes, as in an active matrix display, the volume resistivity of the adhesive layer should not be too low, or lateral conduction of electric current through the continuous adhesive layer may cause undesirable cross-talk between adjacent electrodes. Also, since the volume resistivity of most materials decreases rapidly with increasing temperature, if the volume resistivity of the adhesive is too low, the performance of the display at temperatures substantially above room temperature is adversely affected. For these reasons, there is an optimum range of lamination adhesive resistivity values for use with any given electro-optic medium, this range varying with the resistivity of the electro-optic medium. The volume resistivities of encapsulated electrophoretic media are typically around 10^{10} ohm cm, and the resistivities of other electro-optic media are usually of the same order of magnitude. Accordingly, the volume resistivity of the lamination adhesive should normally be around 10^8 to 10^{12} ohm cm, or about 10^9 to 10^{11} ohm cm, at the operating temperature of the display, typically around 20°C. The lamination adhesive should also have a variation of volume resistivity with temperature which is similar to that of the electro-optic medium itself.

[0019] The number of commercial materials which can meet most of the previously discussed, rather disparate requirements for a lamination adhesive for use in an electro-optic display is small, and in practice a small number of water-dispersed urethane emulsions have been used for this purpose. A similar group of materials have been used as the binder for an encapsulated electrophoretic medium.

[0020] However, the use of such polyester-based urethane emulsions as lamination adhesives is still a not entirely satisfactory compromise between the desired mechanical and electrical properties. Lamination adhesives such as acrylic polymers and pressure sensitive adhesives are available with much better mechanical properties, but the electrical properties of these materials are unsuitable for use in electro-optic displays. Moreover, hitherto there has been no satisfactory way of varying the electrical properties of the urethane emulsions to "fine tune" them to match the electrical properties of a specific electro-optic medium. Accordingly, it would be highly advantageous if some way could be found to "decouple" the mechanical and electrical properties of a lamination adhesive so that each set of properties could be optimized separately, , i.e., in practice, one could choose an adhesive with highly desirable mechanical properties and then optimize its electrical properties for use with a specific electro-optic medium. One aspect of the present invention provides a way of varying the electrical properties of a binder without substantially affecting its mechanical properties. It may also be used to vary the electrical properties of an adhesive without substantially affecting its mechanical properties.

[0021] Furthermore, in considering the choice of a lamination adhesive for use in an electro-optic display, attention must be paid to the process by which the display is to be assembled. Most prior art methods for final lamination of electrophoretic displays are essentially batch methods in which the electro-optic medium, the lamination adhesive and the backplane are only brought together immediately prior to final assembly, and it is desirable to provide methods better adapted for mass production. However, the aforementioned 2004/0027327 describes a method of assembling a solid electro-optic display (including a particle-based electrophoretic display), which is well adapted for mass production. Essentially, this copending application describes a so-called "front plane laminate" ("FPL") which comprises, in order, a light-transmissive electrically-conductive layer; a layer of a solid electro-optic medium in electrical contact with the electrically-conductive layer; an adhesive layer; and a release sheet. Typically, the light-transmissive electrically-conductive layer will be carried on a light-transmissive substrate, which is preferably flexible, in the sense that the substrate can be manually wrapped around a drum (say) 10 inches (254 mm) in diameter without permanent deformation. The term "light-transmissive" is used in this copending application and herein to mean that the layer thus designated transmits sufficient light to enable an observer, looking through that layer, to observe the change in display states of the electro-optic medium, which will be normally be viewed through the electrically-conductive layer and adjacent substrate (if present). The substrate will be typically be a polymeric film, and will normally have a thickness in the range of about 1 to about 25 mil (25 to 634 μm), preferably about 2 to about 10 mil (51 to 254 μm). The electrically-conductive layer is conveniently a thin metal layer of, for example, aluminum or ITO, or may be a conductive polymer. Polyethylene terephthalate (PET) films coated with aluminum or ITO are available commercially, for example as "aluminized Mylar" ("Mylar" is a Registered Trade Mark) from E.I. du Pont de Nemours & Company, Wilmington DE, and such commercial materials may be used with good results in the front plane laminate.

