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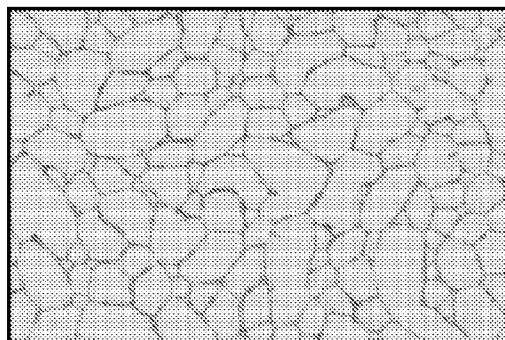
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(54) Title: PROCESSES FOR MAKING TRANSPARENT CONDUCTIVE COATINGS



PATTERN FROM TCC
EMULSION WITH
UV-ACTIVATED
COMPONENTS

FIG. 1

(57) Abstract: A composition for forming a transparent conductive coating on a substrate comprising an organic solvent that is not miscible with water; water, a water-miscible solvent or combination thereof that when mixed with the organic solvent forms an emulsion having a continuous phase and a discontinuous phase; and fine conductive particles dispersed in the solvent forming the continuous phase of the emulsion; a UV-activated oligomer; a UV-activated monomer; and a photo initiator wherein when the composition is coated onto a surface of a substrate, exposed to UV radiation, and dried to remove the solvents, the conductive particles self-assemble to form a transparent and electrically conductive coating in the form of a network-like pattern that includes interconnected traces defining randomly-shaped cells on the surface of the substrate.

Processes for Making Transparent Conductive Coatings

Technical Field

This invention relates to the field of transparent coatings, particularly transparent conductive coatings that are formed from an emulsion containing fine conductive particles that self-assemble into an open-cell, network like conductive pattern after application to a substrate and evaporation of the liquid carrier. The particular field of the invention relates to improved processes for forming such transparent conductive coatings on a substrate including surface treatments to the substrate and emulsion formulations that do not require a special primer layer prior to coating.

Background

Materials and processes for forming transparent conductive coatings are beneficial for the development and manufacture of electronics devices. These coatings provide a number of functions such as electromagnetic (EMI) shielding and electrostatic dissipation, and they serve as light transmitting conductive layers and electrodes in a wide variety of applications. Such applications include, but are not limited to, useful devices or parts of devices such as touch screens, wireless electronic boards, photovoltaic devices, conductive textiles and fibers, displays, OLEDs, and electroluminescent structures such as e-paper.

Emulsions as disclosed in US20050214480 are used to prepare transparent conductive coatings (TCC). A primer layer or pretreatment coating layer applied immediately prior to coating with the emulsion has been used to preferentially alter surface characteristics of the substrate that is to be coated with the emulsion.

In the aforementioned US2005/214480, the process of coating TCC on glass and polyimide substrates involves a preliminary coating step in which silane compounds or other surfactants in acetone are applied to the substrate surface prior to applying the TCC emulsion. These pretreatment coating compositions are referred to as “primers”. After the primer is coated and dries, the TCC coating is applied. Similarly, in WO2006/135735, PET film treated with octyltriethoxysilane primer solution in hexane improved the TCC pattern relative to non-treated film.

There are a number of disadvantages of a process that involves a separate step to apply such primers or other preliminary coating layers immediately prior to deposition of the TCC emulsions. Commercially viable coating processes that deposit a primer or preliminary coating layer and then a TCC formulation require two coating heads and thus a 2-step process. It is preferable that a process operate with a single coating head and in a single step. Also, non-uniformity of the primer layer, as well as emulsion-primer interactions, may lead to defects in the subsequent TCC layer when it is applied immediately after deposition of a primer layer.

An acetone-based primer in particular has additional drawbacks. Acetone is highly flammable; the film quality of acetone-based primers typically influences subsequent uniformity of TCC cell size; and the primer layers produced from acetone-based primers may not retain their properties after intermediate handling steps, e.g. if rolled or otherwise stored prior to a subsequent TCC coating step.

Accordingly the need existed for alternative TCC emulsion formulations or surface treatments to eliminate current primers in commercial scale coating operations without adversely affecting pattern formation.

Summary of the invention

Various improved methods are described for forming TCC on a substrate, two of which eliminate the need to coat a primer onto the substrate immediately prior to coating the TCC emulsion and still obtain acceptable TCC pattern. The third provides a new and more versatile preliminary treatment coating on the substrate. These methods are particularly useful for coating commercially available flexible substrates, including optical PET substrates using large scale coating equipment.

One method involves the incorporation of UV curing components into the TCC emulsion and the application of a UV curing step during the formation of the TCC.

