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(54) **Title:** METHOD OF REPAIRING TRANSPARENT SUBSTRATES AND REPAIRED SUBSTRATES

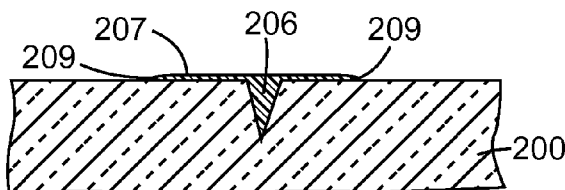


FIG. 4

(57) **Abstract:** A method of repairing a light-transmissive substrate is described comprising: providing a polymeric light-transmissive substrate comprising at least one surface defect; filling the surface defect with a polymerizable resin composition having a viscosity ranging from 25 cps to 50,000 at 25°C; applying a pressure sensitive adhesive coated light-transmissive polymeric cover film to at least the filled surface defect; and curing the polymerizable resin composition before or after applying the pressure sensitive adhesive coated film. Also described are repaired polymeric light-transmissive substrates.



METHOD OF REPAIRING TRANSPARENT SUBSTRATES AND REPAIRED SUBSTRATES**5 SUMMARY**

In one embodiment a method of repairing a light-transmissive substrate is described comprising: providing a polymeric light-transmissive substrate comprising at least one surface defect; filling the surface defect with a polymerizable resin composition having a viscosity ranging from 25 cps to 50,000 at 25°C; applying a pressure sensitive adhesive coated light-transmissive polymeric cover film to at least the filled surface defect; and curing the polymerizable resin composition before or after applying the pressure sensitive adhesive coated film.

Also described are repaired polymeric light-transmissive substrates.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional showing a (e.g. scratch) surface defect in a light-transmissive substrate;
FIG. 2 is a cross-sectional view of an over-filled scratch;
FIG. 3 is cross-sectional view showing the spreading and optional partial removal of the excess polymerizable resin;
FIG. 4 is a cross-section showing the surface defect of FIG. 1 after the surface defect has been filled with polymerizable resin;
FIG. 5 is a planar view of a filled scratch;
FIG. 6 is a cross-sectional showing the filled surface defects after application of a pressure sensitive adhesive coated cover film.

25 DETAILED DESCRIPTION

With reference to FIG. 1, the method described herein is generally useful for repairing surface defects 206 of polymeric light transmissive substrates 200 comprised of thermosetting or thermoplastic polymeric materials. Typical surface defects 206 include scratches, chips, punctures, and cracks. The method is particularly useful for repairing light transmissive substrates that comprise a low surface energy surface coating.

In one embodiment, a method of repairing a light-transmissive substrate is described. The method comprises providing a light-transmissive substrate comprising at least one surface defect, filling the surface defect with a polymerizable resin composition, applying a pressure sensitive adhesive coated

light-transmissive polymeric cover film to at least the filled surface defect; and curing the polymerizable resin composition before or after applying the adhesive coated film.

The light-transmissive substrate for repair should be relatively clean before repair. If it is not relatively clean, visible debris could become trapped in the repaired article and thus compromise the quality of the repaired surface defect. The light-transmissive substrate is typically cleaned with a lint free wipe comprising a suitable solvent, such as isopropanol, that will not mar the surface.

The surface defect is filled with the polymerizable resin composition (also referred to herein as the "repair liquid") using a suitably sized applicator, such as a cotton swab, syringe, pipette, or dental pick. With reference to FIG. 2, the polymerizable resin 207 is applied into and around the surface defect (e.g. scratch) such that the surface area of the light-transmissive substrate that is covered by the repair liquid is typically significantly greater than the surface area of the defect.

The ratio of surface area of light-transmissive substrate that is covered by the polymerizable resin to the surface area of the defect is typically at least 15:1 or 20:1 and may range up to 600:1, 700:1, 800:1, 900:1, or 1000:1. In the case of a typical scratch having a width of about 25 microns the polymerizable resin typically covers an area at least ¼ inch (6 mm) greater than the width of the scratch. In typical embodiments, the ratio of surface area of the light-transmissive substrate that is covered by the polymerizable resin repair liquid to the surface area of the defect ranges from about 50:1 to about 300:1. One advantage of the present invention is that the polymerizable resin repair liquid need not be precisely applied, which improves efficiency. Further, the excess layer of polymerizable resin on the light-transmissive substrate surrounding the filled defect is surmised to reinforce the repair.

With reference to FIG. 3, in some embodiments, excess polymerizable resin is typically spread and optionally partially removed from the surface of the polymeric light-transmissive substrate for example by dragging a planar edge of for example a razor blade 208 across the surface with minimal pressure and at a low angle (e.g. no greater than about 45 degrees). This can also aid in forcing the repair liquid into the surface defect such that the defect is entirely filled with the polymerizable resin. However, such spreading may not be needed when the viscosity of the polymerizable resin is sufficiently low at 25°C. In this embodiment, the excess polymerizable resin on the polymeric light-transmissive substrate is sufficiently thin when applied (e.g. less than 10-12 microns), such as depicted in FIG. 4. Regardless of the viscosity, the application of the adhesive coated cover film can further spread the polymerizable resin when the cover film is applied prior to curing of the polymerizable resin.

For deep defects, the process of applying the polymerizable resin and then spreading an optionally removing the excess resin may be repeated.

In some embodiments, the edges 209 of FIGS 2 and 4 of the applied polymerizable resin can be further thinned out and blended by application of a suitable solvent. However, such edge thinning is also typically not needed when the viscosity of the polymerizable resin is sufficiently low at 25°C.

The excess polymerizable resin 207 on the polymeric light-transmissive substrate 200 after application of the resin and optional spreading illustrated in FIGS. 4 and 5. The ratio of surface area of light-transmissive substrate that is covered by the polymerizable resin to the surface area of the defect is generally about the same or greater than when the polymerizable resin is first applied, yet typically still within the ranges previously described.