[0022] Assembly of an electro-optic display using such a front plane laminate may be effected by removing the release sheet from the front plane laminate and contacting the adhesive layer with the backplane under conditions effective to cause the adhesive layer to adhere to the backplane, thereby securing the adhesive layer, electro-optic medium layer and electrically-conductive layer to the backplane. This process is well-adapted to mass production since the front plane laminate may be mass produced, typically using roll-to-roll coating techniques, and then cut into pieces of any size needed for use with specific backplanes.

[0023] The aforementioned 2004/0027327 also describes a method for testing the electro-optic medium in a front plane laminate prior to incorporation of the front plane laminate into a display. In this testing method, the release sheet is provided with an electrically conductive layer, and a voltage sufficient to change the optical state of the electro-optic medium is applied between this electrically conductive layer and the electrically conductive layer on the opposed side of the electro-optic medium. Observation of the electro-optic medium will then reveal any faults in the medium, thus avoiding laminating faulty electro-optic medium into a display, with the resultant cost of scrapping the entire display, not merely the faulty front plane laminate.

[0024] The aforementioned 2004/0027327 also describes a second method for testing the electro-optic medium in a front plane laminate by placing an electrostatic charge on the release sheet, thus forming an image on the electro-optic medium. This image is then observed in the same way as before to detect any faults in the electro-optic medium.

[0025] The aforementioned 2003/0025855 and the corresponding International Application No. PCT/US03/27686 describe a so-called "double release film" which is essentially a simplified version of the front plane laminate previously described. One form of the double release sheet comprises a layer of a solid electro-optic medium sandwiched between two adhesive layers, one or both of the adhesive layers being covered by a release sheet. Another form of the double release sheet comprises a layer of a solid electro-optic medium sandwiched between two release sheets. Both forms of the double release film are intended for use in a process generally similar to the process for assembling an electro-optic display from a front plane laminate already described, but involving two separate laminations; typically, in a first lamination the double release sheet is laminated to a front electrode to form a front sub-assembly, and then in a second lamination the front sub-assembly is laminated to a backplane to form the final display.

[0026] In view of the advantages of the assembly method using a front plane laminate described in the aforementioned 2004/0027327, it is desirable that a lamination adhesive be capable of being incorporated into such a front plane laminate. It is also desirable that a lamination adhesive be capable of being incorporated into a double release film as previously described.

[0027] The aforementioned 2003/0025855 also describes (see especially Paragraphs [0162] to [0191] thereof) certain polyurethane dispersions especially formulated for use in electro-optic displays.

[0028] The aforementioned copending Applications Nos. 10/810,761 and PCT/US04/09198 describe an electro-optic display comprising first and second substrates, and an adhesive layer and a layer of electro-optic material disposed between the first and second substrates, the adhesive layer comprising a mixture of a polymeric adhesive material and a salt or other polyelectrolyte. The salt may be for example a tetraalkylammonium salt such as tetrabutylammonium chloride, or potassium acetate. (It has also been found that tetrabutylammonium hexafluorophosphate may advantageously be substituted for the chloride on a mole-for-mole basis.) The polyelectrolyte may be a polymeric material, for example the sodium salt of polyacrylic acid. The salt or polyelectrolyte serves to vary the volume resistivity of the adhesive material but typically does not substantially affect the mechanical properties of this material.

[0029] These applications also describe an electrophoretic medium comprising a plurality of capsules, each of the capsules comprising a capsule wall, a suspending fluid encapsulated within the capsule wall and a plurality of electrically charged particles suspended in the suspending fluid and capable of moving therethrough on application of an electric field to the medium, the medium further comprising a binder surrounding the capsules, the binder comprising a mixture of a polymeric adhesive material and a salt or other polyelectrolyte. The salt or polyelectrolyte may be any of those previously described.