Another method involves UV activation or other physical activation of the substrate prior to coating with the TCC emulsion.

Another approach involves pre-treating the substrate with a UV-activated binder that is sufficiently stable on the substrate to allow the substrate

to be stored and later coated with the TCC emulsion in a single pass coating process.

Description of the Drawings

Figure 1 is a photomicrograph of a transparent conductive coating formed from an emulsion containing UV-activated components.

Figure 2 is a photomicrograph of a transparent conductive coating formed on a substrate that had been UV-treated prior to application of the TCC emulsion.

Figure 3 is a photomicrograph of a transparent conductive coating formed on a substrate that had also been UV-treated prior to application of the TCC emulsion.

Detailed Description

When TCC emulsions such as those described in US2005/214480 and WO2006/35735, both of which are incorporated herein by reference, are coated onto preliminary “pretreatment” coating layers or primer layers on a substrate surface, they provide homogeneous patterns with a relatively uniform cell size distribution. But, as noted above, the process of first depositing such a preliminary coating layer or primer layer and then depositing the TCC emulsion has certain drawbacks, particularly in commercial scale coating operations. The ability to deposit the TCC emulsion and form a coating with desired properties in a single step process without a primer applied immediately prior to coating the TCC emulsion is a distinct advantage.

Three approaches have been developed to improve the process of coating of TCC emulsions on substrates.

The first approach involves the use of TCC emulsion compositions that contain UV-activated components. These compositions allow for a 1-coat process without requiring a primer or pretreatment coating immediately prior to deposition of the TCC emulsion.

The UV-activated components within the TCC formulation include, but are not limited to, at least an oligomer component, a monomer component, and a photoinitiator component. Each component may be a single material or a mixture of materials.

The oligomer, or “resin”, component may contain, but is not limited to, epoxy-acrylates, urethane-acrylates, polyester acrylates, polyether acrylates, unsaturated acrylates, acrylic acrylates, vinyl ethers, siloxanes, or combinations thereof. The purpose of the oligomer is to provide the physical properties of the polymerizable material, for example, but not limited to, film-forming, gloss, adhesion, rigidity, weathering, chemical resistance, scratch resistance, and abrasion resistance. The amount of oligomer is preferably 40-80% relative to total UV “binder system” components (consisting of oligomer, monomer, and photo-initiator), more preferably 50-70%, and most preferably 55-65%.

The monomer component of the UV binder system may contain, but is not limited to, styrene, or multifunctional acrylates such as isobornyl acrylate, hexanediol diacrylate (HDDA), dipropylene glycol diacrylate (DPGDA), tripropylene glycol diacrylate (TPGDA), trimethylolpropane triacrylate (TMPTA), polyethylene glycol diacrylate, ditrimethylolpropane tetraacrylate, dipentaerythriol hexaacrylate, oligomeric triacrylate, among others, and combinations thereof. The monomer component may also be referred to as a reactive diluent. The monomers are multifunctional cross-linking agents that react with the oligomers to create polymerized materials. The monomers are typically mono-, di-, or tri-functional, but there are also others available with even higher functionalities

In addition to being reactive diluents, monomers are also used to achieve a variety of desired properties, for example to improve adhesion, reactivity, chemical resistance, or scratch resistance.

The amount of monomer is preferably 25-45% relative to total UV binder system components, more preferably 30-40%, and most preferably 32-37% .

The photoinitiator component may be a free radical type or ionic type. Photoinitiator types include, but are not limited to, hydroxyl-ketones, amino-ketones, benzoin ethers, benzyl dimethyl ketal (BDK), acetophenone derivatives, acylphosphine oxides (e.g. BAPO), metallocenes, benzophenone/amine, titanocene, and thioxanthone derivatives. Photoinitiator concentration is typically less than 10 percent by weight of the UV-activated binder components.

Preferred photoinitiators are those that are activated at UV wavelengths in the range of 240-365nm, and more preferably 250-280nm, such as 2-hydroxy-2-methyl-1-

phenylpropanone (Omnirad 73, IGM Resins) and similar compounds, for example as provided by IGM Resins.

The remaining ingredients of the TCC emulsions are as described in US 2005/214480 and WO/2006/135735, and are primarily the fine conductive particles and the solvent system.

The fine conductive particles in the TCC emulsions may be coated or uncoated, and their composition may include metals, metal alloys, metal salts, or other conductive non-metal components, and mixtures thereof. In a preferred embodiment, the particles are, or include, silver, silver-copper alloy, carbon black or graphite. The particles must be relatively fine in order to form a stable dispersion. Particles having an average particle size less than about three micrometers can be used. Preferably the particles are in the “nano” size range and have an average particle size less than about 100 nanometers.

