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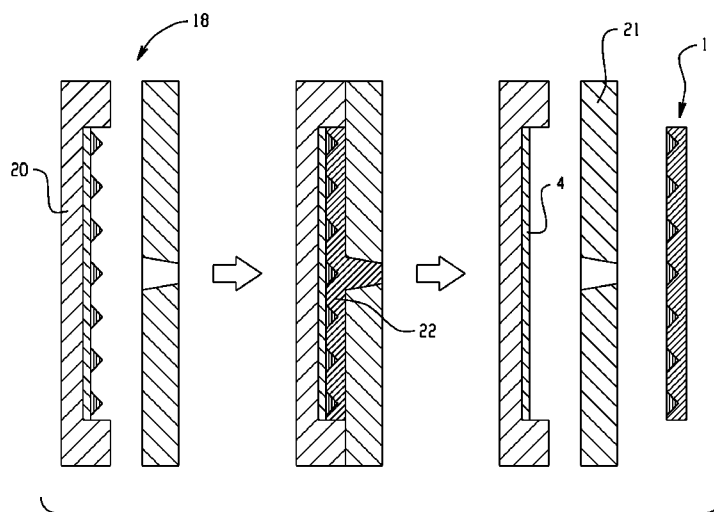


Fig. 2B

(57) Abstract: A method of making an integrated surface heater includes: depositing an integrated conductive film to a resin side of an injection mold, wherein the integrated conductive film includes a polymeric film and a heating medium network extending across a surface of the polymeric film, wherein the heating medium network comprises a conductive coating including nanometer sized metal particles arranged in a network; closing the mold; injecting a polymeric material into the mold to form a mold shaped substrate; injection molding the integrated conductive film and the substrate to form the integrated surface heater; embedding the heating medium network into the substrate; cooling the mold; opening the mold; and ejecting the formed integrated surface heater from the mold, wherein the integrated surface heater has a three-dimensional shape.

INTEGRATED SURFACE HEATER AND COMPONENTS THEREOF AND METHODS OF MAKING THE SAME

BACKGROUND

[0001] Heat can be generated by applying a current to a conductive film. Heating electrodes can be attached to the conductive film with the use of thermal conductive glue. Thermal conductive glue can reduce conductive efficiency and increase assembly cost and provide a complicated assembly process. Conventional electric heaters such as cartridge, tubular, bent, cast heater, etc. are designed to heat only a limited area and circulate air or water to disperse the heat. As a result, these heaters can include a portion of the heater having a very high temperature (e.g., a hot spot), which can require a high heat resistant material surrounding the heater and can provide for limited designs.

[0002] Thus, there is a need in the art for integrated surface heaters with increased conductive efficiency, as well as a less complex and costly assembly process.

BRIEF DESCRIPTION

[0003] An injection molded integrated surface heater, includes: a polymeric film; a heating medium network extending across a surface of the polymeric film, wherein the heating medium network comprises a conductive coating including nanometer sized metal particles arranged in a network; wherein the polymeric film and the heating medium network comprise an integrated conductive film; and a three-dimensional substrate injection molded to the integrated conductive film, wherein the substrate comprises a material selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK), or a combination comprising at least one of the foregoing and wherein the substrate material further includes particles, fibers, wires, or a combination comprising at least one of the foregoing.

[0004] A method of making an integrated surface heater, includes: depositing an integrated conductive film to a resin side of an injection mold, wherein the integrated conductive film includes a polymeric film and a heating medium network extending across a surface of the polymeric film, wherein the heating medium network comprises a conductive coating including nanometer sized metal particles arranged in a network; closing the mold; injecting a polymeric material into the mold to form a mold shaped substrate, wherein the polymeric material is selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone

(PEEK), or a combination comprising at least one of the foregoing and wherein the polymeric material further includes particles, fibers, wires, or a combination comprising at least one of the foregoing; injection molding the integrated conductive film and the substrate to form the integrated surface heater; embedding the heating medium network into the substrate; cooling the mold; opening the mold; and ejecting the formed integrated surface heater from the mold, wherein the integrated surface heater has a three-dimensional shape.

[0005] A method of making an injection molded integrated surface heater, includes: depositing a sheet to a resin side of an injection mold, wherein the sheet comprises a first polymeric film with a heating medium network extending across a surface of the first polymeric film and a second polymeric film comprising a thermally transferable polymer extending across the same surface of the first polymeric film, wherein the heating medium network comprises a conductive coating including nanometer sized metal particles arranged in a network; closing the mold; injecting a polymeric material into the mold to form a mold shaped substrate, wherein the polymeric material is selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK), or a combination comprising at least one of the foregoing and wherein the polymeric material further includes particles, fibers, wires, or a combination comprising at least one of the foregoing; injection molding the sheet to the substrate to form the integrated surface heater; embedding the second polymeric film and the heating medium network into the substrate, wherein the second polymeric film acts as a protective coating over the heating medium network; cooling the mold; opening the mold; and ejecting the formed integrated surface heater from the mold, wherein the integrated surface heater has a three-dimensional shape.

[0006] A method of making a thermoformed integrated heater, includes: depositing an integrated conductive film comprising a polymeric film and a heating medium network extending across a surface of the polymeric film to a first mold having a first mold surface, wherein the heating medium network comprises a conductive coating including nanometer sized metal particles arranged in a network; placing a polymeric sheet on top of the integrated conductive film, wherein the polymeric sheet comprises a material selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK), or a combination comprising at least one of the foregoing and wherein the substrate material further

includes particles, fibers, wires, or a combination comprising at least one of the foregoing; positioning a second mold having an opposing mold surface to the first mold surface over the first mold surface; bringing the first mold and the second mold toward one another with vacuum pressure to form the thermoformed integrated surface heater comprising the integrated conductive film; opening the first mold and the second mold; and extracting the integrated surface heater from the first mold, wherein the integrated surface heater is substantially free of void content.

[0007] A method of making a stamped integrated heater, includes: depositing an integrated conductive sheet to a press, wherein the integrated conductive sheet comprises a first polymeric film with a heating medium network extending across a surface of the first polymeric film and a second polymeric film comprising a thermally transferable polymer extending across the same surface of the first polymeric film, wherein the heating medium network comprises a conductive coating including nanometer sized metal particles arranged in a network; heating a pad stamper; pressing the pad stamper to an opposite surface of the first polymeric film as the heating medium network and the second polymer film; molding the sheet to a substrate to form the integrated heater, wherein the substrate comprises a material selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK), or a combination comprising at least one of the foregoing and wherein the substrate material further includes particles, fibers, wires, or a combination comprising at least one of the foregoing; embedding the second polymeric film and the heating medium network into the substrate by pressing on the pad stamper, wherein the second polymeric film acts as a protective coating over the heating medium network; releasing the pad stamper; and removing the stamped integrated surface heater.

[0008] The above described and other features are exemplified by the following figures and detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Refer now to the figures, which are exemplary embodiments, and wherein the like elements are numbered alike.

[0010] FIG. 1 is a view of one example of a network's shape on a film.

[0011] FIG. 2A is a view of an integrated conductive film without a transfer resin.

[0012] FIG. 2B is a schematic representation of a film insert molding process.

[0013] FIG. 3 is an exploded view of an integrated surface heater with an ultraviolet resin.

[0014] FIG. 4A is a view of an integrated conductive film with a transfer resin.

[0015] FIG. 4B is a schematic representation of another film insert molding process.

[0016] FIG. 5A is a view of an integrated conductive film.

[0017] FIG. 5B is a schematic representation of a thermoforming process.

[0018] FIG. 6 is a schematic representation of a stamping process.

[0019] FIG. 7 is an exploded view of an automotive head lamp.

[0020] FIG. 8 is an exploded view of an automotive side mirror.

[0021] FIG. 9 is a view of a bidet heater having a switch function and a conductive network.

[0022] FIG. 10 is a graphical representation of the temperature increase over time of an integrated surface heater at varying voltages and initial temperatures.

[0023] FIG. 11 is a graphical representation of the temperature rise over time of an integrated surface heater at varying voltages.

DETAILED DESCRIPTION

[0024] The integrated surface heaters disclosed can provide a transparent, surface heating, and thermally conductive solution for various applications including, but not limited to, home appliance, automotive, medical, building and construction, mass transportation, and office supply. The integrated surface heater can include heating medium networks dispersed on or embedded within a surface of the heater. The heating medium networks can vary in shape and can include various shapes, including, but not limited to, particles, wires, fibers, coils, etc., or a combination comprising at least one of the foregoing. The integrated surface heater can be applied to many processable objects, regardless of shape, color, material, etc. The integrated surface heaters can provide defogging/defrosting solutions for a variety of applications including mirrors, glass, housings, etc. which can require both transparency and heating ability in for example, automotive applications. The integrated surface heaters can also provide defogging/defrosting solutions for applications such as bidets, bathroom mirrors, refrigerator windows, hair dryers, water boilers, chair warmers, transparent toasters, etc. in other various appliances. The integrated surface heaters can provide heat dispersion by functioning as a heat sink in mobile housing and thermal chromic sign boards.

[0025] Other heating solutions such as a cartridge heater can include a heating sheet and thermal conductive glue for assembly. However, the use of thermal conductive glue can reduce heat conductive efficiency and can increase the assembly cost and can increase the complexity of

assembly. Other surface heating solutions can have difficulty achieving transparency. Other surface heating solutions (e.g., conventional heating solutions such as a cartridge heater) can heat only a limited area, which is not efficient and often times need a circulating fan to circulate the heat. Other surface heating solutions (e.g., conventional heating solutions such as a cartridge heater) can create “hot-spots”, which can adversely affect surrounding mechanical parts and can require the use of a high heat resistant material. “Hot-spots” can be created in other surface heaters due to the use of a nickel-chromium (Ni-Cr) rod or coil for limited space heating. Other surface heaters can require a longer response time (e.g., lead time) for heating the object to the target temperature. Other surface heaters can only be applied to a planar or bar/band heater, limiting the designs and shapes of the heater and requires a complex circuit design to heat the surface uniformly.

[0026] The integrated surface heaters can improve heat efficiency in a variety of ways. For example, heat efficiency can be improved with the integrated surface heaters disclosed herein. For example, with the use of film insert molding to produce the integrated surface heaters, the heating medium can be embedded directly into the target object thereby removing materials for assembly that can work as heat insulation. For example, insert film molding can eliminate the presence of air bubbles working as a heat insulator that can be found in laminating processes. The removal of air bubbles can improve overall appearance and functionality. Use of insert film molding can remove the need to use an autoclave process to remove the air bubbles, which can be expensive and can add production time.