[0030] The displays and media described in these applications give good results. However, in at least some cases, there are concerns that addition of ionic species to adhesives and/or binders used in electro-optic displays might possibly cause corrosion problems in certain materials used in electro-optic displays, in particular the backplanes thereof which are typically in direct contact with the lamination adhesive. In one aspect, this invention relates to alternative additives which can be used to vary the volume resistivity and enhance the low temperature performance of electro-optic displays. In another aspect, this invention relates to modification of polyurethane adhesives to render them more suitable for use in electro-optic displays.

[0031] As already mentioned, the lamination processes used to manufacture electro-optic displays impose stringent requirements upon both the mechanical and electrical properties of the lamination adhesive. In the final display, the lamination adhesive is located between the electrodes which apply the electric field needed to change the electrical state of the electro-optic medium, so that the electrical properties of the adhesive become crucial. As will be apparent to electrical engineers, the volume resistivity of the lamination adhesive becomes important, since the voltage drop across the electro-optic medium is essentially equal to the voltage drop across the electrodes, minus the voltage drop across the lamination adhesive. If the resistivity of the adhesive layer is too high, a substantial voltage drop will occur within the adhesive layer, requiring an increase in voltage across the electrodes. Increasing the voltage across the electrodes in this manner is undesirable, since it increases the power consumption of the display, and may require the use of more complex and expensive control circuitry to handle the increased voltage involved.

[0032] This invention provides an electrophoretic medium comprising a plurality of droplets, each of the droplets comprising a suspending fluid and a plurality of electrically charged particles suspended in the suspending fluid and capable of moving therethrough on application of an electric field to the medium, the medium further comprising a binder surrounding the droplets, the binder comprising a mixture of a polymeric adhesive material and a hydroxyl containing polymer having a number average molecular weight not greater than about 5000.

[0033] This electrophoretic medium may hereinafter for convenience be referred to as the "low molecular weight polymer" medium. In such a medium, the hydroxyl containing polymer may be a poly(ethylene glycol), typically one having a number average molecular weight not greater than about 2000. The poly(ethylene glycol) may be present at a concentration of from about 10^{-6} to about 10^{-5} moles per gram of polymeric adhesive material. The electrophoretic medium may be an encapsulated electrophoretic medium in which the droplets are provided with capsule walls surrounding the suspending fluid and the electrically charged particles.

[0034] Figure 1 of the accompanying drawings is a graph showing the variation of volume resistivity with temperature for certain polyurethane adhesives useful in low molecular weight polymer displays of the invention.

Low molecular weight polymer display and medium

[0035] An electro-optic display may have an adhesive layer comprising a mixture of a polymeric adhesive material and a low number average molecular weight (M_n not greater than about 5000) hydroxyl containing polymer. A preferred polymer for this purpose is poly(ethylene glycol) (PEG). desirably having Mn not greater than about 2000. In effect, the polymer additive serves the same function as the salt or other polyelectrolyte used in the aforementioned copending Application Serial No. 10/810,761. However, the use of the polymer additive appears likely to cause fewer corrosion problems that the use of a salt. It has also been found that the use of the polymer additive improves the operating temperature range of the display by reducing the variation of the volume resistivity of polyurethane adhesive materials with temperature in a way which the use of salt additives does not. The optimum concentration of hydroxyl containing polymer additive for any particular system is best determined empirically, but by way of general guidance it may be said that the optimum concentration of typically around 10^{-6} to 10^{-5} moles per gram of polymeric adhesive material cf. the relevant Examples below.

[0036] The low molecular weight polymer display of the invention may make use of any of the types of electro-optic media discussed above.