The solvent system may include apolar organic solvents and/or polar solvents. Typically the particles are dispersed in a continuous organic solvent phase, and the second or discontinuous phase is a water or polar solvent phase, to create a water-in-oil emulsion. However, it is also possible to form a water-phase dispersion of the particles to which an organic phase is added to make an oil-in-water emulsion. For optimum pattern formation, it is desirable that the particles be dispersed in the continuous phase and that the solvent system forming the continuous phase evaporates faster than the solvent system forming the discontinuous phase of the emulsion.

Mixing of the particles with the desired solvent to form the dispersion can be accomplished by mechanical stirring, ball mill mixing, or by means of homogenizers or ultrasonic mixing equipment. Mixing order, times, and temperature can be optimized for each formulation.

In a preferred embodiment, the UV-activated components are added to the dispersion prior to the addition of the second phase by which the emulsion state is formed.

Other additives may be present in the emulsion formulations. For example, additives can include, but are not limited to, reactive or non-reactive diluents, oxygen scavengers, hard coat components, inhibitors, stabilizers, colorants, pigments, IR

absorbers, surfactants, wetting agents, leveling agents, flow control agents, thixotropic or other rheology modifiers, slip agents, dispersion aids, defoamers, and corrosion inhibitors. Additional binder or adhesion components may also be present in the formulation, for example thermally-activated binders or adhesion promoters.

After preparation and prior to coating on the selected substrates, the emulsions may be stored until they are needed for the coating process. The emulsions may be mixed and possibly heated prior to use in order to optimize the emulsion properties immediately prior to coating.

Characterization of the dispersion and emulsions may include particle-size distribution, metal loading, stability, and determination of rheological properties such as viscosity, for example by Zahn cup method, viscometers, and/or Casson plot analysis.

Substrates onto which the TCC emulsions are coated may be rigid, flexible, polymeric, paper, ceramic, glass, or semiconductor materials. The substrate may be used directly or pretreated, for example in order to clean the surface or otherwise alter it by physical means or chemical means. Physical means include, but are not limited to, corona, plasma, UV-exposure, or flame treatment. The substrate may have a coating or surface treatment to improve certain properties. For example, it may have a hard-coat layer applied in order to provide mechanical resistance to scratching and damage. The treatment and processes described here can be applied to neat substrates or to substrates for which the film supplier has already placed a primer, preliminary coating, or otherwise pretreated the surface that will receive TCC emulsion.

Coating can be performed by batch coating equipment or continuous coating equipment, on small laboratory scale or on larger industrial scales, including roll-to-roll processes. The coating apparatus may be any of a variety of contact or non-contact coaters known in the art, such as comma coaters, die coaters, gravure coaters, reverse roll coaters, knife coaters, rod coaters, extrusion coaters, curtain coaters, or any other coating device or metering device.

After coating of the substrate with the TCC emulsion, the solvent is removed by evaporation (drying at room conditions or thermal treatment) and then exposed to a UV-lamp for polymerization, curing, and fixation. The preferred UV lamp source activates at wavelengths in the range of 240-365nm, more preferably 250-280nm. Preferred

conditions for treatment include a conveyor system. Speed is a function of photoinitiator type and concentration and functionality of the selected components. For the work described in the examples below, a bench-top conveyor system equipped with an H-bulb (Model LC6B, Fusion UV System, Inc min.) was used with Omnirad 73 photoinitiator. Preferable operation speeds were 0.5-4 m/, more preferred conveyor speeds were 1-3 m/min.

Additional post-coating treatment steps for curing, sintering, adhesion, or other property improvement can then be applied, for example secondary thermal, laser, microwave, ultraviolet, or chemical exposure steps. Washing steps may be applied, for example, washing with water and/or other chemical wash solutions such as, but not limited to, acid solution, acetone, or organic solvent wash steps.

Post-treatment of the coating can be performed by batch process equipment or continuous coating equipment, on small laboratory scales or on larger industrial scales, including roll-to-roll processes.

The resulting TCC films can then be characterized in terms of dry film thickness, homogeneity of the coating on the substrate, average TCC cell size, cell size distribution, light transmittance, haze, electrical sheet resistance, line height of the TCC cells, thickness of the TCC lines, surface energy, adhesion of the coating to the substrate, EMI shielding effect, and resistance to scratching, rubbing, rolling, and pressing.

TCC compositions that contain UV-activated components were exposed to UV-curing conditions gave resistance values <12 ohm/sq, light transmittance >80%, haze <5%, without the use of a preliminary coating or primer layer.