[0027] The use of film insert molding can allow the heater to be made in a one step process using, for example, injection molding. Ultraviolet curing or thermal transfer of the heating medium to a substrate can be used, which is simpler than the use of thermally conductive glue. The integrated surface heaters can achieve greater than or equal to 50% transparency with the use of transparent materials such as, polycarbonate, polymethyl (methacrylate), etc. The integrated surface heater can heat an entire surface or surrounding space. In other words, the integrated surface heater can heat wherever needed, as opposed to other surface heaters, which heat only the neighboring space around the heater. As a result, this means that there is no “hot-spot” and that a larger space can be heated with lower temperatures. Since the heating medium can be embedded beneath the target surface or object, and since surface heating can be utilized, overall efficiency and response times can be improved compared to glue-assembled surface heaters or an electrical rod heating method. Heating performance can be adjusted in several ways including controlling electric resistance of the network, distance of any bus-bars, supplying electric power, etc.

[0028] Through the use of a hot stamping or roller pressing method with heat or ultraviolet curing after pressing, the heating medium network can be transferred to any shape target surface, for example, a curved target surface. An insert film can be coated or printed with a conductive medium. The insert film can be molded to achieve a curved or otherwise three-dimensional shape, which can give more flexibility to the shape of an integrated surface heater than a heater assembled with glue. Total weight of the integrated surface heater can be less as compared to a heater using a heater sheet and thermally conductive glue.

[0029] Use of a thermochromic polymer or an electro-chromo polymer can enable surface decorations on the integrated surface heater. The use of ultraviolet curable resin and thermally transferable resin layers can assist in preventing wash-out in film insert molding by adjusting the layer thickness. Adhesion between the network and the film substrate can be adjustable to control the peel-off performance of the polymeric film from the integrated surface heater after forming, for example, after forming by film insert molding.

[0030] Possible thermally transferable materials (and thermally transferable fillers for the plastic) include aluminum (e.g., AlN (aluminum nitride)), BN (boron nitride), MgSiN₂ (magnesium silicon nitride), SiC (silicon carbide), graphite, or a combination comprising at least one of the foregoing. For example, ceramic-coated graphite, expanded graphite, graphene, carbon fiber, carbon nanotubes (CNT), graphitized carbon black, or a combination comprising at least one of the foregoing. For example, the thermally transferable material can include KONDUIT™ resin, commercially available from SABIC's Innovative Plastics business.

[0031] The polymeric material used in the thermally transferable plastic can be selected from a wide variety of thermoplastic resins, blend of thermoplastic resins, thermosetting resins, or blends of thermoplastic resins with thermosetting resins, as well as combinations comprising at least one of the foregoing. The polymer may also be a blend of polymers, copolymers, terpolymers, or combinations comprising at least one of the foregoing. The organic polymer can also be an oligomer, a homopolymer, a copolymer, a block copolymer, an alternating block copolymer, a random polymer, a random copolymer, a random block copolymer, a graft copolymer, a star block copolymer, a dendrimer, or the like, or a combination comprising at least one of the foregoing. Examples of the organic polymer include polyacetals, polyolefins, polyacrylics, poly(arylene ether) polycarbonates, polystyrenes, polyesters (e.g., cycloaliphatic polyester, high molecular weight polymeric glycol terephthalates or isophthalates, and so forth), polyamides (e.g., semi-aromatic polyamide such as PA4.T, PA6.T, PA9.T, and so forth), polyamideimides, polyarylates, polyarylsulfones, polyethersulfones, polyphenylene sulfides, polyvinyl chlorides, polysulfones, polyimides, polyetherimides, polytetrafluoroethylenes,

polyetherketones, polyether etherketones, polyether ketone ketones, polybenzoxazoles, polyphthalides, polyacetals, polyanhydrides, polyvinyl ethers, polyvinyl thioethers, polyvinyl alcohols, polyvinyl ketones, polyvinyl halides, polyvinyl nitriles, polyvinyl esters, polysulfonates, polysulfides, polythioesters, polysulfones, polysulfonamides, polyureas, polyphosphazenes, polysilazanes, styrene acrylonitrile, acrylonitrile-butadiene-styrene (ABS), polyethylene terephthalate, polybutylene terephthalate, polyurethane, ethylene propylene diene rubber (EPR), polytetrafluoroethylene, fluorinated ethylene propylene, perfluoroalkoxyethylene, polychlorotrifluoroethylene, polyvinylidene fluoride, or the like, or a combination comprising at least one of the foregoing organic polymers. Examples of polyolefins include polyethylene (PE), including high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), mid-density polyethylene (MDPE), glycidyl methacrylate modified polyethylene, maleic anhydride functionalized polyethylene, maleic anhydride functionalized elastomeric ethylene copolymers (like EXXELOR VA1801 and VA1803 from ExxonMobil), ethylene-butene copolymers, ethylene-octene copolymers, ethylene-acrylate copolymers, such as ethylene-methyl acrylate, ethylene-ethyl acrylate, and ethylene butyl acrylate copolymers, glycidyl methacrylate functionalized ethylene-acrylate terpolymers, anhydride functionalized ethylene-acrylate polymers, anhydride functionalized ethylene-octene and anhydride functionalized ethylene-butene copolymers, polypropylene (PP), maleic anhydride functionalized polypropylene, glycidyl methacrylate modified polypropylene, and a combination comprising at least one of the foregoing polymers.

[0032] Examples of blends of thermoplastic resins include acrylonitrile-butadiene-styrene/nylon, polycarbonate/acrylonitrile-butadiene-styrene, acrylonitrile butadiene styrene/polyvinyl chloride, polyphenylene ether/polystyrene, polyphenylene ether/nylon, polysulfone/acrylonitrile-butadiene-styrene, polycarbonate/thermoplastic urethane, polycarbonate/polyethylene terephthalate, polycarbonate/polybutylene terephthalate, thermoplastic elastomer alloys, nylon/elastomers, polyester/elastomers, polyethylene terephthalate/polybutylene terephthalate, acetal/elastomer, styrene-maleicanhydride/acrylonitrile-butadiene-styrene, polyether etherketone/polyethersulfone, polyether etherketone/polyetherimide polyethylene/nylon, polyethylene/polyacetal, or the like.

[0033] Examples of thermosetting resins include polyurethane, natural rubber, synthetic rubber, epoxy, phenolic, polyesters, polyamides, silicones, or the like, or a combination comprising at least one of the foregoing thermosetting resins. Blends of thermoset resins as well as blends of thermoplastic resins with thermosets can be utilized.

[0034] For example, the polymer that can be used in the thermally transferable material can be polyarylene ether. The term poly(arylene ether) polymer includes polyphenylene ether (PPE) and poly(arylene ether) copolymers; graft copolymers; poly(arylene ether) ionomers; and block copolymers of alkenyl aromatic compounds with poly(arylene ether)s, vinyl aromatic compounds, and poly(arylene ether), and the like; and combinations including at least one of the foregoing.

[0035] An integrated surface heater can include a polymeric film and a heating medium network extending across a surface of the polymeric film forming an integrated conductive film and a three-dimensional (3D) substrate molded to the integrated conductive film. The heating medium network can include a conductive coating including nanometer sized metal particles arranged in a network. The network can include a hexagonal-like structure as illustrated in Figure 1. It is to be understood, however, the network can include any shape and is not limited to that illustrated in Figure 1. The nanometer sized metal particles can have a height of 1 to 20 micrometers, for example, 2.5 to 15 micrometers, for example, 5 to 10 micrometers. It is to be understood, however, that the height of the network can vary depending upon the surface resistance of the heating medium network and its overall purpose. After processing, the networks can be transferred to the object part from the polymeric film. The substrate can include any material that will provide the desired end shape for the integrated surface heater. For example, substrate can include a material selected from polymeric material, metallic material, stone, glass, wood, or a combination comprising at least one of the foregoing. The substrate material can further include particles, fibers, wires, or a combination comprising at least one of the foregoing. The integrated surface heater can be formed by injection molding. For example, the integrated conductive film and the three-dimensional substrate can be injection molded to form the integrated surface heater.

[0036] Based upon the material chosen for the substrate, the integrated surface heater can be transparent, translucent, or opaque. For example, an opaque sheet generally refers to a sheet that has less than or equal to 3% light transmission, specifically, less than or equal to 1% light transmission, more specifically, less than or equal to 0.5% light transmission, and even more specifically, less than or equal to 0.25% light transmission. With regards to the transparency or opacity of the multilayer sheet, it is briefly noted that end user specifications can specify that the component satisfy a particular predetermined threshold. Haze values, as measured by ANSI/ASTM D1003-00, can be a useful determination of the optical properties of a transparent sheet. The lower the haze levels, the higher the light transmission value of the finished sheet. Haze can be measured using ASTM D1003-00, procedure B, using CIE

(International Commission on Illumination) standard illuminant C. Translucent lightweight sheet would be defined as a condition whereby light can pass through the sample; and transparent would be a subset of translucent whereby an optical image may also pass through the sheet with the light.

[0037] The integrated surface heater can have greater than or equal to 50% transparency when applied to a transparent substrate. The heating medium network can include a transfer resin disposed adjacent to a surface of the polymeric film. The transfer resin can be disposed onto a surface of the polymeric film after the conductive coating. The transfer resin can be adhered to a surface of the polymeric film with the conductive coating being at least partially surrounded by the transfer resin.

[0038] Various articles can be made utilizing the integrated surface heaters disclosed herein. Any article desiring surface heating can utilize the integrated surface heaters. For example, the article can include automotive, home appliance, medical device, building and construction, mass transportation, or office supplies. For example, the article can include lamps, mirrors, glasses, steering wheels, ovens, toasters, warmers, bidets, irons, dryers, dryer ducts, blood warmers, refrigerator visibility windows, and laser printed drums. The integrated surface heater can be capable of defogging, antifogging, defrosting, antifrosting, or a combination comprising at least one of the foregoing.

[0039] The conductive coating can contain an electromagnetic capability (EMC) shielding material. The conductive coating can include pure metals such as silver (Ag), nickel (Ni), copper (Cu), or similar shielding metal, metal oxides thereof, combinations comprising at least one of the foregoing, or metal alloys comprising at least one of the foregoing, or metals or metal alloys produced by the Metallurgic Chemical Process (MCP) described in U.S. Pat. No. 5,476,535. Metals of the conductive coating can be nanometer sized, e.g., such as where 90% of the particles can have an equivalent spherical diameter of less than 100 nanometers (nm). The metals of the conductive coating can form a network of interconnected metal traces defining openings on the substrate surface to which it is applied. The surface resistance of the conductive coating can be less than or equal to 100 ohms per square (ohm/sq), for example, less than or equal to 25 ohm/sq, or, less than or equal to 10 ohm/sq.

[0040] A polymer of the integrated surface heater, including the polymeric film or the substrate, or used in the manufacture of the integrated conductive film (e.g., transfer sheet), can include a thermoplastic resin, a thermoset resin, or a combination comprising at least one of the foregoing.