In some embodiments, the polymerizable resin is cured prior to application of the pressure sensitive adhesive coated light-transmissive polymeric cover film. Further, the polymerizable resin utilized to fill the surface defect is typically not a pressure sensitive adhesive. Thus, the cured polymerizable resin utilized to fill the surface defect is non-tacky after curing. This combination of attributes can be amenable to being able to replace the pressure sensitive adhesive coated light-transmissive polymeric cover film without removal of the cured repair liquid. Alternatively, the polymerizable resin of the filled surface defect can be cured after applying the pressure sensitive adhesive coated light-transmissive polymeric cover film. In some embodiments, such later technique can prevent oxygen inhibition during curing of the polymerizable resin. Further, it is surmised that this later technique can also improve the bonding force between the cured polymerizable resin of the repair and the pressure-sensitive adhesive of the cover film.

The thickness of the excess cured polymerizable resin disposed on the light-transmissive substrate is preferably no greater than 10-12 microns. When the height is too high, the cured polymerizable resin creates surface topography that can be visible when viewed off angle (an angle other than 90 degrees relative to the surface). In some embodiments, the thickness of the excess cured polymerizable resin disposed on the light-transmissive substrate is no greater than 9, 8, 7, 6, or 5 microns.

Various light-transmissive substrates can be repaired as described herein such as light-transmissive optical films that are utilized in illuminated display devices. Illustrative optical films include but are not limited to, multilayer optical films, (e.g. the planar surface of) microstructured films such as retroreflective sheeting and brightness enhancing films, (e.g. reflective or absorbing) polarizing films, diffusive films, as well as (e.g. biaxial) retarder films and compensator films such as described in U.S. Patent Application Publication No. 2004/0184150. In some embodiments, the light transmissive optical substrates are multilayer reflective polarizing films, such as described is U.S. Patent Application Publication 2003/0217806; U.S. Pat. No. 5,882,774 (Jonza et al.), and PCT Publications WO 95/17303 (Ouderkirk et al.) and WO 99/39224 (Ouderkirk et al.).

Such optical films are utilized in a variety of portable and non-portable illuminated display articles. These articles include PDAs, cell phones (including combination PDA/cell phones), LCD televisions (direct lit and edge lit), touch sensitive screens, wrist watches, car navigation systems, global positioning systems, depth finders, calculators, electronic books, computer monitors, and notebook computer displays. The viewing surfaces can have any conventional size and shape and can be planar or non-planar, although flat panel displays are most typical.

In some embodiments, the light transmissive substrate being repaired (inclusive of optical films) comprises a polymeric material such as polycarbonate, acrylic (e.g., polymethyl methacrylate or "PMMA"), polyolefins (e.g., polypropylene or "PP"), polyurethane, polyesters (e.g., polyethylene terephthalate or "PET"), polyamides, polyimides, phenolic resins, cellulose diacetate, cellulose triacetate, polystyrene.

In contrast to glass, reported to have a surface energy of about 250-500 dynes/cm², polymeric materials such as plastics generally have a surface energy of less than 100 dynes/cm², 75 dynes/cm², or 50 dynes/cm². For example, polyester is reported to have surface energy of 43 dynes/cm²; polycarbonate 42 dynes/cm²; polyvinyl chloride 39 dynes/cm²; and acrylic 38 dynes/cm². Even lower surface energy materials have a surface energy of less than 37 dynes/cm². These include for example polyvinyl acetate, polystyrene, acetal, ethylene vinyl acetate, and polyethylene reported to have a surface energy of 31 dynes/cm².

Light transmissive films that are typically exposed to the outdoor environment during use often comprise a low surface energy coating that typically comprises fluorinated or silicone additives. In some embodiments, a substrate with a low surface energy coating exhibits an advancing contact angle with water of at least 80, 90, or 100 degrees. Low surface energy materials can complicate the repair process. For example, it has been found that when one attempts to fill a surface defect, such as a scratch, with a low viscosity material, the material tends to bead up rather than fill the surface defect.

Thus one favored characteristic of the present invention is to utilize a polymerizable resin having a sufficiently high viscosity to overcome the repellency of the low surface energy surface. The viscosity of the polymerizable resin is at least 25, 30, 35, 40, 45, 50, 55, or 60 cps at 25°C (e.g. for a surface having a surface energy of 36-38 dynes/cm). It is surmised that for even lower surface energy surfaces, the minimum viscosity may be even higher. In some embodiments, the viscosity is at least 75, 100, 125, 150, 175, 200 or 225 cps at 25°C. The viscosity of the polymerizable resin can range up to 50,000 cps at 25°C, yet is typically no greater than 25,000; 20,000; 15,000; or 10,000 cps at 25°C. When the viscosity is too high, it can be difficult to spread the polymerizable resin such that the thickness is below 10-12 microns, as previously described. In some favored embodiments, the polymerizable resin has a viscosity no greater than 5,000; 4,000; 3,000; or 2,000 cps or 1,000 at 25°C.

The refractive index of the polymerizable resin generally ranges from about 1.4 to 1.6 for common polymeric light-transmissive substrates. To minimize the visibility of a repaired scratch, it is preferred that the kinds and amounts of components of the polymerizable resin are selected such that the refractive index of the polymerizable resin is sufficiently matched to the refractive index of the light-transmissive substrate. The difference in refractive index is typically no greater than 0.05.

In some embodiments, the polymerizable resin composition is a substantially solvent free polymerizable composition. "Substantially solvent free" refer to the polymerizable composition having

less than 5 wt-%, 4 wt-%, 3 wt-%, 2 wt-%, 1 wt-%, and 0.5 wt-% of (e.g. organic) solvent. The concentration of solvent can be determined by known methods, such as gas chromatography. Solvent concentrations of less than 0.5 wt-% are preferred. When the polymerizable resin comprises high solvent concentrations, the surface defect can be less than 100% filled after evaporation of the solvent. Thus, substantially solvent free polymerizable compositions are amenable to sufficiently filling the surface defects in a single application.