A second approach for improving the process of coating TCC emulsions without the need for in-line application of a primer involves UV activation or other physical activation of the substrate prior to coating with the TCC emulsion. The surface is preferably exposed to UV activation with a UV source with primary wavelength in the range of 240-365nm, more preferably 250-280nm, for example as with an H-bulb. Such activation can be used alternatively or in addition to the incorporation of UV activated ingredients in the emulsion formulation.

Physical activation methods in addition to UV activation to pre-treat the substrate include treatment with plasma, laser, microwave, or chemical exposure. Pretreatment step or steps can be performed off-line or on-line immediately prior to subsequent coating steps. As an example of pre-treating on-line, PET films can be treated with UV radiation and then immediately coated with a suitable TCC formulation in a single 1-pass 1-coat continuous process.

The treatment and processes described here can be applied to neat substrates or to substrates for which the film supplier has already placed a primer, preliminary coating, or otherwise pretreated the surface that will receive TCC emulsion deposition.

Such physical treatment of the substrate prior to applying the TCC coating can be performed by batch process equipment or continuous coating equipment, on small laboratory scales or on larger industrial scales, including roll-to-roll processes.

Another method of improving the process of coating TCC emulsions involves the use of UV-activated binder compositions to pre-treat the substrate. Such pre-treatments have been found to improve subsequent coated TCC patterns, particularly on flexible substrates such as PET substrates, and yield a binder layer that is homogeneously coated and adheres well to the substrate.

The UV-activated binder composition may include, but is not limited to, at least an oligomer component, a monomer component, and a photoinitiator component. Each component may be a single material or may be a mixture of materials.

The oligomer, or “resin”, component may contain, but is not limited to, epoxy-acrylates, urethane-acrylates, polyester acrylates, polyether acrylates, unsaturated acrylates, acrylic acrylates, vinyl ethers, siloxanes, or combinations thereof. The amount of oligomer is preferably 40-80% relative to total UV-activated components (consisting of oligomer, monomer, and photo-initiator), more preferably 50-70%, most preferably 55-65%

The monomer component may contain, but is not limited to, styrene, or multifunctional acrylates such as isobornyl acrylate, hexanediol diacrylate (HDDA), dipropylene glycol diacrylate (DPGDA), tripropylene glycol diacrylate (TPGDA), trimethylolpropane triacrylate (TMPTA), polyethylene glycol diacrylate, ditrimethylolpropane tetraacrylate, dipentaerythriol hexaacrylate, oligomeric triacrylate,

among others, and combinations thereof. The monomer component may also be referred to as a reactive diluent. Monomers are typically mono-, di-, or tri-functional, but there are also others available with even higher functionalities. The amount of monomer is preferably 25-45% to total UV-activated components in the binder formulation, more preferably 30-40%, most preferably 32-37%

The photoinitiator component may be free radical type or ionic type. They may include, but are not limited to, hydroxyl-ketones, amino-ketones, benzoin ethers, benzyl dimethyl ketal (BDK), acetophenone derivatives, acylphosphine oxides (e.g. BAPO), metallocenes, benzophenone compounds, benzophenone/amine, camphorquinone, benzil, titanocene, and fluorenone, anthraquinone, zanthone, and/or thioxanthone derivatives. Photoinitiator concentration is typically less than 10 percent by weight of the UV-activated components. Preferred photoinitiators are those that are activated at UV wavelengths in the range of 240-365nm, and more preferably 250-280nm, such as 2-hydroxy-2-methyl-1-phenylpropanone (Omnirad 73, IGM Resins) and similar compounds, for example as provided by IGM Resins.

Preferably, the UV-activated binder pre-treatment compositions also include additional components, for example surfactants, that are able to chemically interact with the UV-activated components in the binder formulation. For example, Maxemul 5011 and 5010 (Uniqema) are surfactants with unsaturated alkenyl groups that are able to react chemically with the UV-activated component in the binder formulation during UV-initiated polymerization. The surfactant increases the wettability of the substrate. By reacting with the polymerizable components in the binder formulation, the surfactant becomes fixed to the surface and does not migrate on the surface with time after application.

The binder components may be dispersed or diluted in a solvent, preferably a water-based or alcohol-based solvent or diluent. Total solids content is preferably less than 20% by weight. The binder composition may also include additional additives, for example reactive or non-reactive diluents, stabilizers, oxygen scavengers, hard coat components, inhibitors, colorants, pigments, IR absorbers, surfactants, wetting agents, leveling agents, flow control agents, thixotropic or other rheology modifiers, slip agents, dispersion aids, defoamers, and corrosion inhibitors. Additional binder or

adhesion components may also be present in the formulation, for example thermally-activated binders or adhesion promoters.