[0041] Possible thermoplastic resins include, but are not limited to, oligomers, polymers, ionomers, dendrimers, copolymers such as graft copolymers, block copolymers (e.g., star block copolymers, random copolymers, and the like) or a combination comprising at least one of the foregoing. Examples of such thermoplastic resins include, but are not limited to, polycarbonates (e.g., blends of polycarbonate (such as, polycarbonate-polybutadiene blends, copolyester polycarbonates)), polystyrenes (e.g., copolymers of polycarbonate and styrene, polyphenylene ether-polystyrene blends), polyimides (PI) (e.g., polyetherimides (PEI)), acrylonitrile-styrene-butadiene (ABS), polyalkylmethacrylates (e.g., polymethylmethacrylates (PMMA)), polyesters (e.g., copolyesters, polythioesters), polyolefins (e.g., polypropylenes (PP) and polyethylenes, high density polyethylenes (HDPE), low density polyethylenes (LDPE), linear low density polyethylenes (LLDPE)), polyamides (e.g., polyamideimides), polyarylates, polysulfones (e.g., polyarylsulfones, polysulfonamides), polyphenylene sulfides, polytetrafluoroethylenes, polyethers (e.g., polyether ketones (PEK), polyether etherketones (PEEK), polyethersulfones (PES)), polyacrylics, polyacetals, polybenzoxazoles (e.g., polybenzothiazinophenothiazines, polybenzothiazoles), polyoxadiazoles, polypyrazinoquinoxalines, polypyromellitimides, polyquinoxalines, polybenzimidazoles, polyoxindoles, polyoxoisindolines (e.g., polydioxoisindolines), polytriazines, polypyridazines, polypiperazines, polypyridines, polypiperidines, polytriazoles, polypyrazoles, polypyrrolidones, polycboranes, polyoxabicyclononanes, polydibenzofurans, polyphthalamide, polyacetals, polyanhydrides, polyvinyls (e.g., polyvinyl ethers, polyvinyl thioethers, polyvinyl alcohols, polyvinyl ketones, polyvinyl halides, polyvinyl nitriles, polyvinyl esters, polyvinylchlorides), polysulfonates, polysulfides, polyureas, polyphosphazenes, polysilazanes, polysiloxanes, fluoropolymers (e.g., polyvinyl fluorides (PVF), polyvinylidene fluorides (PVDF), fluorinated ethylene-propylenes (FEP), polyethylene tetrafluoroethylenes (ETFE)), polyethylene naphthalates (PEN), cyclic olefin copolymers (COC), or a combination comprising at least one of the foregoing.

[0042] More particularly, a thermoplastic resin can include, but is not limited to, polycarbonate resins (e.g., LEXANTM resins, including LEXANTM CFR resins, commercially available from SABIC's Innovative Plastics business), polyphenylene ether-polystyrene resins (e.g., NORYLTM resins, commercially available from SABIC's Innovative Plastics business), polyetherimide resins (e.g., ULTEMTM resins, commercially available from SABIC's Innovative Plastics business), polybutylene terephthalate-polycarbonate resins (e.g., XENOYTM resins, commercially available from SABIC's Innovative Plastics business), copolyestercarbonate resins (e.g., LEXANTM SLX resins, commercially available from SABIC's Innovative Plastics business), or a combination comprising at least one of the foregoing resins. Even more

particularly, the thermoplastic resins can include, but are not limited to, homopolymers and copolymers of a polycarbonate, a polyester, a polyacrylate, a polyamide, a polyetherimide, a polyphenylene ether, or a combination comprising at least one of the foregoing resins. The polycarbonate can comprise copolymers of polycarbonate (e.g., polycarbonate-polysiloxane, such as polycarbonate-polysiloxane block copolymer, polycarbonate-dimethyl bisphenol cyclohexane (DMBPC) polycarbonate copolymer (e.g., LEXANTM DMX and LEXANTM XHT resins commercially available from SABIC's Innovative Plastics business), polycarbonate-polyester copolymer (e.g., XYLEXTM resins, commercially available from SABIC's Innovative Plastics business),), linear polycarbonate, branched polycarbonate, end-capped polycarbonate (e.g., nitrile end-capped polycarbonate), acrylonitrile butadiene styrene resins (e.g., CYCOLACTM resins, commercially available from SABIC's Innovative Plastics business), polycarbonate-acrylonitrile butadiene styrene resins (PC-ABS resins; e.g., CYCOLOYTM resins, commercially available from SABIC's Innovative Plastics business), or a combination comprising at least one of the foregoing, for example, a combination of branched and linear polycarbonate.

[0043] For example, the substrate can comprise a material selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK), or a combination comprising at least one of the foregoing and wherein the substrate material further includes particles, fibers, wires, or a combination comprising at least one of the foregoing.

[0044] For example, the polymeric material can comprise a material selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polystyrene, polyimide, polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK) or a combination comprising at least one of the foregoing.

[0045] A polymer of the integrated surface heater, including, but not limited to, the polymeric film or the substrate can include various additives ordinarily incorporated into polymer compositions of this type, with the proviso that the additive(s) are selected so as to not significantly adversely affect the desired properties of the polymeric composition. Such additives can be mixed at a suitable time during the mixing of the components for forming the composition. Exemplary additives include fillers, reinforcing agents, antioxidants, heat stabilizers, light stabilizers, ultraviolet (UV) light stabilizers, plasticizers, lubricants, mold release agents, antistatic agents, colorants such as titanium dioxide, carbon black, and organic

dyes, surface effect additives, radiation stabilizers, flame retardants, and anti-drip agents. A combination of additives can be used, for example a combination of a heat stabilizer, mold release agent, and ultraviolet light stabilizer. The total amount of additives (other than any impact modifier, filler, or reinforcing agents) is generally 0.01 to 5 wt.%, based on the total weight of the composition.

[0046] Light stabilizers and/or ultraviolet light (UV) absorbing stabilizers can also be used. Exemplary light stabilizer additives include benzotriazoles such as 2-(2-hydroxy-5-methylphenyl)benzotriazole, 2-(2-hydroxy-5-tert-octylphenyl)-benzotriazole and 2-hydroxy-4-n-octoxy benzophenone, or combinations comprising at least one of the foregoing light stabilizers. Light stabilizers are used in amounts of 0.01 to 5 parts by weight, based on 100 parts by weight of the total composition, excluding any filler.

[0047] UV light absorbing stabilizers include triazines, dibenzoylresorcinols (such as TINUVIN[®] 1577 commercially available from BASF and ADK STAB LA-46 commercially available from Asahi Denka), hydroxybenzophenones; hydroxybenzotriazoles; hydroxyphenyl triazines (e.g., 2-hydroxyphenyl triazine); hydroxybenzotriazines; cyanoacrylates; oxanilides; benzoxazinones; 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)-phenol (CYASORB[®] 5411); 2-hydroxy-4-n-octyloxybenzophenone (CYASORB[®] 531); 2-[4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl]-5-(octyloxy)-phenol (CYASORB[®] 1164); 2,2'-(1,4-phenylene)bis(4H-3,1-benzoxazin-4-one) (CYASORB[®] UV-3638); 1,3-bis[(2-cyano-3,3-diphenylacryloyl)oxy]-2,2-bis[[2-cyano-3,3-diphenylacryloyl)oxy]methyl]propane (UVINUL[®] 3030); 2,2'-(1,4-phenylene) bis(4H-3,1-benzoxazin-4-one); 1,3-bis[(2-cyano-3,3-diphenylacryloyl)oxy]-2,2-bis[[2-cyano-3,3-diphenylacryloyl)oxy]methyl]propane; nano-size inorganic materials such as titanium oxide, cerium oxide, and zinc oxide, all with a particle size less than or equal to 100 nanometers, or combinations comprising at least one of the foregoing UV light absorbing stabilizers. UV light absorbing stabilizers are used in amounts of 0.01 to 5 parts by weight, based on 100 parts by weight of the total composition, excluding any filler.

[0048] The heating medium network can include a transfer resin. The transfer resin can include a multifunctional acrylate oligomer and an acrylate monomer. The transfer resin can include a photoinitiator. The multifunctional acrylate oligomer can include an aliphatic urethane acrylate oligomer, a pentaerythritol tetraacrylate, an aliphatic urethane acrylate, an acrylic ester, a dipentaerythritol dhexaacrylate, an acrylated resin, a trimethylolpropane triacrylate (TMPTA), a dipentaerythritol pentaacrylate ester, or a combination comprising at least one of the foregoing. In an embodiment, the multifunctional acrylate can include DOUBLEMER[™] 5272 (DM5272) (commercially available from Double Bond Chemical Ind., Co., LTD., of Taipei, Taiwan,

R.O.C.) which includes an aliphatic urethane acrylate oligomer in an amount from 30 weight percent (wt.%) to 50 wt.% of the multifunctional acrylate and a pentaerythritol tetraacrylate in an amount from 50 wt.% to 70 wt.% of the multifunctional acrylate.

[0049] The transfer resin can optionally include a polymerization initiator to promote polymerization of the acrylate components. The optional polymerization initiators can include photoinitiators that promote polymerization of the components upon exposure to ultraviolet radiation.

[0050] The transfer resin can include the multifunctional acrylate oligomer in an amount of 30 wt.% to 90 wt.% for example, 30 wt.% to 85 wt.%, or, 30 wt.% to 80 wt.%; the acrylate monomers in an amount of 5 wt.% to 65 wt.%, for example, 8 wt.% to 65 wt.%, or, 15 wt.% to 65 wt.%; and the optional polymerization initiator present in an amount of 0 wt.% to 10 wt.%, for example, 2 wt.% to 8 wt.%, or, 3 wt.% to 7 wt.%, wherein weight is based on the total weight of the transfer resin.

[0051] An aliphatic urethane acrylate oligomer can include 2 to 15 acrylate functional groups, for example, 2 to 10 acrylate functional groups. The acrylate monomer (e.g., 1,6-hexanediol diacrylate, meth(acrylate) monomer) can include 1 to 5 acrylate functional groups, for example, 1 to 3 acrylate functional group(s). In an embodiment, the acrylate monomer can be 1,6-hexanediol diacrylate (HDDA).

[0052] The multifunctional acrylate oligomer can include a compound produced by reacting an aliphatic isocyanate with an oligomeric diol such as a polyester diol or polyether diol to produce an isocyanate capped oligomer. This oligomer can then be reacted with hydroxy ethyl acrylate to produce the urethane acrylate.

[0053] The multifunctional acrylate oligomer can be an aliphatic urethane acrylate oligomer, for example, a wholly aliphatic urethane (meth)acrylate oligomer based on an aliphatic polyol, which is reacted with an aliphatic polyisocyanate and acrylated. In one embodiment, the multifunctional acrylate oligomer can be based on a polyol ether backbone. For example, an aliphatic urethane acrylate oligomer can be the reaction product of (i) an aliphatic polyol; (ii) an aliphatic polyisocyanate; and (iii) an end capping monomer capable of supplying reactive terminus. The polyol (i) can be an aliphatic polyol, which does not adversely affect the properties of the composition when cured. Examples include polyether polyols; hydrocarbon polyols; polycarbonate polyols; polyisocyanate polyols, and mixtures thereof.