In other embodiments, the polymerizable resin composition is combined with an organic solvent. In this embodiment, the polymerizable resin in combination with the solvent has a viscosity ranging from 25 to 50,000 cps at 25°C. The concentration of solvent may be at least 5 wt-%, 6 wt-%, 7 wt-%, 8 wt-%, 9 wt-%, or 10 wt-% of the total composition. The solvent concentration is typically no greater than 50 wt-% and in some embodiments no greater than 45 wt-%, 40 wt-%, 35 wt-%, 30 wt-%, 25 wt-%, 20 wt-%, or 15 wt-%. Various organic solvent may be utilized such as alcohols (e.g. IPA).

The polymerizable resin composition comprises one or more ethylenically unsaturated monomers or oligomers. The polymerizable resin composition may comprise a (meth)acrylated urethane monomer or oligomer, a (meth)acrylated polyester monomer or oligomer, a (meth)acrylated phenolic monomer or oligomer, a (meth)acrylated acrylic monomer or oligomer, and mixtures thereof. In typical embodiments the polymerizable composition and thus components thereof comprises solely acrylate functionality and thus is substantially free of methacrylate functional groups. In some embodiments, the polymerizable resin and thus components thereof are non-halogenated (e.g. non-brominated).

Suitable aromatic (e.g. epoxy) (meth)acrylates are commercially available from Sartomer under the trade designations "CN104" and "CN120". In some embodiments, the aromatic epoxy acrylate is derived from bisphenol A. A suitable urethane (meth)acrylate is commercially available from UCB under the trade designations "Ebecryl 4883". Suitable phenolic (meth)acrylates are commercially available from Sartomer under the trade designation "SR601" and "SR602". Suitable polyester (meth)acrylates are commercially available from Sartomer under the trade designation "CN2297A" and "CN2261". Various bisphenol A and biphenyl di(meth) acrylate monomers and polymerizable resins comprising such are described in PCT Publication WO2008/112451; incorporated herein by reference

In some embodiments, the polymerizable composition may comprise a single di(meth)acrylate ethylenically unsaturated monomer having a number average molecular weight of greater than 450 g/mole. In other embodiments, the polymerizable composition may comprise a single (e.g. lower molecular weight) crosslinker having at least two and preferably at least three (meth)acrylate functional groups. In some embodiments, the polymerizable composition comprise at least one di(meth)acrylate ethylenically unsaturated monomer having a number average molecular weight of greater than 450 g/mole in combination with a (e.g. lower molecular weight) crosslinking agent.

The crosslinking agent comprises at least two and preferably at least three (meth)acrylate functional groups. Crosslinking agents include hexanediol diacrylate (HDDA), pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate, trimethylolpropane tri(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, and mixtures thereof.

5 Pentaerythritol triacrylate (PETA) and dipentaerythritol pentaacrylate are commercially available from Sartomer Company, Exton, PA under the trade designations "SR444" and "SR399LV" respectively; from Osaka Organic Chemical Industry, Ltd. Osaka, Japan under the trade designation "Viscoat #300"; from Toagosei Co. Ltd., Tokyo, Japan under the trade designation "Aronix M-305"; and from Eternal Chemical Co., Ltd., Kaohsiung, Taiwan under the trade designation "Etermer 235". Trimethylol propane triacrylate
10 (TMPTA) and ditrimethylol propane tetraacrylate (di-TMPTA) are commercially available from Sartomer Company under the trade designations "SR351" and "SR355". TMPTA is also available from Toagosei Co. Ltd. under the trade designation "Aronix M-309". Further, ethoxylated trimethylolpropane triacrylate and ethoxylated pentaerythritol triacrylate are commercially available from Sartomer under the trade designations "SR454" and "SR494" respectively.

15 When utilized in a mixture with at least one di(meth)acrylate ethylenically unsaturated monomer having a number average molecular weight of greater than 450 g/mole, the crosslinking agent may be present in the polymerizable composition in an amount of at least about 5 or 10 wt-%. Typically, the amount of crosslinking agent is not greater than about 95 wt-%. In some favored embodiments, the crosslinking agent may be present in an amount ranging from about 20 wt-% to no greater than 75, 70, or
20 65 wt-%.

In some embodiments, the polymerizable resin may comprise monofunctional diluents. Diluents having a refractive index greater than 1.50 (e.g. greater than 1.55) can be utilized to increase the refractive index of the polymerizable resin. Such reactive diluents may contain aromatic groups and/or sulfur atoms and/or be halogenated. Diluents typically have a number average molecular weight no greater than 450
25 g/mole include

Suitable reactive diluents include for example phenoxy ethyl (meth)acrylate; phenoxy-2-methylethyl (meth)acrylate; phenoxyethoxyethyl (meth)acrylate, 3-hydroxy-2-hydroxypropyl (meth)acrylate; benzyl (meth)acrylate, 4-(1-methyl-1-phenethyl)phenoxyethyl (meth)acrylate; phenylthio ethyl acrylate; 2-naphthylthio ethyl acrylate; 1-naphthylthio ethyl acrylate; 2,4,6-tribromophenoxy ethyl
30 acrylate; 2,4-dibromophenoxy ethyl acrylate; 2-bromophenoxy ethyl acrylate; 1-naphthyloxy ethyl acrylate; 2-naphthyloxy ethyl acrylate; phenoxy 2-methylethyl acrylate; phenoxyethoxyethyl acrylate; 3-phenoxy-2-hydroxy propyl acrylate; biphenyl monomers such as 2-phenylphenoxy ethyl acrylate and 4-phenylphenoxy ethyl acrylate; 2,4-dibromo-6-sec-butylphenyl acrylate; 2,4-dibromo-6-isopropylphenyl acrylate; benzyl acrylate; phenyl acrylate; 2,4,6-tribromophenyl acrylate. Other high refractive index
35 monomers include pentabromobenzyl acrylate and pentabromophenyl acrylate.