Mixing of the components of the binder composition can be accomplished by mechanical stirring, ball mill mixing, or by means of homogenizers or ultrasonic mixing equipment. Mixing order, times, and temperature can be optimized for each formulation. Characterization of the binder formulation may include determination of viscosity, for example by viscometers or other methods such as Zahn cup method.

The binder pre-treatment can be applied to neat substrates or to substrates for which the film supplier has already placed a primer, preliminary coating, or otherwise pretreated the surface that will receive the TCC emulsion .

An example of a UV-polymerizable binder pre-treatment, for example for a touch screen application, that can be applied to HF1C21 PET film (Teijin Dupont) with hard-coat, is diluted LUV-PET-004 binder (Today's Suntech, Ltd.) at a ratio of 1:20 by weight in ethyl acetate or ethanol.

Coating of the binder composition on the substrate can be performed by batch process equipment or continuous coating equipment, on small laboratory scales or on larger industrial scales, including roll-to-roll processes. The coating apparatus may be any of a variety of contact or non-contact coaters known in the art, such as comma coaters, die coaters, gravure coaters, reverse roll coaters, knife coaters, rod coaters, extrusion coaters, curtain coaters, or any other coating device or metering device.

Wet thickness of the binder layer is typically less than 30 microns, preferably less than 16 microns, and most preferably less than 12 microns. After coating of the substrate with the binder composition, the solvent is removed by evaporation, for example by drying at room conditions or by thermal treatment as in an oven, and then the coated film is exposed to a UV-lamp for polymerization, curing, and fixation, typically in the 240-365 nm range

Additional treatment steps can then be applied to the binder pre-treatment coating in order to improve adhesion or add patterning or other properties prior to coating with the TCC emulsion formulation.

After applying the binder pretreatment coating, and optional post-coating treatment, the films can be rolled, wound, stacked, pressed, and stored until subsequent coating with TCC emulsion formulations at a future time.

The binder layer after drying and the coated substrate can be characterized in terms of dry film thickness, homogeneity of the coating on the surface, adhesion, transmittance, haze, surface energy, contact angle, and stability over time.

Example 1:

A 1-step, 1-pass TCC deposition process was executed in which UV-polymerizable components were incorporated within the TCC emulsion formulation. A solution of UV-curable oligomer, monomer, and photo-initiator components in ethyl acetate was prepared ("S-UV"). The monomer was HDDA (1,6 hexanediol diacrylate), the oligomer was an aliphatic urethane acrylate (Etercure 6161-100, Eternal Chem. Co, Taiwan), and the photoinitiator was Omnirad 73 (IGM Resins, Waalwijk, Netherlands). The ratio of oligomer: monomer: photoinitiator was 60:35:5 by weight, and the proportion of these materials to ethyl acetate solvent was 40:60 by weight. This UV-additive solution was then added at a level of 1% by weight to the TCC dispersion. Water phase solution was then added to create the final TCC emulsion, as shown in Table 1.

Ingredient	%
Byk 410	0.1
Byk106	0.02
2-amino-1-butanol	0.2
5% sodium dioctyl sulfosuccinate (AOT) in toluene	0.3
Aniline	0.5
Cyclohexanone	2.9
Toluene	44.4
S-UV	1
Span 60	0.1
Methylcyclohexane	9.9
P204 silver nanopowder	3.7
BS16 (Wacker)	0.4

0.02% 1-octane-sulfonic acid sodium salt in water	36.5
total	100

The TCC emulsion was then coated on commercial Lumirror U46 PET film (Toray) for an EMI shielding application. The emulsion was applied to the film surface using a K202 K Control Coater (RK Print, England) equipped with Meyer coating bars at $\sim 22^{\circ}\text{C}$ and $\sim 50\%$ humidity. The film was not coated with a primer or preliminary coating layer prior to deposition of the emulsion. Wet thickness of the emulsion was 30 microns. After coating with the emulsion, the film was heated at 150°C for 12 seconds, and then passed through a UV chamber (LC6B Benchtop Conveyor, Fusion UV System, Inc.) at a speed of 2m/min, with H-bulb at 120 W/cm at a distance of 53.3 mm from the sample surface. After UV exposure, the film was treated by successive dipping in acetone for 30 seconds followed by dipping in 1M HCl solution for 1 min, and then rinsing in deionized water for 30 seconds. The film was then heated in a closed oven at 150°C for 2 minutes.

Resistance of the TCC coating was 6 – 9 ohm/sq, as determined with a Loresta GP resistivity meter equipped with an ESP-type probe. Average transmission and haze measured with a HazeGard Plus (Byk-Gardner) hazemeter were 82% and 4.6%, respectively. A micrograph of a resulting TCC coating is shown in Figure 1, as taken with a Nikon SMZ800 Stereo Microscope at 4X magnification.