Example 1

[0037] Three different commercially available PEG's (with number average molecular weights, Mn of 300, 1000, and 8000 g/mole respectively, purchased from Aldrich Chemical) were used at a concentration of 4400 ppm in a custom polyurethane adhesive. The concentration of 4400 ppm corresponds a molar concentration of 5.17×10^{-6} for PEG-300, 1.55×10^{-6} for PEG-1000, and 1.94×10^{-7} for PEG-8000. To provide experimental samples closely simulating an encapsulated electrophoretic display, each polyurethane/PEG mixture was coated at a thickness of 30 ± 2 µm on to a 7 mil (177 µm) poly(ethylene terephthalate) (PET) film coated with ITO, the mixture being coated on to the ITO-covered surface of the film. To provide experimental test units suitable for use in these experiments, pieces of the resultant adhesive-coated film were then laminated at 120°C and 65 psig (approximately 0.5 mPa) at a speed of 6 inches/minute (approximately 2.5 mm/sec) to a 5 cm by 5 cm PET film covered with a carbon black layer, which served as the rear electrode of the test unit (which was essentially an encapsulated electrophoretic display with the capsule layer itself omitted). At least four test units were used for each experiment and all test units were conditioned at 30°C and 30 per cent relative humidity for 116 hours before testing; previous experiments had shown that this conditioning was sufficient for the adhesive to reach relative humidity equilibrium. The volume resistivity (Vr) of the adhesive in each test unit was then tested at 25°C and 30 per cent relative humidity using a standard industrial testing apparatus. To provide controls, test units were prepared containing the same polyurethane adhesive with no additive, and the same polyurethane adhesive with the addition of 4400 ppm of tetrabutylammonium hexafluorophosphate (abbreviated "NBu_4PF_6" in the Table below). The results are shown in the Table below. For simplicity, experimental uncertainty in each sample is omitted; however, the error is, in general, no greater than ±15%.

[0038] The last column of the Table shows the theoretical maximum moisture content of each material assuming that in the PEG-containing samples the site for moisture uptake is the terminal hydroxyl groups, since it appears unlikely that any significant amount of water will be bound by the ether linkages within the polymer chain. The maximum moisture content of the sample containing tetrabutylammonium hexafluorophosphate was calculated assuming from 1 to 5 moles of water of crystallization.

Table 1

Dopant	Conc. (x10 ^{6} mole/g, dispersion)	Vr (x10^{-9}Ω cm)	Moisture content (ppm)
None	0.00	60	N/A
NBu_4PF_6	6.40	0.68	50-230
PEG (300)	5.17	0.42	500

(continued)

Dopant	Conc. (x10 ^{6} mole/g, dispersion)	Vr (x10$^{-9}\Omega$ cm)	Moisture content (ppm)
PEG (1000)	1.55	0.46	160
PEG (8000)	0.19	44	20

[0039] From the data in Table 1, it will be seen that the PEG-300 and PEG-1000 were at least as effective as the tetrabutylammonium hexafluorophosphate in reducing the volume resistivity of the polyurethane adhesive, whereas the PEG-8000 had little effect on the volume resistivity. This is consistent with the maximum theoretical water content of the samples. An alternative explanation is that the PEG-8000 is far less effective than the PEG-300 and PEG-1000 in plasticizing the polyurethane adhesive.

Example 2

[0040] As already mentioned, the addition of low molecular weight hydroxyl-containing polymers improves the variation of the volume resistivity of polyurethane adhesives with temperature in a manner which the addition of salts does not. A second series of experiments were conducted to illustrate this behavior. Test units were prepared and conditioned in the same way as in Example 1 except that the conditioning was performed for a minimum of only 100 hours, and that the test units contained only no additive, 4400 ppm of tetrabutylammonium hexafluorophosphate, or 166 or 2658 ppm of PEG-300. Volume resistivity measurements were then conducted at temperatures from -5°C to 50°C, in all cases at 30 per cent relative humidity. The results are shown in Figure 1 of the accompanying drawings; no error bars are shown in this Figure since experimental error is in general less than the size of the symbols used to mark the data points.

[0041] From Figure 1, it will be seen that the volume resistivity of the undoped adhesive falls by about two orders of magnitude over the 55C° temperature range used; this behavior is typical for polyurethane adhesives. The tetrabutylammonium hexafluorophosphate doped adhesive has a volume resistivity about two orders of magnitude lower than that of the undoped adhesive at the same temperature, but the overall shape of the volume resistivity curve for the salt doped adhesive closely resembles that of the curve for the undoped adhesive. In contrast, both PEG doped adhesives show a volume resistivity which varies little with temperature over the temperature range used; indeed, the volume resistivity of the PEG doped adhesive increased slightly with temperature. Since the increase in volume resistivity of polyurethane adhesives at low temperatures is a major factor limiting the performance of electro-optic displays using such adhesives at low temperatures, the results shown in Figure 1 indicate that use of PEG doped polyurethane adhesives should result in a significant improvement in the low temperature performance of such electro-optic displays.