In some embodiments, the polymerizable resin composition further comprises nanoparticles. The inclusion of silica nanoparticles can improve the durability of the cured polymerizable resin composition. The inclusion of high refractive index particles, such as zirconia, can increase the refractive index for the purpose of index matching the polymerizable resin to the substrate being repaired, as previously
5 described. Polymerizable resins that comprise zirconia nanoparticles and monofunctional diluents that may be suitable for use in repairing (high refractive index) light transmissive substrate are described for example in WO 2008/121465; incorporated herein by reference.

The nanoparticles typically comprise a surface treatment agent. In general a surface treatment agent has a first end that will attach to the particle surface (covalently, ionically or through strong
10 physisorption) and a second end that imparts compatibility of the particle with the resin and/or reacts with resin during curing. Examples of surface treatment agents include alcohols, amines, carboxylic acids, sulfonic acids, phosphonic acids, silanes and titanates. The preferred type of treatment agent is determined, in part, by the chemical nature of the metal oxide surface. Silanes are preferred for silica and other for siliceous fillers. Silanes and carboxylic acids are preferred for metal oxides such as zirconia. The surface
15 modification can be done either subsequent to mixing with the monomers or after mixing. It is preferred in the case of silanes to react the silanes with the particle or nanoparticle surface before incorporation into the resin. The required amount of surface modifier is dependent upon several factors such as particle size, particle type, modifier molecular wt, and modifier type. In general it is preferred that approximately a monolayer of modifier is attached to the surface of the particle. The attachment procedure or reaction
20 conditions required also depend on the surface modifier used. For silanes it is preferred to surface treat at elevated temperatures under acidic or basic conditions for from 1-24 hr approximately. Surface treatment agents such as carboxylic acids may not require elevated temperatures or extended time.

The surface modified colloidal nanoparticles can be oxide particles having a primary particle size or associated particle size of greater than 1 nm or 5 nm and less than 100 nm, 75 nm or 50 nm. It is
25 preferred that the nanoparticles are unassociated. Their measurements can be based on transmission electron microscopy (TEM). The nanoparticles can include metal oxides such as, for example, alumina, tin oxides, antimony oxides, silica, zirconia, titania, mixtures thereof, or mixed oxides thereof. Surface modified colloidal nanoparticles can be substantially fully condensed.

Silica nanoparticles can be present in the durable article or optical element in an amount from 10
30 to 60 wt-%, or 10 to 40 wt-%. Silicas for use in the polymerizable resins are commercially available from Nalco Chemical Co., Naperville, IL under the trade designation "Nalco Colloidal Silicas" such as products 1040, 1042, 1050, 1060, 2327 and 2329. Suitable fumed silicas include for example, products commercially available from DeGussa AG, (Hanau, Germany) under the trade designation, "Aerosil series OX-50", as well as product numbers -130, -150, and -200. Fumed silicas are also commercially
35 available from Cabot Corp., Tuscola, I, under the trade designations CAB-O-SPERSE 2095", "CAB-O-SPERSE A105", and "CAB-O-SIL M5". The UV curable polymerizable compositions comprise at least one photoinitiator.

A single photoinitiator or blends thereof may be employed in the polymerizable resin. In general the photoinitiator(s) are at least partially soluble (e.g. at the processing temperature of the resin) and substantially colorless after being polymerized. The photoinitiator may be (e.g. yellow) colored, provided that the photoinitiator is rendered substantially colorless after exposure to the UV light source.

5 Suitable photoinitiators include monoacylphosphine oxide and bisacylphosphine oxide. Commercially available mono or bisacylphosphine oxide photoinitiators include 2,4,6-trimethylbenzoyldiphenylphosphine oxide, commercially available from BASF (Charlotte, NC) under the trade designation "Lucirin TPO"; ethyl-2,4,6-trimethylbenzoylphenyl phosphinate, also commercially available from BASF under the trade designation "Lucirin TPO-L"; and bis (2,4,6-trimethylbenzoyl)-
10 phenylphosphine oxide commercially available from Ciba Specialty Chemicals under the trade designation "Irgacure 819". Other suitable photoinitiators include 2-hydroxy-2-methyl-1-phenyl-propan-1-one, commercially available from Ciba Specialty Chemicals under the trade designation "Darocur 1173" as well as other photoinitiators commercially available from Ciba Specialty Chemicals under the trade designations "Darocur 4265", "Irgacure 651", "Irgacure 1800", "Irgacure 369", "Irgacure 1700", and
15 "Irgacure 907".

The photoinitiator can be used at a concentration of about 0.1 to about 10 weight percent. More preferably, the photoinitiator is used at a concentration of about 0.5 to about 5 wt-%.

The polymerizable resin can optionally further comprise one or more additives including but not limited to those selected from the group consisting of flame retardants, ultraviolet light absorbers,
20 antioxidants, and hindered amine stabilizers.

After the surface defect is filled with polymerizable resin, a pressure sensitive adhesive coated light-transmissive cover film is applied to at least the filled surface defect and typically to the entire surface of the substrate being repaired. Thus, the pressure sensitive adhesive of the cover film is contacted with the polymerizable resin of the filled defect and the surface of the repaired light-
25 transmissive substrate. In some embodiments, a major portion (i.e. at least 50%) of the light-transmissive substrate surface lacks polymerizable resin of the filled surface defects and directly contacts the pressure sensitive adhesive of the cover film.

Although the polymerizable resin utilized to fill the defect(s) can be cured or uncured when the cover film is applied, the polymerizable resin is cured during the repair process. Thus, the repaired
30 polymeric light transmissive substrate comprises at least one surface defect filled with cured polymerizable resin.

The purpose of the cover film is to provide a new undamaged surface in place of the damaged substrate surface. The cover film may also provide protection of the repaired substrate. The cover film is transparent such that it does not detract from the observer's ability to distinguish (e.g. illuminated)
35 images underlying the cover film. The cover film is not applied as a gel or a flowable liquid but is rather a "solid" preformed film. The "solid" nature of the cover film facilitates and expedites application

thereof. Uniformity of the cover film is helpful in providing a final laminate article in which the underlying filled surface defects (e.g. repaired scratch) are not apparent.