[0054] The multifunctional acrylate oligomer can include an aliphatic urethane tetraacrylate (i.e., a maximum functionality of 4) that can be diluted 20% by weight with a acrylate monomer, e.g., 1,6-hexanediol diacrylate (HDDA), tripropyleneglycol diacrylate

(TPGDA), and trimethylolpropane triacrylate (TMPTA). A commercially available urethane acrylate that can be used in forming the transfer resin can be EBECRYL™ 8405, EBECRYL™ 8311, or EBECRYL™ 8402, each of which is commercially available from Allnex.

[0055] Another component of the transfer resin can be an optional polymerization initiator such as a photoinitiator. Generally, a photoinitiator can be used if the coating composition is to be ultraviolet cured; if it is to be cured by an electron beam, the coating composition can comprise substantially no photoinitiator.

[0056] When the transfer resin is cured by ultraviolet light, the photoinitiator, when used in a small but effective amount to promote radiation cure, can provide reasonable cure speed without causing premature gelation of the coating composition. Further, it can be used without interfering with the optical clarity of the cured coating material. Still further, the photoinitiator can be thermally stable, non-yellowing, and efficient.

[0057] The photoinitiator can be chosen such that the curing energy is less than 2.0 Joules per square centimeter (J/cm^2), and specifically less than $1.0 \text{ J}/\text{cm}^2$, when the photoinitiator is used in the designated amount.

[0058] The polymerization initiator can include peroxy-based initiators that can promote polymerization under thermal activation. Examples of useful peroxy initiators include benzoyl peroxide, dicumyl peroxide, methyl ethyl ketone peroxide, lauryl peroxide, cyclohexanone peroxide, t-butyl hydroperoxide, t-butyl benzene hydroperoxide, t-butyl peroctoate, 2,5-dimethylhexane-2,5-dihydroperoxide, 2,5-dimethyl-2,5-di(t-butylperoxy)-hex-3-yne, di-t-butylperoxide, t-butylcumyl peroxide, alpha,alpha'-bis(t-butylperoxy-m-isopropyl)benzene, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, dicumylperoxide, di(t-butylperoxy isophthalate, t-butylperoxybenzoate, 2,2-bis(t-butylperoxy)butane, 2,2-bis(t-butylperoxy)octane, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane, di(trimethylsilyl)peroxide, trimethylsilylphenyltriphenylsilyl peroxide, and the like, and combinations comprising at least one of the foregoing polymerization initiators.

[0059] Turning now to Figures 2A and 2B, a film insert molding method to make the integrated surface heater is illustrated without a transfer resin (e.g., direct transfer). For example, a method of making an integrated surface heater 1 can include depositing an integrated conductive film 12 including a polymeric film 4 and a heating medium network 2 extending across a surface 14 of the polymeric film 4 to a resin side 20 of an injection mold 18. The injection mold 18 includes a mold side 21 opposite the resin side 20. The heating medium network 2 can include a conductive coating including nanometer sized metal particles arranged in a network. Once the integrated conductive film has been deposited to the resin side 20 of the

injection mold 18, the mold 18 can be closed. A polymeric material can then be injected into the mold 18 to form a mold shaped substrate 22. The polymeric material can be selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK), or a combination comprising at least one of the foregoing and wherein the substrate material can further include particles, fibers, wires, or a combination comprising at least one of the foregoing. The integrated conductive film 12 and the substrate 22 can be injection molded to form an integrated surface heater 1. The heating medium network 2 can be embedded into the substrate 22 during the injection molding process. Once the integrated surface heater 1 has been formed, the mold can be cooled and opened. The formed integrated surface heater 1 can be ejected from the injection mold 18. The integrated surface heater 1 can have a three-dimensional shape. The polymeric film 4 can remain on the resin side 20 of the injection mold 18 so that the integrated surface heater 1 includes the heating medium network 2 embedded into a surface of the substrate 22.

[0060] The heating medium network 2 can optionally include a transfer resin film disposed adjacent to a surface 14, 16 of the polymeric film 4. The transfer resin film can be removed from the integrated surface heater 1 after removal from the mold 18 or the transfer resin film can be removed from the integrated surface heater 1 during ejection of the integrated surface heater 1 from the mold. The heating medium network 2 remains embedded in the integrated surface heater 1.

[0061] As illustrated in Figure 3, an ultraviolet light curable resin 6 can be deposited onto the same surface 14 of the polymeric film 4 as the heating medium network 2 before molding to form an integrated conductive film 24. During molding, the ultraviolet light curable resin 6 can be activated with an ultraviolet light radiation source. The polymeric film 4 can remain on the resin side of the injection mold so that the integrated surface heater 1 includes the heating medium network 2 embedded into a surface of the substrate 22. After molding and ejection from the ejection mold, the polymeric film 4 can be removed from the integrated surface heater 1 by peeling the polymeric film 4 from the integrated surface heater 1.

[0062] As illustrated in Figures 4A and 4B, a method of making an injection molded integrated surface heater can include depositing an integrated conductive film 26 including a sheet 8 to a resin side 20 of an injection mold 18. The sheet 8 can include a first polymeric film 4 with a heating medium network 2 extending across a surface 14 of the first polymeric film 4. The sheet 8 can include a second polymeric film 10 including a thermally transferable polymer

extending across the same surface 14 of the first polymeric film 4 as the heating medium network 2. The polymeric film 4 can include another surface 16 opposite surface 14. The heating medium network 2 can include a conductive coating including nanometer sized metal particles arranged in a network. After depositing the sheet 8 to the resin side 20 of the injection mold 18, the mold can be closed and a polymeric material can be injected into the mold to form a mold shaped substrate 22. The polymeric material can be selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK), or a combination comprising at least one of the foregoing and wherein the substrate material can further include particles, fibers, wires, or a combination comprising at least one of the foregoing. The sheet 8 can then be injection molded to the substrate 22 to form the integrated surface heater 1. The second polymeric film 10 and the heating medium network 2 can then be embedded into the substrate 22. The second polymeric film 10 can function as a protective coating over the heating medium network 2. The mold 18 can then be cooled and opened with the formed integrated surface heater 1 ejected from the mold 18. The integrated surface heater 1 can have a three-dimensional shape.

[0063] The method can comprise removing the first polymeric film 4 from the integrated surface heater 1 after removal from the mold 18 or removing the first polymeric film 4 from the integrated surface heater 1 during ejection of the integrated surface heater 1 from the mold. The heating medium network 2 and the second polymeric film 10 remain embedded in the integrated surface heater. The first polymeric film 4 can optionally remain on the resin side 20 of the injection mold 18 when the integrated surface heater 1 is ejected and thereafter removed from the injection mold 18 prior to molding an additional heater. The first polymeric film 4 can optionally remain on the mold side 21 of the injection mold 18 when the integrated surface heater 1 is ejected and thereafter removed from the injection mold 18 prior to molding an additional heater.

[0064] Turning now to Figures 5A and 5B, a thermoforming method of making an integrated surface heater is illustrated. The method can include depositing an integrated conductive film 12 including a polymeric film 4 and a heating medium network 2 extending across a surface 14 of the polymeric film 4 to a first mold 28 having a first mold surface 30. The heating medium network 2 can include a conductive coating including nanometer sized metal arranged in a network. A polymeric sheet 32 can be placed over the integrated conductive film 12 such that the polymeric film 4 faces the first mold surface 30. The polymeric sheet 32 can

include a material selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK), or a combination comprising at least one of the foregoing and wherein the substrate material can further include particles, fibers, wires, or a combination comprising at least one of the foregoing. A second mold 34 having an opposing mold surface 36 to the first mold surface 30 can be positioned over the first mold surface 30. The first mold 28 and the second mold 34 can be brought toward one another with vacuum pressure and a ram 40 pressing on the second mold 34 to form a thermoformed integrated surface heater 38. Air vents 42 can be located in the first mold 28. The first mold 28 and the second mold 34 can be opened and the integrated surface heater 38 can be extracted from the first mold 30. The integrated surface heater 38 can be substantially free of void content. For example, the integrated surface heater 38 can have a void content of less than or equal to 10%, for example, less than or equal to 5%, for example, less than or equal to 2.5%. The integrated surface heater 38 can have a two-dimensional shape. The integrated surface heater 38 can have a two and a half-dimensional shape. The integrated surface heater 38 can have a three-dimensional shape.

[0065] A pad stamping process to make an integrated surface heater 44 is illustrated in Figure 6. For example, a method of making a stamped integrated surface heater can include depositing a sheet 8, including an integrated conductive film 26, to a press 46. The integrated conductive film 26 can include a first polymeric film 4 with a heating medium network 2 extending across a surface 14 of the first polymeric film 4 and a second polymeric film 10 with a thermally transferable polymer extending across the same surface 14 of the first polymeric film 4 as the heating medium network 2. The heating medium network 2 can include nanometer sized metal particles arranged in a network. A pad stamper 48, for example, a rubber pad stamper, can be heated and pressed to an opposite surface 16 of the first polymeric 4 as the heating medium network 2 and the second polymer film 10. The pad stamper 48 can include a rigid material such as aluminum or metal or can include a flexible material such as rubber to press evenly onto a non-flat shaped surface. The sheet 8 can be molded to a substrate 50 to form the integrated surface heater 44. The substrate can include a material selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK), or a combination comprising at least one of the foregoing and wherein the substrate material can further include particles, fibers, wires, or a combination comprising at least one of the foregoing. The second polymeric film 10

and the heating medium network 2 can be embedded into the substrate 50 by pressing on the pad stamper 48. The second polymeric film 10 can function as a protective coating over the heating medium network. The pad stamper 48 can be released and the stamped integrated surface heater 44 can be removed from the pad stamper 48. Rolls 52 can be present to facilitate forming of the sheet 8 to the substrate 50. The substrate 8 can be straight, curved, semi-curved, etc. Using a rubber pad can assist in transferring the network to a curved substrate.

[0066] A decorative image can be applied to the first polymeric film 4 before stamping. The decorative image can be formed from a thermochromic polymeric material. The first polymeric film 4 can be removed from the integrated surface heater 44 after removal from the mold. The heating medium network 2 and the second polymeric film 10 remain embedded in the integrated surface heater 44. The integrated surface heater 44 can have a two-dimensional shape. The integrated surface heater 44 can have a two and a half-dimensional shape. The integrated surface heater 44 can have a three-dimensional shape.