Example 2:

Optical grade HF1C21 PET films with hard coat surface (Teijin DuPont, Japan) were exposed to UV treatment on the non-hard coat side by passing through a LC6B Bench top Conveyor chamber (Fusion UV System, Inc.) at various conveyor speeds ranging from 1.5 to 2.7 m/min. Afterward, TCC emulsion as described in Table 2 below, was coated onto the films on the non-hard-coat side at a wet thickness of 40 microns. No primer or preliminary coating material was applied prior to deposition of the TCC emulsion. Following the coating step, the film was heat treated at 150°C for 3 minutes and subsequently washed with acetone for 30-40 seconds and then dried in air. The resulting TCC coatings had sheet resistance of 200-300 ohm/sq, light transmittance

above 85%, and haze of ~4% and are suitable for touch screen applications. Adhesion of the TCC to the substrate was good, as determined by repeat measurement of the sheet resistance after application and removal of adhesive tape (Permacel P-99) to the pattern surface. Figure 2 shows a TCC pattern obtained on one such film UV-treated at a conveyor speed of 1.5m/min.

Table 2: TCC emulsion, components

Ingredient	Weight (%)
Cymel 1168	0.1
K flex 307 xm	0.1
Nacure 2501	0.1
Byk 410	0.2
Span 60	0.2
Aniline	0.1
Byk 106	0.1
2 Amino Butanol	0.2
Cyclohexane	8.0
Cyclohexanone	4.1
Toluene	53.9
P204 silver nanopowder	1.0
0.04% sodium dodecyl sulfate (SDS) in water	31.9
Total	100

Relative to the HF1C21 films described above, another commercial hard-coat PET film (Toyobo A4300) required a higher UV exposure in order to result in a good TCC pattern when the films were subsequently coated with TCC emulsion on the non-hard coat side. Good results were obtained with 2 passes through the UV chamber at a speed of 1.1 m/min, when followed by coating of the TCC emulsion at a wet thickness of 40 micron. Films were post-treated with the same conditions given above for the HF1C21 films.

PET film Skyrol SH34 (SKC) and Lumirror U46 PET film (Toray), neither of which have hard-coat surfaces, were UV-treated on the same equipment as above at conveyor rates of 1 m/min and 2 m/min. When subsequently coated with TCC emulsion as described in Table 3, network-like patterns were obtained as in Figure 3.

Table 3: TCC emulsion, components

Ingredient	Weight (%)
Byk 410	0.2
Span 60	0.2
Aniline	0.2
Byk 106	0.4
2 Amino Butanol	0.1
5% sodium dioctyl sulfosuccinate (AOT) in toluene	0.1
Cyclohexanone	4.1
Cyclohexane	28.1
Cymel 303	0.2
K flex 307xm	0.1
Nacure 2501	0.2
Toluene	30.1
Oleic Acid	0.1
0.08% Byk106 in Toluene	0.2
P 204	1.2
0.04% sodium dodecyl sulfate (SDS) in water	34.5
Total	100

Example 3

For a touch screen application, a 2-step, 2-pass process with a UV-polymerizable binder pre-treatment was developed for HF1C21 optical PET film (Teijin Dupont). A binder formulation was prepared comprised of 0.3g of a reactive surfactant having double bonds (Maxemul 5011), 4.0 g LUV-PET-004 (Today's Suntech, Ltd), and 45.7 g ethanol. LUV-PET-004 is a commercially available UV curable hard-coat resin for PET. Its chemistry is proprietary to the supplier but includes acrylic-type oligomer, monomer, and photoinitiator. This binder composition was coated to a wet thickness of 12 microns on the HF1C21 film and then dried at room temperature for 1 minute. The binder coating was then heat-treated at 150°C for 1 minute and then exposed to UV radiation on the LC6B conveyor at 2 m/min with 120 W/cm and H-bulb at a distance of 53.3 mm from the sample surface. Dry thickness was ~0.5 microns after drying and UV polymerization. Transmission and haze properties were not adversely affected relative to untreated film. It is thought that the double bonded

surfactant is able to polymerize with or bond to the curable acrylic hard-coat components in the LUV-PET-004 material. The resulting coated binder layer was homogeneous as determined by visual and microscope inspection and well-fixed on the substrate surface.

TCC emulsion as described above in Table 1, gave a good pattern with light transmission >80% when applied on this binder pre-treatment layer. The binder layer was stable over time in tests up to 18 days after being coated on the substrate. Furthermore, when the substrate was coated with the binder composition and then held in a stack of films under pressure of a 20 kg weight for 18 days, TCC coatings that were subsequently coated on top of it in the manner described above gave acceptable sheet resistance and light transmission of >80%.