The cover film is typically comprised of a polymeric material, such as the previously described light transmissive substrate polymeric material. The thickness of the cover film (inclusive of the pressure sensitive adhesive) is typically at least about 1, 1.5 or 2 mils and generally no greater than about 10 mils. When the cover film is applied such that it covers substantially the entire repaired substrate, the cover film typically has substantially the same length and width as the repaired substrate.

The transmission of both the light-transmissive substrate and the cover film is typically at least about 90%. In some embodiments, the cover film is a light transmissive film in the optical path of the display that substantially alters at least one optical property as compared to viewing the display in the absence of the over film. Thus the cover film may be an antiglare film, an antireflective film, as well as certain films having a coating that reduces the visibility of fingerprints such as described in U.S. Application Serial No. 13/307,137, filed 30 November 2011; incorporated herein by reference. Films that reduce the visibility of fingerprints exhibit a ratio of initial simulated fingerprint visibility to simulated fingerprint visibility at 20 minutes of less than 0.80, 0.70, 0.60, or 0.50.

Various antiglare films have been described in the art. As described at paragraph 0039 of U.S. Publication No. 2007/0286994, matte antireflective films typically have lower transmission and higher haze values than equivalent gloss films. For examples the haze is generally at least 5%, 6%, 7%, 8%, 9%, or 10% as measured according to ASTM D1003. Further gloss surfaces typically have a gloss of at least 130 as measured according to ASTM D 2457-03 at 60°; whereas matte surfaces have a gloss of less than 120. Gloss film also typically have a haze of less than 4%, 3% or 2%.

There are several approaches for obtaining matte films. For example, matte coating can be prepared by adding matte particles, such as described in U.S. 6,778,240. In yet another approach, the surface of an antiglare film can be roughened or textured to provide a matte surface. According to U.S. Patent No. 5,820,957; "the textured surface of the anti-reflective film may be imparted by any of numerous texturing materials, surfaces, or methods. Non-limiting examples of texturing materials or surfaces include: films or liners having a matte finish, microembossed films, a microreplicated tool containing a desirable texturing pattern or template, a sleeve or belt, rolls such as metal or rubber rolls, or rubber-coated rolls." In some embodiments, the antiglare film may have certain microstructure characteristics that can be obtained by microreplication, such as described in WO2010/141345; incorporated herein by reference.

Various antireflective films have also been described in the art. As used herein, antireflective film refers to a film that provides an average reflectance of no greater than about 2% or about 1.5% at 550 nm as measured with a spectrophotometer. Antireflective films generally comprise at least two layers having differing refractive indices. Some illustrated antireflective films are described in U.S. Patent Publication No. US2010/0232021 and PCT Publication No. WO2011/140018; incorporated herein by reference.

The cover film may optionally further comprise additives such as, for example, flame retardants, ultraviolet light absorbers, antioxidants, and hindered amine stabilizers, and combinations thereof. The cover film may optionally further comprise an abrasion resistant coating (e.g. hardcoat) on the exposed surface (i.e. that is not in contact with the repaired substrate surface). Further, the cover film may
5 comprise a (e.g. fluorinated or silicone-containing) low surface energy coating.

The cover film may optionally be primed to enhance adhesion with the applied pressure sensitive adhesive. The primers may include, for example, surface treatments such as corona treatments or flame treatments.

Various permanent and removable grade pressure sensitive adhesive compositions may be coated
10 on the cover film. The pressure sensitive adhesive is generally self-adherent to the light transmissive substrate being repaired, compliant, and at least somewhat tacky. Suitable adhesive compositions include (e.g. hydrogenated) block copolymers such as those commercially available from Kraton Polymers of Westhollow, Texas under the trade designation "Kraton G-1657", as well as other (e.g. similar) thermoplastic rubbers. Other exemplary adhesives include acrylic-based, urethane-based, silicone-based,
15 and epoxy-based adhesives. Preferred adhesives are of sufficient optical quality and light stability such that the adhesive does not yellow with time or upon weather exposure so as to degrade the viewing quality of the optical display. The adhesive can be applied using a variety of known coating techniques such as transfer coating, knife coating, spin coating, die coating and the like. Exemplary adhesives are described in U.S. Patent Application Publication No. 2003/0012936. Several of such adhesives are
20 commercially available from 3M Company, St. Paul, MN under the trade designations 8141, 8142, and 8161. Other exemplary adhesives include urea-based and urethane-based "self wetting adhesives", such as described in WO2009/085662 and WO2010/132176; incorporated herein by reference.

The pressure sensitive adhesive of the cover film is chosen such that the peel force to the repaired surface of the light-transmissive substrate is at least 5, 10, or 15 g/ inch. If the peel force is too low, the
25 pressure sensitive adhesive can "release" from the repair light-transmissive, allowing air bubbles to form along the edge of the repair causing the repair to become visible. In some embodiments, the peel force is no greater than about 3,000 or 2,000 g/inch (or sufficiently low such that the light-transmissive substrate is not damaged upon removal of the cover film) to facilitate subsequent replacement of the pressure-sensitive adhesive coated cover film.

The thickness of the pressure-sensitive adhesive layer is typically at least 0.5 or 1 mil to about 2
30 mils. The thickness of the pressure-sensitive adhesive layer is generally greater than the thickness of the excess cure polymerizable resin of the repaired substrate surface.

Prior to application a release liner protects the surface of the pressure sensitive adhesive layer of the cover film. Useful release liners include, for example, polyester or polyolefin films. These films may

be coated with silicone or fluorinated release surfaces to facilitate release from the bonding layer. For added dimensional stability, the release liner may comprise a film and paper laminate.

Suitable (e.g. polyester) cover films that comprise a pre-applied pressure sensitive adhesive include for example “ARMR220 NC Protection Film”, “Natural View Antiglare Protection Film”, and “Smooth Cling Films 7717SW, 7718SW, and 7719SW”; all available from 3M, St. Paul, MN.

5

Examples

All parts, percentages, ratios, etc. in the examples are by weight, unless noted otherwise.