[0067] Figures 7 and 8 illustrate automotive components containing an integrated surface heater. For example, as can be seen in Figure 7, a head lamp 53 can include a lamp housing 56 and an integrated surface heater 54. When the integrated surface heater 54 is integrated behind the lamp housing 56, defogging can be realized. When the integrated surface heater 54 is integrate in front of the lamp housing 56, defrosting can be realized. Figure 8 illustrates a side mirror 57 of an automobile. The side mirror 57 can include a housing 58, an integrated surface heater 60, and a mirror 62. As can be seen from both Figures 7 and 8, no adhesive is required to attach the assembly because the integrated surface heater 54 and the integrated surface heater 60 can be molded with the lamp housing 56 and the housing 58 to form the head lamp 53 and the side mirror 57, respectively. The integrated surface heater 54 can cover at least a portion of the lamp housing 56 and can use convection to spread the heat throughout the head lamp 53. For example, the integrated surface heater 54 can cover greater than or equal to 35% of the head lamp 53, for example, greater than or equal to 50%, for example, greater than or equal to 75%, for example, greater than or equal to 90%, for example, 100%. The integrated surface heater 60 can cover at least a portion of the mirror 62 of the side mirror 57 of Figure 8 using convection to spread the heat across the mirror 62. For example, the integrated surface heater 60 can cover greater than or equal to 35% of the mirror 62, for example, greater than or equal to 50%, for example, greater than or equal to 75%, for example, greater than or equal to 90%, for example 100%. A bidet 64 is illustrated in Figure 9 with an integrated surface heater 66 integrally formed with the bidet housing 68. The bidet 64 with the integrated surface

heater 66 can reduce assembly cost and time by removing the need for a separate heating rod to be installed in the bidet after formation.

[0068] The following examples are merely illustrative of the device disclosed herein and are not intended to limit the scope hereof.

EXAMPLES

[0069] In the following examples, an integrated surface heater was tested for various properties. The integrated surface heater tested was one as illustrated in Figure 1, containing a polymeric film comprising polycarbonate and a heating medium network as disclosed herein, wherein the heating medium network extended across a surface of the polymeric film. The integrated surface heater was subjected to a voltage test to determine the degree of heating that can be accomplished over a period of time. Results are demonstrated in Figure 10, which is a graph of temperature, measured in degrees Celsius ($^{\circ}\text{C}$), versus time, measured in seconds. Reference no. 70 illustrates a 3 Volt (V) room temperature test, reference no. 72 illustrates a 3 V ice chamber test, reference no. 74 illustrates a 12 V room temperature test, and reference no. 76 illustrates a 12 V ice chamber test. For the tests conducted at room temperature, the temperature increased to 105°C from room temperature under 12 V within 20 seconds (see e.g., reference no. 74). Conversely, at 3 V, the temperature increased slowly and showed only a 25°C difference over a six minute period. These results demonstrate that a surface can reach a preset temperature with low energy consumption and the response time of the integrated surface heater also demonstrates efficiency. For example, these results demonstrate that the integrated surface heater can be used for defrosting or defogging applications for example in automotive applications.

[0070] Figure 11 illustrates the temperature distribution for the integrated surface heater. As can be seen from Figure 11, heating of the integrated surface heater is faster at 12 V (reference no. 80) than at 6 V (reference no. 78). The heating performance can be controlled by controlling the surface resistance of the integrated surface heater.

[0071] The integrated surface heaters disclosed herein and methods of making can provide a heating function to various applications in a short amount of time where the integrated surface heaters can be applied to any kind of heating applications. Examples include, but are not limited to, hair dryers, bidets, air conditioners, water boilers, automotive applications such as headlamps and side mirrors, windshield glass replacement, refrigerator visibility windows, etc.

[0072] The disclosed integrated surface heaters and methods of making include at least the following embodiments:

[0073] Embodiment 1: An injection molded integrated surface heater, comprising: a polymeric film; a heating medium network extending across a surface of the polymeric film, wherein the heating medium network comprises a conductive coating including nanometer sized metal particles arranged in a network; wherein the polymeric film and the heating medium network comprise an integrated conductive film; and a three-dimensional substrate injection molded to the integrated conductive film, wherein the substrate comprises a material selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK), or a combination comprising at least one of the foregoing and wherein the substrate material further includes particles, fibers, wires, or a combination comprising at least one of the foregoing.

[0074] Embodiment 2: The integrated heater of Claim 1, wherein the polymeric film is transparent, translucent, or opaque.

[0075] Embodiment 3: The integrated heater of any of Claims 1 – 2, wherein the polymeric film comprises a material selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polystyrene, polyimide, polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK) or a combination comprising at least one of the foregoing.

[0076] Embodiment 4: The integrated heater of any of Claims 2 – 3, wherein the heater has greater than or equal to 50% transparency when applied to a transparent substrate.

[0077] Embodiment 5: The integrated heater of any of Claims 1 – 4, wherein the heating medium network further comprises a transfer resin disposed adjacent to a surface of the polymeric film.

[0078] Embodiment 6: The integrated heater of any of Claims 1 - 5, wherein the transfer resin is disposed onto a surface of the polymeric film after the conductive coating.

[0079] Embodiment 7: The integrated heater of any of Claims 1 - 6, wherein the transfer resin is adhered to a surface of the polymeric film and the conductive coating is at least partially surrounded by the transfer resin.

[0080] Embodiment 8: An article comprising the integrated heater of any of Claims 1 – 7.

[0081] Embodiment 9: The article of Claim 8, wherein the article is selected from automotive, home appliances, medical devices, building, construction, mass transportation, and office supplies.

[0082] Embodiment 10: The article of Claim 9, wherein the article is selected from lamps, mirrors, glasses, steering wheels, ovens, toasters, warmers, bidets, irons, dryers, dryer ducts, blood warmers, refrigerator visibility windows, and laser printed drums.

[0083] Embodiment 11: The article of any of Claims 8 – 10, wherein the integrated heater is capable of defogging, antifogging, defrosting, antifrosting, or a combination comprising at least one of the foregoing.

[0084] Embodiment 12: A method of making an integrated surface heater, comprising: depositing an integrated conductive film to a resin side of an injection mold, wherein the integrated conductive film includes a polymeric film and a heating medium network extending across a surface of the polymeric film, wherein the heating medium network comprises a conductive coating including nanometer sized metal particles arranged in a network; closing the mold; injecting a polymeric material into the mold to form a mold shaped substrate, wherein the polymeric material is selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK), or a combination comprising at least one of the foregoing and wherein the polymeric material further includes particles, fibers, wires, or a combination comprising at least one of the foregoing; injection molding the integrated conductive film and the substrate to form the integrated surface heater; embedding the heating medium network into the substrate; cooling the mold; opening the mold; and ejecting the formed integrated surface heater from the mold, wherein the integrated surface heater has a three-dimensional shape.

[0085] Embodiment 13: The method of Claim 12, wherein the heating medium network further comprises a transfer resin film disposed adjacent to a surface of the polymeric film.

[0086] Embodiment 14: The method of Claim 13, further comprising removing the transfer resin film from the integrated surface heater during the ejection process from the mold, wherein the heating medium network remains embedded in the integrated surface heater.

[0087] Embodiment 15: The method of any of Claims 12 – 14, further comprising depositing an ultraviolet light curable resin onto the same surface of the polymeric film as the heating medium network before molding.

[0088] Embodiment 16: The method of Claim 15, comprising activating the ultraviolet light curable resin with an ultraviolet light radiation source.

[0089] Embodiment 17: A method of making an injection molded integrated surface heater, comprising: depositing a sheet to a resin side of an injection mold, wherein the sheet comprises a first polymeric film with a heating medium network extending across a surface of the first polymeric film and a second polymeric film comprising a thermally transferable polymer extending across the same surface of the first polymeric film, wherein the heating medium network comprises a conductive coating including nanometer sized metal particles arranged in a network; closing the mold; injecting a polymeric material into the mold to form a mold shaped substrate, wherein the polymeric material is selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK), or a combination comprising at least one of the foregoing and wherein the polymeric material further includes particles, fibers, wires, or a combination comprising at least one of the foregoing; injection molding the sheet to the substrate to form the integrated surface heater; embedding the second polymeric film and the heating medium network into the substrate, wherein the second polymeric film acts as a protective coating over the heating medium network; cooling the mold; opening the mold; and ejecting the formed integrated surface heater from the mold, wherein the integrated surface heater has a three-dimensional shape.

[0090] Embodiment 18: The method of Claim 17, further comprising removing the first polymeric film from the integrated surface heater during the ejection process, wherein the heating medium network and the second polymeric film remain embedded in the integrated surface heater.

[0091] Embodiment 19: A method of making a thermoformed integrated heater, comprising: depositing an integrated conductive film comprising a polymeric film and a heating medium network extending across a surface of the polymeric film to a first mold having a first mold surface, wherein the heating medium network comprises a conductive coating including nanometer sized metal particles arranged in a network; placing a polymeric sheet on top of the integrated conductive film, wherein the polymeric sheet comprises a material selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK), or a combination comprising at least one of the foregoing and wherein the substrate material further includes particles, fibers, wires, or a combination comprising at least one of the foregoing; positioning a second mold having an opposing mold surface to the first mold surface

over the first mold surface; bringing the first mold and the second mold toward one another with vacuum pressure to form the thermoformed integrated surface heater comprising the integrated conductive film; opening the first mold and the second mold; and extracting the integrated surface heater from the first mold, wherein the integrated surface heater is substantially free of void content.

[0092] Embodiment 20: The method of Claim 19, wherein the void content in the integrated heater is less than or equal to 5%.

[0093] Embodiment 21: A method of making a stamped integrated heater, comprising: depositing an integrated conductive sheet to a press, wherein the integrated conductive sheet comprises a first polymeric film with a heating medium network extending across a surface of the first polymeric film and a second polymeric film comprising a thermally transferable polymer extending across the same surface of the first polymeric film, wherein the heating medium network comprises a conductive coating including nanometer sized metal particles arranged in a network; heating a pad stamper; pressing the pad stamper to an opposite surface of the first polymeric film as the heating medium network and the second polymer film; molding the sheet to a substrate to form the integrated heater, wherein the substrate comprises a material selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK), or a combination comprising at least one of the foregoing and wherein the substrate material further includes particles, fibers, wires, or a combination comprising at least one of the foregoing; embedding the second polymeric film and the heating medium network into the substrate by pressing on the pad stamper, wherein the second polymeric film acts as a protective coating over the heating medium network; releasing the pad stamper; and removing the stamped integrated surface heater.

[0094] Embodiment 22: The method of Claim 21, further comprising applying a decorative image to the first polymeric film before molding.

[0095] Embodiment 23: The method of Claim 22, wherein the decorative image is formed from a thermochromic polymeric material.

[0096] Embodiment 24: The method of any of Claims 21 – 23, wherein the pad stamper comprises a rigid or flexible material.

[0097] Embodiment 25: The method of any of Claims 12 – 24, wherein the integrated surface heater includes a 2-dimensional shape, a 2.5-dimensional shape, or a 3-dimensional shape.