What is claimed is:

1. A composition for forming a transparent conductive coating on a substrate comprising:

an organic solvent that is not miscible with water ;

water, a water-miscible solvent or combination thereof that when mixed with the organic solvent forms an emulsion having a continuous phase and a discontinuous phase; and

fine conductive particles dispersed in the solvent forming the continuous phase of the emulsion;

a UV-activated oligomer;

a UV-activated monomer; and

a photoinitiator

wherein when the composition is coated onto a surface of a substrate, exposed to UV radiation, and dried to remove the solvents, the conductive particles self-assemble to form a transparent and electrically conductive coating in the form of a network-like pattern that includes interconnected traces defining randomly-shaped cells on the surface of the substrate.

2. The composition of claim 1 wherein the conductive particles have an average particles size less than 100 nanometers.

3. The composition of claim 1 wherein the conductive particles are selected from silver, silver-copper alloy, carbon black and graphite.

4. A method of forming a transparent conductive coating on a substrate comprising:

applying the composition of claim 1 to a surface of a substrate;

exposing the coated composition to UV radiation; and

drying the composition to remove the solvents and form an article comprising the particles in the form of an electrically conductive network-like pattern that includes interconnected traces forming randomly-shaped cells on the surface of the substrate.

5. A method of forming a transparent conductive coating on a substrate comprising:

Pre-treating the substrate with a UV-activated binder composition comprising a UV-activated oligomer, a UV-activated monomer, and a photoinitiator;

exposing the pre-treated substrate to UV radiation;

coating the pre-treated and exposed substrate with a composition in the form of an emulsion comprising fine conductive particles, an organic solvent that is not miscible with water, and water or a water-miscible solvent, or combination thereof;

drying the emulsion to remove the solvents to form an article comprising the conductive particles in the form of an electrically conductive network on the surface of the substrate.

6. The method of claim 5 wherein the UV-activated binder composition further comprises a surfactant that is capable of chemically interacting with the UV-activated components of the composition.

7. The method of claim 6 wherein said surfactant comprises unsaturated alkenyl groups.

8. A composition for forming a UV-activated binder layer on a substrate comprising:

a UV-activated oligomer;

a UV-activated monomer;

a photoinitiator; and

a surfactant that is capable of chemically interacting with the UV-activated components of the composition

9. The composition of claim 8 wherein said surfactant comprised unsaturated alkenyl groups.

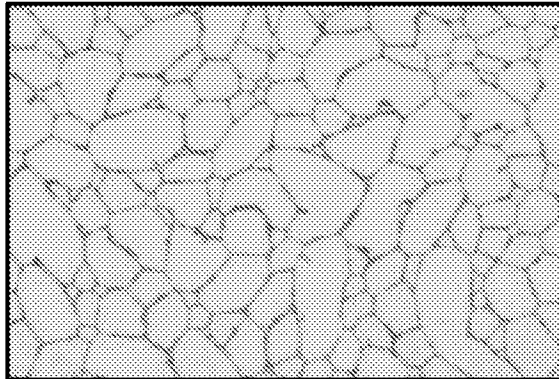
10. A method of forming a transparent conductive coating on a substrate comprising;

pre-treating the substrate by exposure to UV radiation;

coating the treated and exposed substrate with a composition in the form of an emulsion comprising fine conductive particles, an organic solvent that is not miscible with water, and water or a water-miscible solvent, or combination thereof;

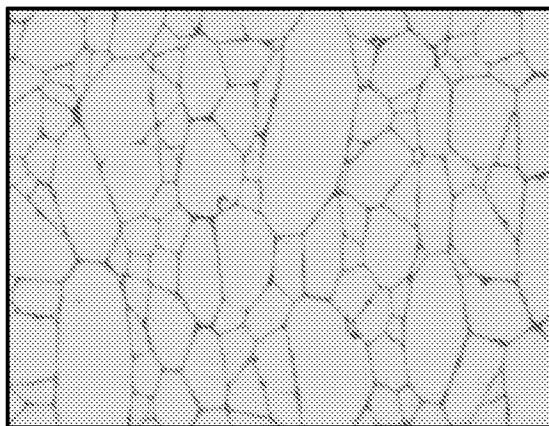
drying the emulsion to remove the solvents to form an article comprising the conductive particles in the form of an electrically conductive network on the surface of the substrate.