Materials

Trade Designation or Abbreviation	Material	Supplier
CN104A60	Difunctional bisphenol A based epoxy acrylate blended with tripropylene glycol diacrylate	Sartomer Company, Exton, PA
CN2297A	Polyester acrylate	Sartomer Company, Exton, PA
DAROCUR 4265	Photoinitiator	BASF, Mount Olive, NJ
EPONEX 1510	Epoxy resin	Momentive Specialty Chemicals, Inc. Houston, TX
GLR310	Low reflection film	3M Company, St. Paul, MN
JEFFAMINE T-403	Amine curing agent	Huntsman Performance Products, Conroe, TX
MFSP	Methacrylate functionalized silica particles	Prepared as described in U.S. Patent Publication No. US2012/0154811
SR238B	1,6 hexanediol diacrylate	Sartomer Company, Exton, PA
SR351LV	Low viscosity trimethylolpropane triacrylate	Sartomer Company, Exton, PA
SR415	Ethoxylated(20) trimethylolpropane triacrylate	Sartomer Company, Exton, PA
SR444	Pentaerythritol triacrylate	Sartomer Company, Exton, PA
SR494	Ethoxylated Pentaerythritol tetraacrylate	Sartomer Company, Exton, PA
SR602	Ethoxylated bisphenol A diacrylate	Sartomer Company, Exton, PA
TRPGDA	Tri(propylene glycol) diacrylate	Available as SR306F from Sartomer Company, Exton, PA

Examples 1-14 and Comparative Example C1

A scratched LCD display panel (model B141EW05 V3 14.1" WXGA Color TFT-LCD with LED Backlight design, by AU Optonics Corporation of Hsinchu Taiwan, manufactured in China) having a TAC polarizer as the outer surface was obtained. The scratches were examined with a high resolution optical microscope and found to have widths varying from about 8 microns to about 150 microns and lengths varying from about 1 mm to about 30 mm.

Mixtures were prepared according to the table below. The viscosities for Examples 2-7 were estimated by interpolating based on weight percent between the values specified by the manufacturer for SR602 and SR351LV. Viscosities for Examples 9, 12-14 and Comparative Example C1 were measured with a Brookfield model DV-E viscometer (available from Brookfield Engineering Laboratories, Inc., Middleboro, MA) at 25°C. For the other Examples the viscosities are as specified by the manufacturer.

A cotton swab was dipped into the polymerizable resin described in the table below and then wiped across a scratch, overfilling the scratch with the polymerizable resin. A cover film (GLR310 cover film for Examples 1-8 and ARMR220 cover film for Examples 9-14 and Comparative Example C1) was applied over the filled scratch and a hand roller was used to flatten the film against the display. This caused the resin to spread out well beyond the edges of the scratch. For Example 13, a razor blade was used to spread out the polymerizable resin prior to applying the cover film.

After the cover film was applied, the polymerizable resin was cured. For Examples 1-8, the solution was UV cured by passing the filled screen under H and D bulbs at 12.8 m/min (42 ft/min). The UV dose (in the UVA, UVB, UVC and UVV wavelength bands) was measured by a UV Power Puck (available from EIT Inc., Sterling VA) and found to be UVA: 1.568 J/cm², UVB: 0.443 J/cm², UVC: 0.105 J/cm², and UVV: 0.901 J/cm². For Example 14, the epoxy formulation was not UV cured but cured upon standing at 25°C. For all other Examples, a UV cure was performed by placing the samples 5 cm (2 inches) from the bulb of a Spectroline SB-100P UV Lamp (Spectronics Corporation, Westbury, NY) for 1 minute.

The repaired area was inspected to determine the visibility of the scratch and the visibility of the edge of the cured polymerizable resin on the substrate surface typically caused from the cover film lifting off the repaired substrate. The results are provided in the table below.

Ex.	Resin	Viscosity at 25 °C (cps)	Repaired scratch visible?	Repair edge visible?
1	100:0.5 w/w SR351LV and DAROCUR 4265	65	Yes	No
2	7:93:0.5 w/w SR602, SR351LV and DAROCUR 4265	103	Yes	No
3	25:75:0.5 w/w SR602, SR351LV and DAROCUR 4265	201	Yes	No
4	35:65:0.5 w/w SR602, SR351LV and DAROCUR 4265	256	No	No
5	44:56:0.5 w/w SR602, SR351LV and DAROCUR 4265	305	No	No
6	62:38:0.5 w/w SR602, SR351LV and DAROCUR 4265	403	No	No
7	80:20:0.5 w/w SR602, SR351LV and DAROCUR 4265	501	No	No
8	100:0.5 w/w SR602 and DAROCUR 4265	610	No	No
9	100:1 w/w CN104A60 and DAROCUR 4265	3450	No	No
10	100:1 w/w SR415 and DAROCUR 4265	225	No	No
11	100:1 w/w SR494 and DAROCUR 4265	150	No	No
12	100:1 w/w CN2297A and DAROCUR 4265	6430	No	No
13	30:70:1 w/w MFSP, SR444 and DAROCUR 4265	778	No	No
14	2:1 w/w EPONEX 1510 and JEFFAMINE T-403	750	No	No
C1	100:1 w/w TRPGDA and DAROCUR 4265	19	Yes	Yes

Example 11 shows that using polymerizable resins with viscosities less than about 200 cps can result in an invisible repaired scratch. In Examples 1-3 the scratch was visible because air was entrapped in the scratches surmised to be created by repellency of the low viscosity polymerizable resin. This illustrates that it is more difficult to achieve an invisible scratch using

polymerizable resins with viscosities less than about 200 cps than it is when higher viscosity solutions are used. Using an even lower viscosity as in Comparative Example C1 resulted in both the scratch being visible and the edge of the applied solution being visible. Examples 9 and 12 show that using higher viscosity polymerizable resins can result in an invisible repaired scratch.

5 However, it is increasingly difficult to flatten the deposited polymerizable resin when the cover film is laminated as the viscosity of the polymerizable resin increases.