[0098] Embodiment 26: The method of any of Claims 12 – 25, wherein the polymeric film comprises a material selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polystyrene, polyimide, polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK) or a combination comprising at least one of the foregoing.

[0099] Unless otherwise specified herein, any reference to standards, testing methods and the like, such as ASTM D1003, ASTM D3359, ASTM D3363, refer to the standard, or method that is in force at the time of filing of the present application.

[0100] In general, the invention may alternately comprise, consist of, or consist essentially of, any appropriate components herein disclosed. The invention may additionally, or alternatively, be formulated so as to be devoid, or substantially free, of any components, materials, ingredients, adjuvants or species used in the prior art compositions or that are otherwise not necessary to the achievement of the function and/or objectives of the present invention.

[0101] All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other (e.g., ranges of “up to 25 wt.%, or, more specifically, 5 wt.% to 20 wt.%”, is inclusive of the endpoints and all intermediate values of the ranges of “5 wt.% to 25 wt.%,” etc.). “Combination” is inclusive of blends, mixtures, alloys, reaction products, and the like. Furthermore, the terms “first,” “second,” and the like, herein do not denote any order, quantity, or importance, but rather are used to denote one element from another. The terms “a” and “an” and “the” herein do not denote a limitation of quantity, and are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The suffix “(s)” as used herein is intended to include both the singular and the plural of the term that it modifies, thereby including one or more of that term (e.g., the film(s) includes one or more films). Reference throughout the specification to “one embodiment”, “another embodiment”, “an embodiment”, and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the embodiment is included in at least one embodiment described herein, and may or may not be present in other embodiments. In addition, it is to be understood that the described elements may be combined in any suitable manner in the various embodiments.

[0102] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or may be presently unforeseen may arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and

as they may be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

[0103] I/we claim:

CLAIMS:

1. An injection molded integrated surface heater, comprising:
a polymeric film;
a heating medium network extending across a surface of the polymeric film, wherein the heating medium network comprises a conductive coating including nanometer sized metal particles arranged in a network;
wherein the polymeric film and the heating medium network comprise an integrated conductive film; and
a three-dimensional substrate injection molded to the integrated conductive film, wherein the substrate comprises a material selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK), or a combination comprising at least one of the foregoing and wherein the substrate material further includes particles, fibers, wires, or a combination comprising at least one of the foregoing.
2. The integrated heater of Claim 1, wherein the polymeric film is transparent, translucent, or opaque.
3. The integrated heater of any of Claims 1 – 2, wherein the polymeric film comprises a material selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polystyrene, polyimide, polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK) or a combination comprising at least one of the foregoing.
4. The integrated heater of any of Claims 2 – 3, wherein the heater has greater than or equal to 50% transparency when applied to a transparent substrate.
5. The integrated heater of any of Claims 1 – 4, wherein the heating medium network further comprises a transfer resin disposed adjacent to a surface of the polymeric film.
6. The integrated heater of any of Claims 1 - 5, wherein the transfer resin is disposed onto a surface of the polymeric film after the conductive coating.
7. The integrated heater of any of Claims 1 - 6, wherein the transfer resin is adhered to a surface of the polymeric film and the conductive coating is at least partially surrounded by the transfer resin.
8. An article comprising the integrated heater of any of Claims 1 – 7.

9. The article of Claim 8, wherein the article is selected from automotive, home appliances, medical devices, building, construction, mass transportation, and office supplies.

10. The article of Claim 9, wherein the article is selected from lamps, mirrors, glasses, steering wheels, ovens, toasters, warmers, bidets, irons, dryers, dryer ducts, blood warmers, refrigerator visibility windows, and laser printed drums.

11. The article of any of Claims 8 – 10, wherein the integrated heater is capable of defogging, antifogging, defrosting, antifrosting, or a combination comprising at least one of the foregoing.

12. A method of making an integrated surface heater, comprising:

depositing an integrated conductive film to a resin side of an injection mold, wherein the integrated conductive film includes a polymeric film and a heating medium network extending across a surface of the polymeric film, wherein the heating medium network comprises a conductive coating including nanometer sized metal particles arranged in a network;

closing the mold;

injecting a polymeric material into the mold to form a mold shaped substrate, wherein the polymeric material is selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK), or a combination comprising at least one of the foregoing and wherein the polymeric material further includes particles, fibers, wires, or a combination comprising at least one of the foregoing;

injection molding the integrated conductive film and the substrate to form the integrated surface heater;

embedding the heating medium network into the substrate;

cooling the mold;

opening the mold; and

ejecting the formed integrated surface heater from the mold, wherein the integrated surface heater has a three-dimensional shape.

13. The method of Claim 12, wherein the heating medium network further comprises a transfer resin film disposed adjacent to a surface of the polymeric film.

14. The method of Claim 13, further comprising removing the transfer resin film from the integrated surface heater during the ejection process from the mold, wherein the heating medium network remains embedded in the integrated surface heater.

15. The method of any of Claims 12 – 14, further comprising depositing an ultraviolet light curable resin onto the same surface of the polymeric film as the heating medium network before molding.

16. The method of Claim 15, comprising activating the ultraviolet light curable resin with an ultraviolet light radiation source.

17. A method of making a stamped integrated heater, comprising:

depositing an integrated conductive sheet to a press, wherein the integrated conductive sheet comprises a first polymeric film with a heating medium network extending across a surface of the first polymeric film and a second polymeric film comprising a thermally transferable polymer extending across the same surface of the first polymeric film, wherein the heating medium network comprises a conductive coating including nanometer sized metal particles arranged in a network;

heating a pad stamper;

pressing the pad stamper to an opposite surface of the first polymeric film as the heating medium network and the second polymer film;

molding the sheet to a substrate to form the integrated heater, wherein the substrate comprises a material selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK), or a combination comprising at least one of the foregoing and wherein the substrate material further includes particles, fibers, wires, or a combination comprising at least one of the foregoing;

embedding the second polymeric film and the heating medium network into the substrate by pressing on the pad stamper, wherein the second polymeric film acts as a protective coating over the heating medium network;

releasing the pad stamper; and

removing the stamped integrated surface heater.

18. The method of Claim 17, further comprising applying a decorative image to the first polymeric film before molding, wherein the decorative image is formed from a thermochromic polymeric material.

19. The method of any of Claims 12 – 18, wherein the integrated surface heater includes a 2-dimensional shape, a 2.5-dimensional shape, or a 3-dimensional shape.

20. The method of any of Claims 12 – 19, wherein the polymeric film comprises a material selected from polycarbonate, poly(methyl methacrylate) (PMMA), polyethylene

terephthalate (PET), polyethylene naphthalate (PEN), a cyclic olefin copolymer (COC), polyetherimide (PEI), polystyrene, polyimide, polypropylene (PP), polyethylene (PE), poly(p-phenylene oxide) (PPO), polyether ether ketone (PEEK) or a combination comprising at least one of the foregoing.

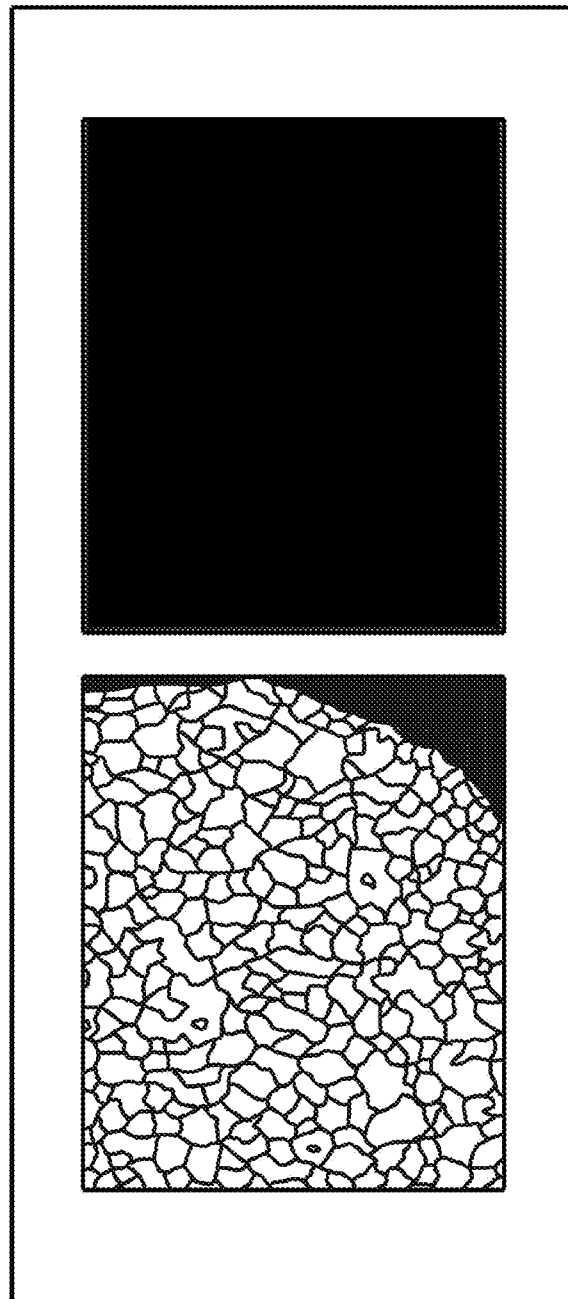
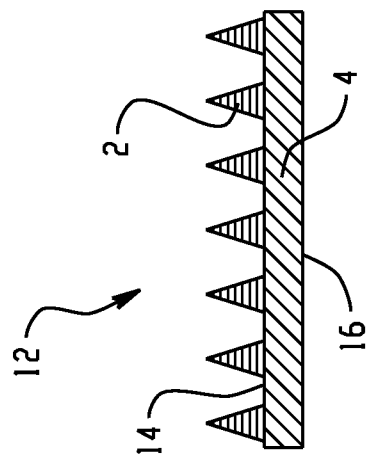
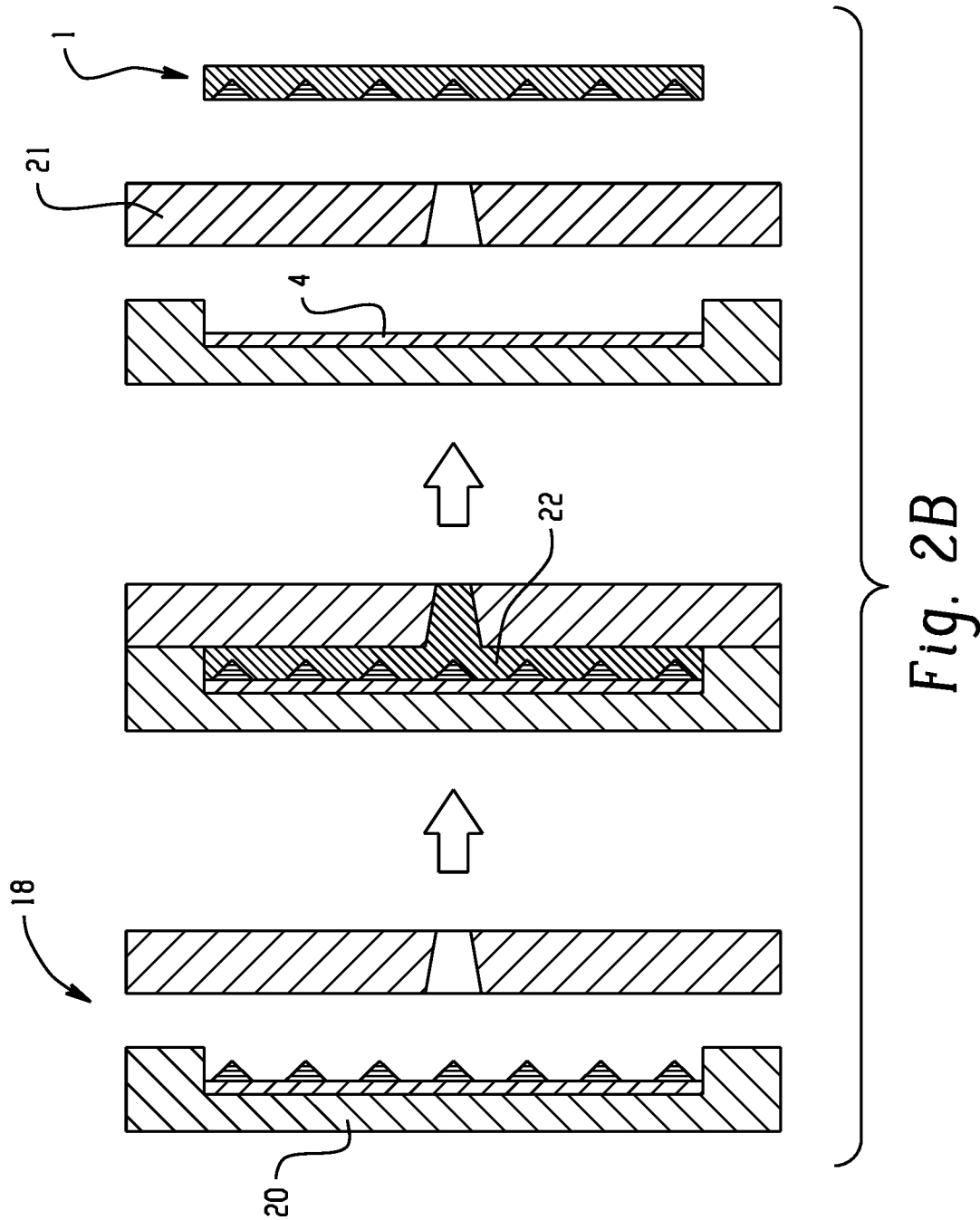