1/1



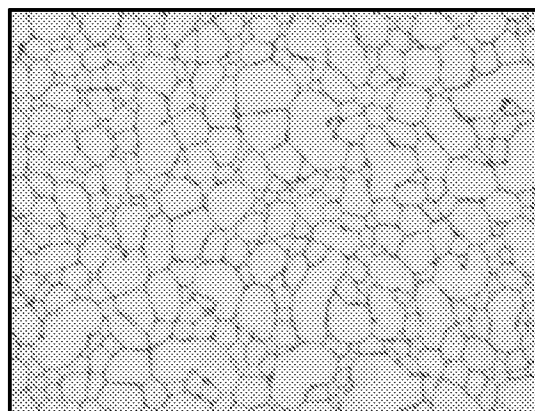
PATTERN FROM TCC
EMULSION WITH
UV-ACTIVATED
COMPONENTS

FIG. 1



PATTERN ON HF1C21
FILM FOLLOWING
UV-TREATMENT
OF FILM SUBSTRATE
AT 1.5 M/MIN

FIG. 2



PATTERN ON U46
FILM FOLLOWING
UV-TREATMENT
OF FILM SUBSTRATE
AT 2 M/MIN

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 09/46243

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B05D 1/12, 1/36 (2009.01)

USPC - 427/180,407.1

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)
USPC - 427/180,407.1Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 427/180,385.5,407.1 (text search - see search terms below)

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

PubWEST (PGPB,USPT,OC,EPAB,JPAB); DialogPro (General Research); Google Patents
too, transparent, conductive, coat, solvent, miscible, water, aqueous, emulsion, UV, activate, photo, initiate, oligomer, monomer, expose, dry, network, pattern, interconnect, trace, random, shape, particle, nm, Ag, Cu, carbon black, treat, pretreat, surfactant, alkeny

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2005/0238804 A1 (GARBAR et al.) 27 October 2005 (27.10.2005), abstract, para [0006], [0010]-[0021], [0026], [0027], [0032], [0050]-[0058] [0073], [0079]-[0086], [0089]-[0092], [0112]-[0115].	1-7 and 10
Y	US 2007/0079869 A1 (YUKINOBU) 12 April 2007 (12.04.2007), abstract, Fig. 3, para [0001], [0013]-[0016], [0034]-[0044], [0048], [0051]-[0056], [0060], [0062]-[0064], [0090], [0135].	1-7 and 10
Y	US 2006/0204718 A1 (KAWAKAMI) 14 September 2006 (14.09.2006), para [0041], [0042], [0046], [0056]-[0061], [0080]-[0084], [0121]-[0123], [0127], [0128], [0152], [0153], [0163], [0266], [0328], [0331]-[0333].	7
A	US 2006/0197814 A1 (DOI) 07 September 2006 (07.09.2006), entire document.	7
A	US 2006/0292311 A1 (KILBURN et al.) 28 December 2006 (28.12.2006), entire document.	1-7 and 10
A	US 2005/0263909 A1 (FUKUTA et al.) 01 December 2005 (01.12.2005), para [0082] (benzotriazole binders).	1-7 and 10

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

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

17 September 2009 (17.09.2009)

Date of mailing of the international search report

24 SEP 2009

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

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PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 09/46243

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
See supplemental sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-7 and 10

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US 09/46243

Box. No. III: Observations where unity of invention is lacking

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

Group I: claims 1-7 and 10: directed to a composition for forming a transparent conductive coating on a substrate comprising water, a water-miscible solvent or combination thereof that when mixed with an organic solvent forms an emulsion; and fine conductive particles; a UV-activated oligomer; a UV-activated monomer; and a photoinitiator; wherein when the composition is coated onto a surface of a substrate, exposed to UV radiation, and dried to remove the solvents, the conductive particles self-assemble to form a transparent and electrically conductive coating.

Group II: claims 8 and 9: directed to a composition for forming a UV-activated binder layer on a substrate comprising a UV-activated oligomer; a UV-activated monomer; a photoinitiator; and a surfactant that is capable of chemically interacting with the UV-activated components of the composition

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

Group I does not include the inventive concept of a surfactant that is capable of chemically interacting with the UV-activated components of the composition as required by Group II.

Group II does not include the inventive concept of an emulsion when coated onto a surface of a substrate, exposed to UV radiation, and dried to remove the solvents, the conductive particles self-assemble to form a transparent and electrically conductive coating, as required by Group I.

Groups I and II share the technical feature of a UV-activated transparent layer or coating comprising a UV-activated oligomer, a UV-activated monomer, and a photoinitiator. However, this shared technical feature does not represent a contribution over the prior art of US 2007/0079869 A1 (Yukinobu) 12 April 2007 (12.04.2007) which discloses the feature at the Abstract, and para [0039], [0049], and [0053].

Groups I and II therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.