Comparative Example C2

10 For Comparative Example C2, a sample was prepared as in Example 11 except that the polymerizable resin was not cured. Initially the scratch was not visible, but after 24 hours the scratch became visible. In Example 11, the scratch was still invisible after 24 hours.

Comparative Example C3

15 A polymerizable resin was prepared by blending 18.35 grams of SR238B, which has a manufacturer specified viscosity of 9 cps at 25°C, with 0.14 grams of DAROCUR 4265. The polymerizable resin was applied to an LCD panel and laminated with a cover film as described in Example 1. Within 2 minutes of laminating and before curing the sample, the filled scratch was visible.

What is claimed is:

1. A method of repairing a light-transmissive substrate comprising:

providing a polymeric light-transmissive substrate comprising at least one surface defect;

5 filling the surface defect with a polymerizable resin composition having a viscosity ranging from 25 cps to 50,000 at 25°C;

applying a pressure sensitive adhesive coated light-transmissive polymeric cover film to at least the filled surface defect; and

curing the polymerizable resin composition before or after applying the adhesive coated film.

10 2. The method of claim 1 wherein the light-transmissive substrate comprises a low surface energy coating comprising silicone or fluorine.

15 3. The method of claims 1-2 wherein the surface defect is filled with an excess of polymerizable resin such that a ratio of the surface defect surface area to area of substrate covered by the polymerizable resin is at least about 1 to 15.

4. The method of claims 1-3 wherein the polymerizable resin has a viscosity ranging from 100 cps to 1,000 at 25°C.

20 5. The method of claims 1-4 wherein the polymerizable resin is non-tacky after curing.

25 6. The method of claims 1-5 wherein the polymeric light-transmissive substrate is selected from polycarbonate, acrylic, polyolefin, polyurethane, polyesters, polyamides, polyimides, phenolic resins, cellulose diacetate, cellulose triacetate, polystyrene.

7. The method of claims 1-6 wherein the polymerizable resin is substantially solvent free.

30 8. The method of claim 1-6 wherein the polymerizable resin in combination with a solvent has a viscosity ranging from 25 cps to 50,000 at 25°C.

9. The method of claims 1-8 wherein the polymerizable resin comprises at least one di(meth)acrylate monomer or oligomer.

35 10. The method of claim 9 wherein the di(meth)acrylate monomer or oligomer is a bisphenol A or biphenyl di (meth)acrylate.

11. The method of claim 10 wherein the di(meth)acrylate monomer or oligomer is an ethoxylated or propoxylated (meth)acrylate monomer.

12. The method of claims 1-11 wherein the di(meth)acrylate monomer or oligomer is an epoxy or urethane.

13. The method of claims 1-12 wherein the polymerizable resin comprises at least one crosslinker comprising at least three (meth)acrylate groups.

14. The method of claims 1-13 wherein the polymerizable resin comprising comprises at least one di(meth)acrylate monomer and at least one crosslinker comprising at least three (meth)acrylate groups.

15. The method of claims 1-14 wherein the pressure sensitive adhesive coated cover film has a peel force to the polymeric light-transmissive of at least 5 g/inch.

16. The method of claims 1-15 wherein the surface defect is filled with an excess of polymerizable resin and the excess resin is spread and partially removed from the light transmissive substrate surface.

17. The method of claims 1-16 wherein the surface defect is filled with an excess of polymerizable resin and solvent is applied to edges of the excess polymerizable resin to thin edges.

18. The method of claims 1-17 wherein the polymerizable resin is cured after applying a pressure sensitive adhesive coated light-transmissive polymeric cover film.

19. The method of claims 1-18 wherein the pressure sensitive adhesive coated light-transmissive polymeric cover film is applied such that it covers an entire surface of the light-transmissive substrate.

20. The method of claim 19 wherein a major portion of the light-transmissive surface lacks cured polymerizable resin of the filled surface defects and directly contacts the pressure sensitive adhesive of the cover film.

21. The method of claims 1-20 wherein the light-transmissive cover film is a matte or gloss film.

22. A repaired light-transmissive substrate comprising:

a polymeric light-transmissive substrate comprising a low surface energy coating and at least one surface defect filled with a cured polymerizable resin composition having a viscosity ranging from 25 cps to 50,000 at 25°C prior to curing; and

a pressure sensitive adhesive coated light-transmissive polymeric cover film disposed upon the light-transmissive substrate such that it cover the filled surface defect.

23. A repaired light-transmissive substrate comprising:

- 5 a polymeric light-transmissive substrate comprising at least one surface defect filled with a cured non-tacky polymerizable resin composition having a viscosity ranging from 25 cps to 50,000 at 25°C prior to curing; and
- a pressure sensitive adhesive coated light-transmissive polymeric cover film disposed upon the light-transmissive substrate such that it cover the filled surface defect.

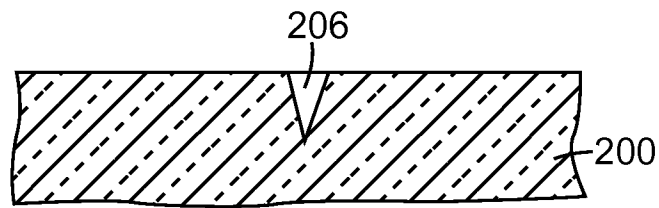
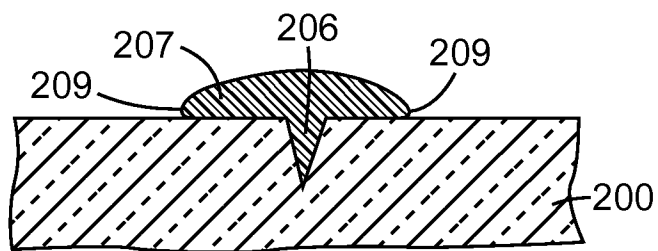
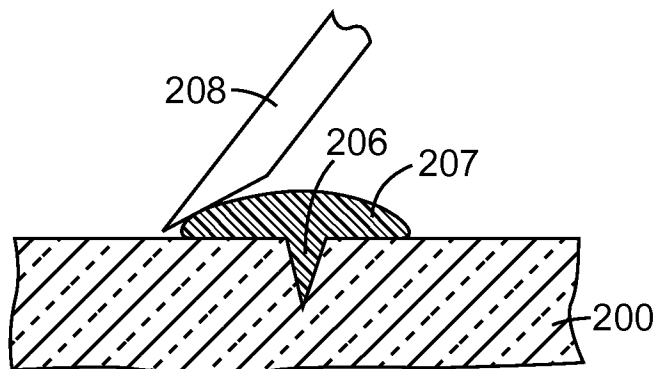
10

24. The repaired light-transmissive substrate of claims 22-23 wherein the substrate, polymerizable resin, or cover film are further characterized by any one or combination of features of claims 1-21.