Fig. 1



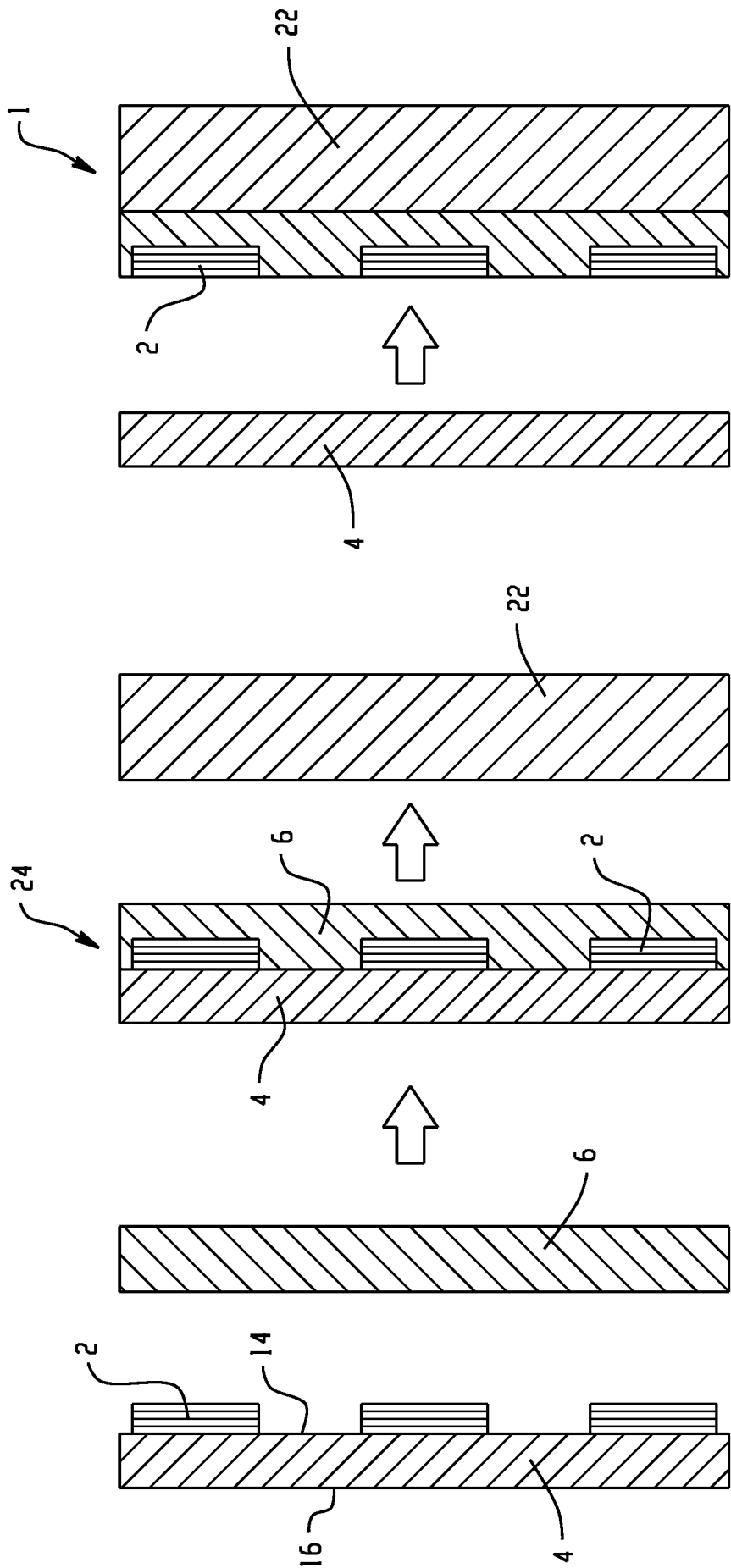


Fig. 3

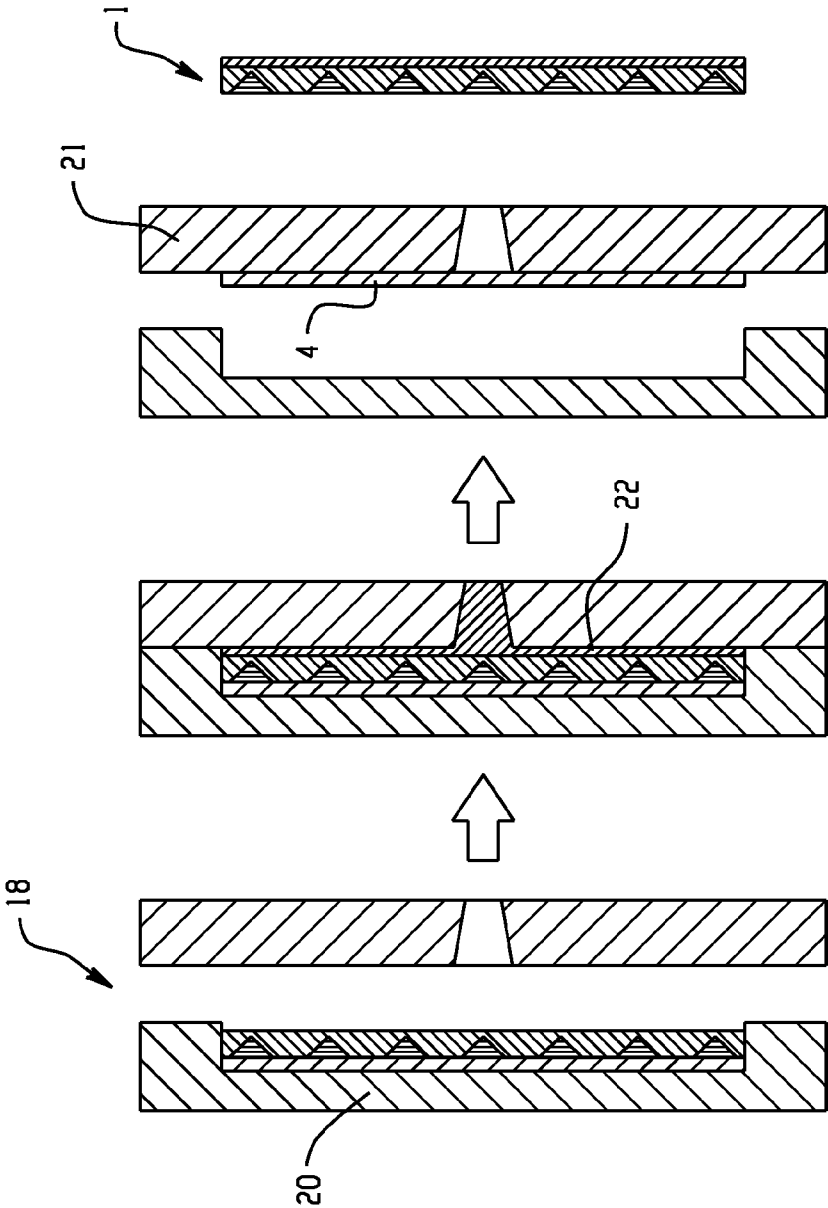


Fig. 4B

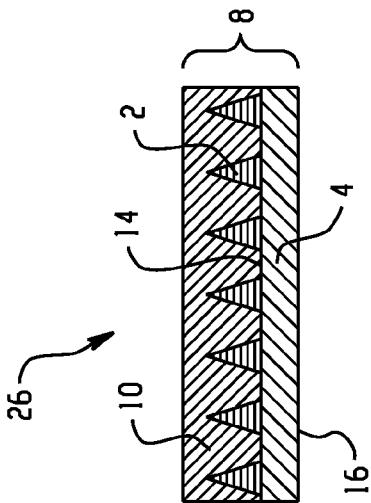


Fig. 4A

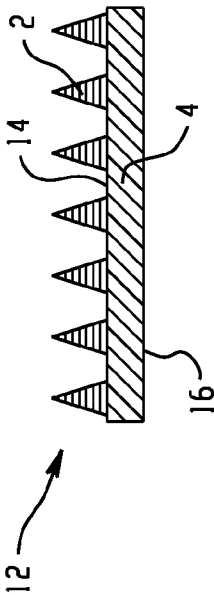