[0042] From the foregoing, it will be seen that the low molecular weight polymer display and electro-optic medium of the present invention provides a means for controlling the volume resistivity of adhesives used in electro-optic displays which reduces any possible corrosion problems which may be associated with the addition of salts to such adhesives. Also, they provide a means for rendering the volume resistivity of adhesives used in electro-optic displays relatively insensitive to temperature changes, thereby potentially improving the range of conditions under which such displays can operate. Finally, because of the relationship between the properties required in an adhesive and a binder for use in an encapsulated electrophoretic medium, the use of a low molecular weight polymer medium of the present invention as a binder in encapsulated electrophoretic media used in electro-optic displays should give advantages similar to those achieved to its use as an adhesive in electro-optic displays.

Claims

1. An electrophoretic medium comprising a plurality of droplets, each of the droplets comprising a suspending fluid and a plurality of electrically charged particles suspended in the suspending fluid and capable of moving therethrough on application of an electric field to the medium, the medium further comprising a binder surrounding the droplets, the electrophoretic medium being **characterized in that** the binder comprises a mixture of a polymeric adhesive material and a hydroxyl containing polymer having a number average molecular weight not greater than 5000.

2. An electrophoretic medium according to claim 1 wherein the hydroxyl containing polymer is a poly(ethylene glycol).

3. An electrophoretic medium according to claim 2 wherein the poly(ethylene glycol) has a number average molecular weight not greater than about 2000.

4. An electrophoretic medium according to claim 2 wherein the poly(ethylene glycol) is present at a concentration of from 10^{-6} to 10^{-5} moles per gram of polymeric adhesive material.

5. An electrophoretic medium according to claim 1 wherein the droplets are surrounded by capsule walls surrounding the suspending fluid and the electrically charged particles and wherein the capsule walls are themselves held within the binder.

Patentansprüche

1. Elektrophoretisches Medium mit einer Vielzahl von Tröpfchen, wobei jedes der Tröpfchen ein Suspensionsfluid und eine Vielzahl elektrisch geladener Teilchen, die im Suspensionsfluid suspendiert sind und sich beim Anlegen eines elektrischen Felds an das Medium dadurch bewegen können, umfasst, wobei das Medium ferner ein die Tröpfchen umgebendes Bindemittel umfasst, wobei das Medium **dadurch gekennzeichnet ist, dass** das Bindemittel eine Mischung eines polymerischen Klebematerials und eines hydroxylhaltigen Polymers mit einem durchschnittlichen Molekulargewicht von höchstens 5000 umfasst.

2. Elektrophoretisches Medium nach Anspruch 1, wobei das hydroxylhaltige Polymer Poly(ethylenglykol) ist.

3. Elektrophoretisches Medium nach Anspruch 2, wobei das Poly(ethylenglykol) ein durchschnittliches Molekulargewicht von höchstens etwa 2000 aufweist.

4. Elektrophoretisches Medium nach Anspruch 2, wobei das Poly(ethylenglykol) mit einer Konzentration von 10^{-6} bis 10^{-5} Mol pro Gramm des polymerischen Klebematerials vorhanden ist.

5. Elektrophoretisches Medium nach Anspruch 1, wobei die Tröpfchen von Kapselwänden umgeben sind, welche das Suspensionsfluid und die elektrisch geladenen Teilchen umgeben, und wobei die Kapselwände selbst innerhalb des Bindemittels gehalten werden.

Revendications

1. Milieu électrophorétique comprenant une pluralité de gouttelettes, chacune des gouttelettes comprenant un fluide de mise en suspension et une pluralité de particules électriquement chargées en suspension dans le fluide de mise en suspension et pouvant s'y déplacer lors de l'application d'un champ électrique au milieu, le milieu comprenant en outre un liant entourant les gouttelettes, le milieu électrophorétique étant **caractérisé en ce que** le liant comprend un mélange d'une matière adhésive polymère et d'un polymère contenant un groupe hydroxyle ayant une masse moléculaire moyenne en nombre de pas plus de 5000.