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1/2

**FIG. 1****FIG. 2****FIG. 3**

2/2

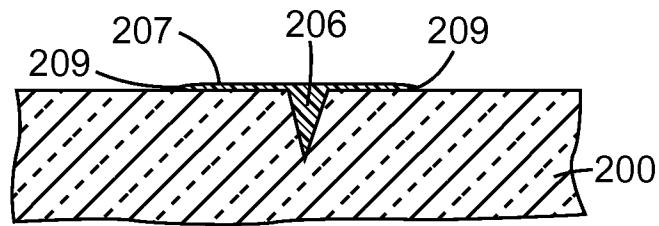


FIG. 4

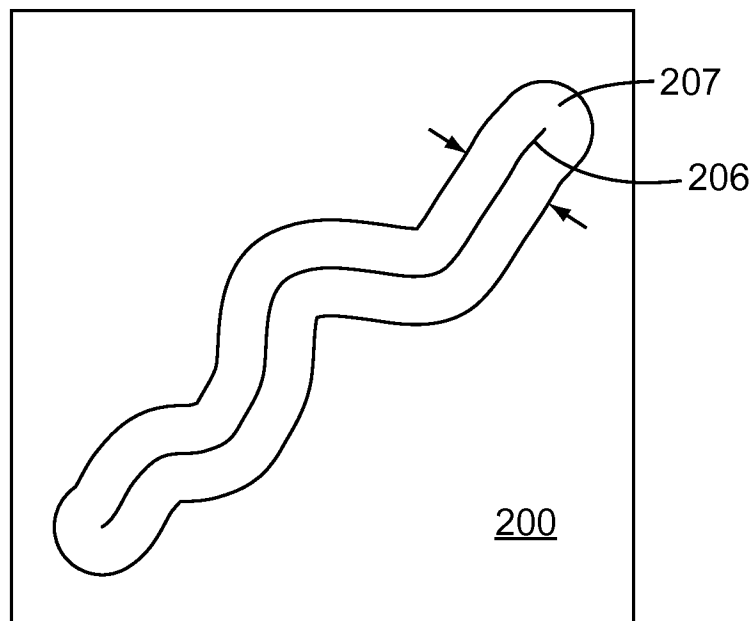


FIG. 5

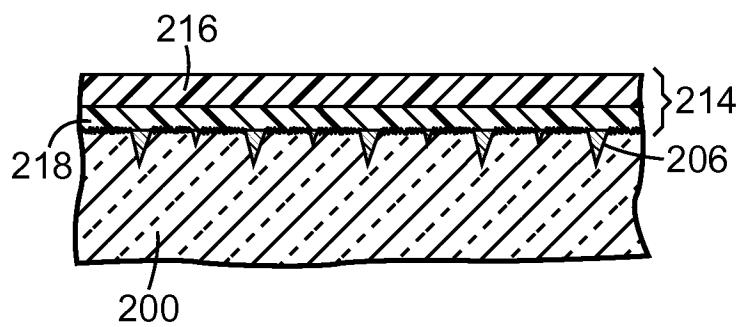


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/030113**A. CLASSIFICATION OF SUBJECT MATTER****B29C 73/02(2006.01)i, C08J 7/04(2006.01)i**

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)

B29C 73/02

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: repair, substrate, plate, film, panel, defect, scratch, chip, puncture, crack, fault, flaw, resin, viscosity, pressure sensitive, adhesive**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 05-150205 A (SHARP CORP.) 18 June 1993 See abstract; claim 1 and figures 1-5.	1, 2, 22, 23
A	US 2007-0014984 A1 (STOUT, G. M. et al.) 18 January 2007 See abstract; claim 19 and figure 2.	1, 2, 22, 23
A	JP 10-000426 A (KANSAI PAINT CO., LTD.) 06 January 1998 See abstract and claim 1.	1, 2, 22, 23
A	US 2007-0139607 A1 (NAM, S. H. et al.) 21 June 2007 See abstract; claim 1 and figure 3.	1, 2, 22, 23
A	JP 06-280400 A (NATL HOUSE IND CO., LTD.) 04 October 1994 See abstract; claim 1 and figure 1.	1, 2, 22, 23
A	JP 2006-336188 A (KONISHI CO., LTD.) 14 December 2006 See abstract; claims 1-3, figures 1-2.	1, 2, 22, 23



Further documents are listed in the continuation of Box C.



See patent family annex.

* 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 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

19 June 2013 (19.06.2013)

Date of mailing of the international search report

20 June 2013 (20.06.2013)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
189 Cheongsu-ro, Seo-gu, Daejeon Metropolitan City,
302-701, Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

HONG, Sung Ran

Telephone No. 82-42-481-5405



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/030113

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.: 10, 11, 20
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:
Claims 10, 11 and 20 are unclear because they refer to multiple dependent claims 9, 10 and 19 which do not comply with PCT Rule 6.4(a)

3. ☒ Claims Nos.: 3-9, 12-19, 21, 24
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:

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 an additional fee, this Authority did not invite payment of any additional fee.

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.:

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/US2013/030113

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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JP 2006-336188 A	14.12.2006	JP 4629501 B2	09.02.2011