2. Milieu électrophorétique selon la revendication 1 dans lequel le polymère contenant un groupe hydroxyle est un polyéthylène glycol.

3. Milieu électrophorétique selon la revendication 2 dans lequel le polyéthylène glycol a une masse moléculaire moyenne en nombre de pas plus d'environ 2000.

4. Milieu électrophorétique selon la revendication 2 dans lequel le polyéthylène glycol est présent en une concentration de 10^{-6} à 10^{-5} mole par gramme de matière adhésive polymère.

5. Milieu électrophorétique selon la revendication 1 dans lequel les gouttelettes sont entourées de parois de capsules entourant le fluide de mise en suspension et les particules électriquement chargées et dans lequel les parois de capsules sont elles-mêmes contenues dans le liant.

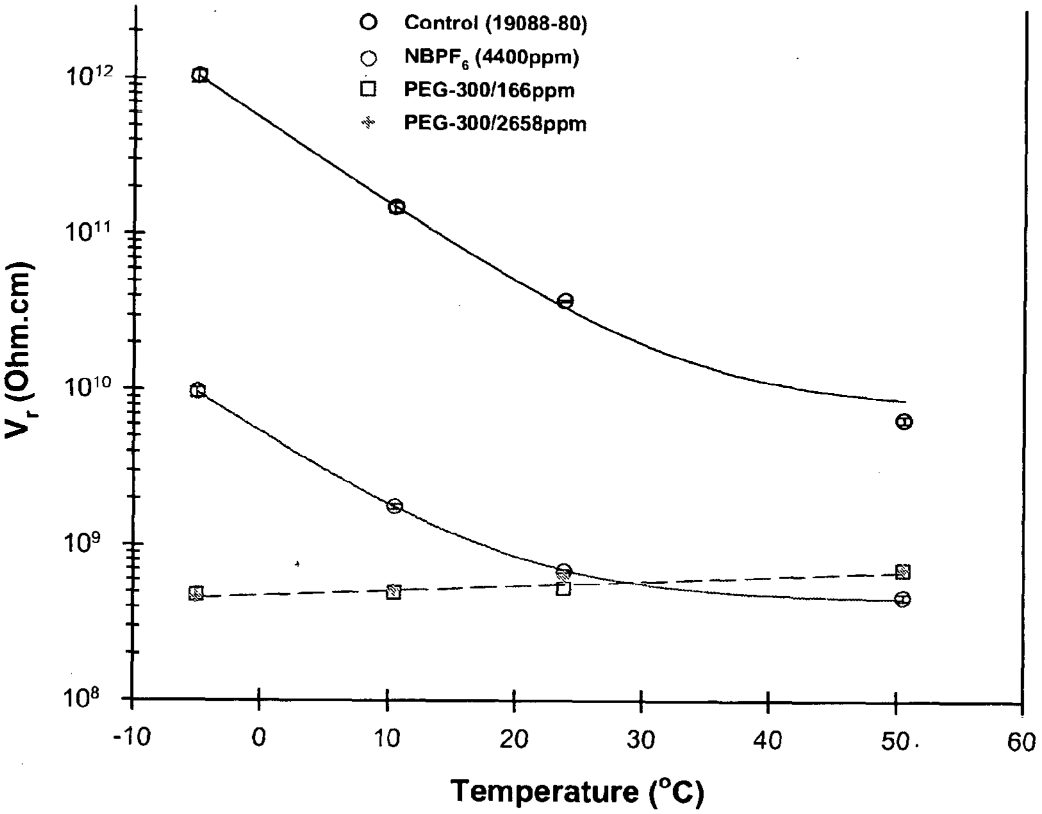
Control (19088-80)
NBPF$_6$ (4400ppm)
PEG-300/166ppm
PEG-300/2658ppm
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
V_r (Ohm.cm)
-10
0
10
20
30
40
50
60
Temperature (°C)

Figure 1

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