Fig. 5A

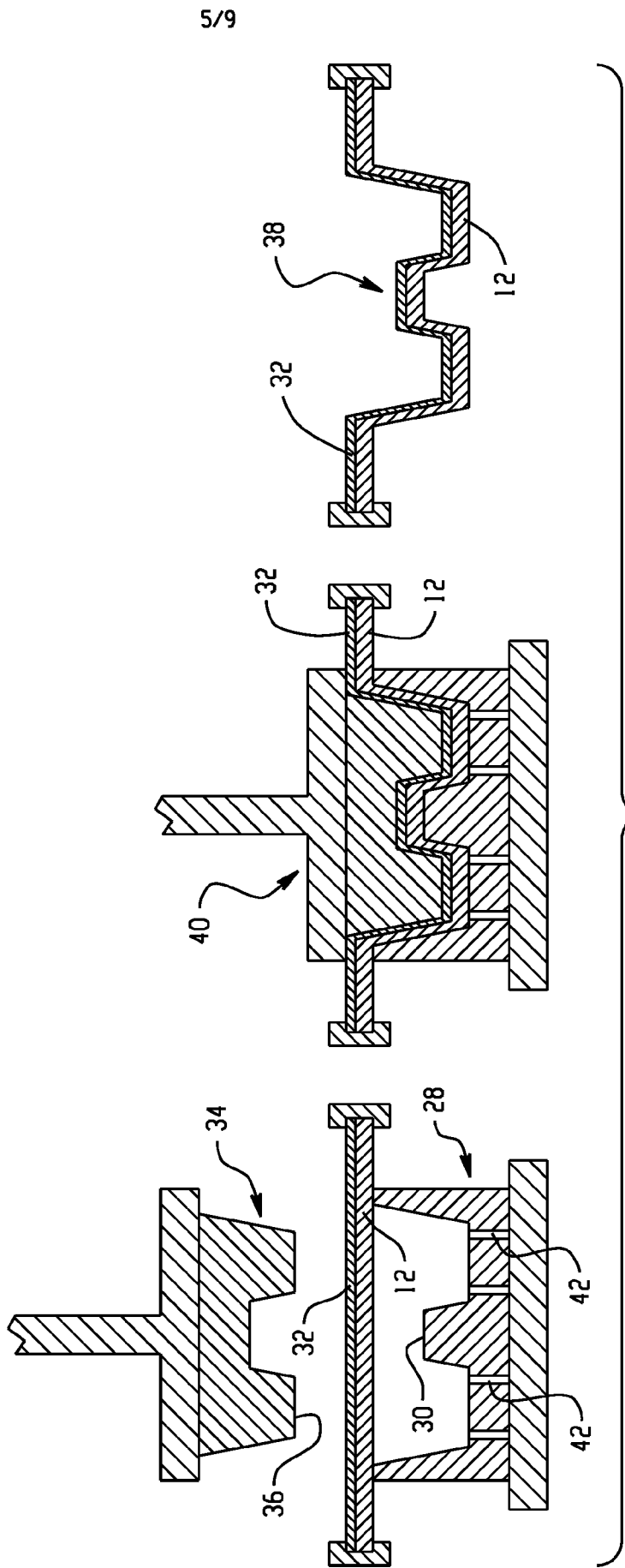
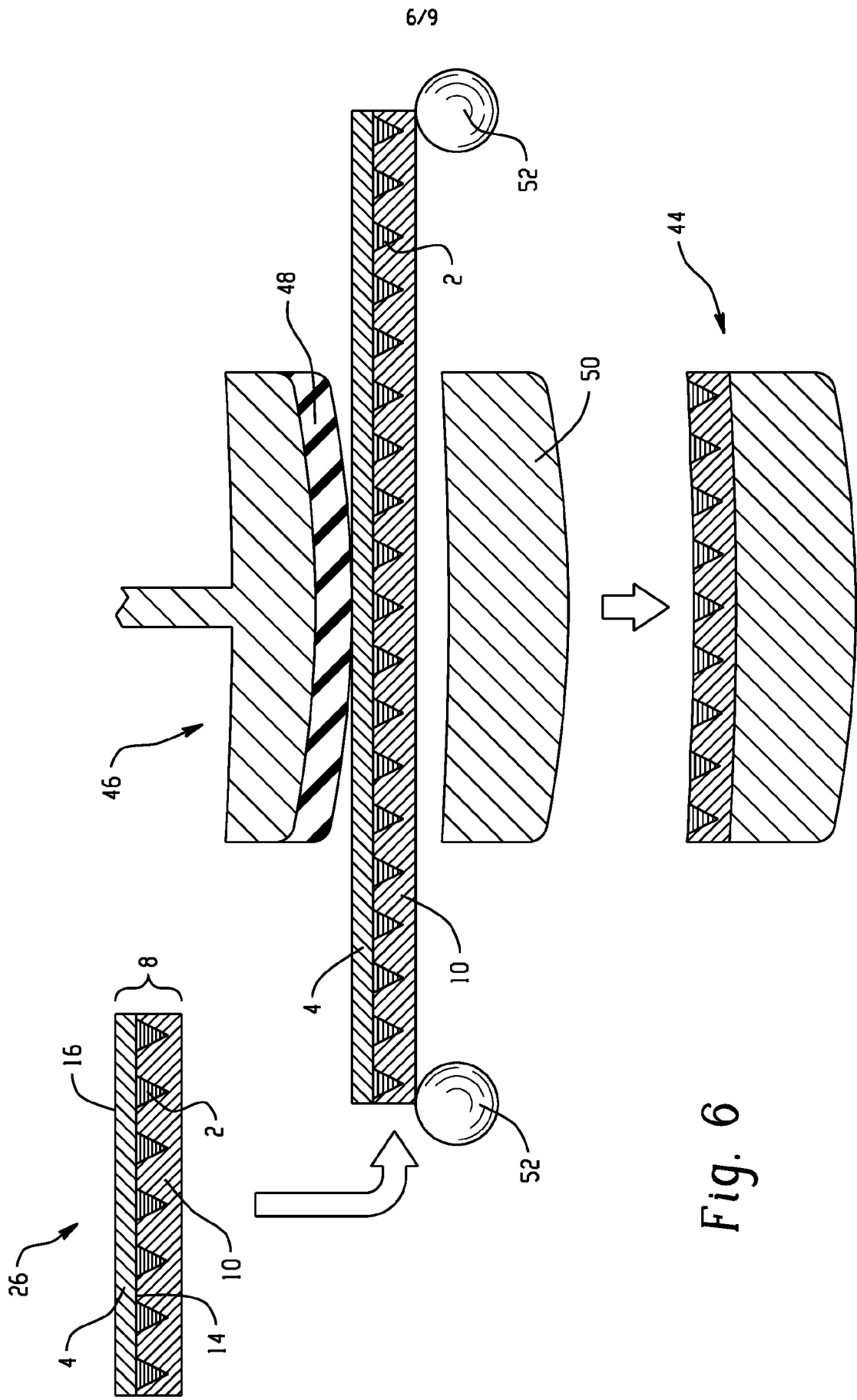
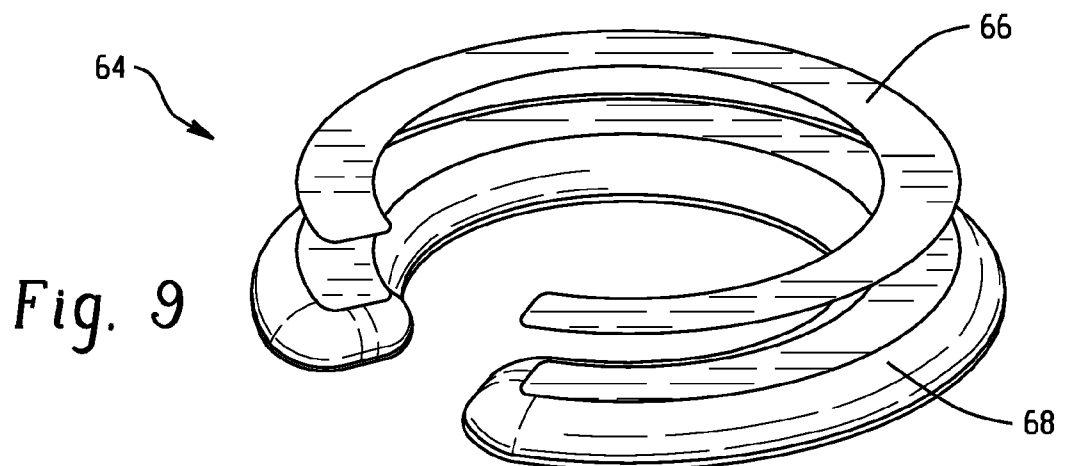
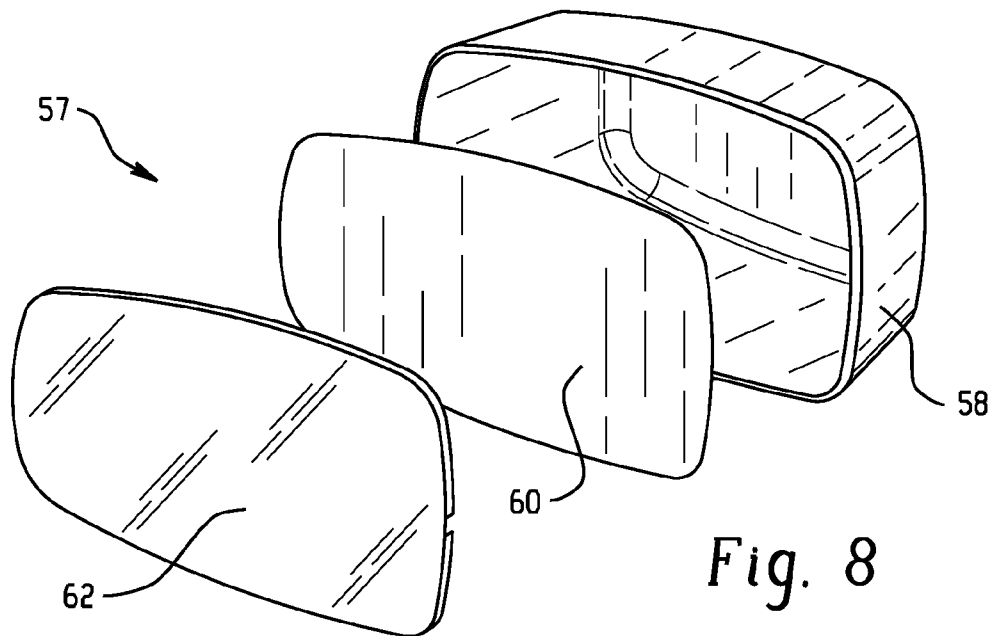
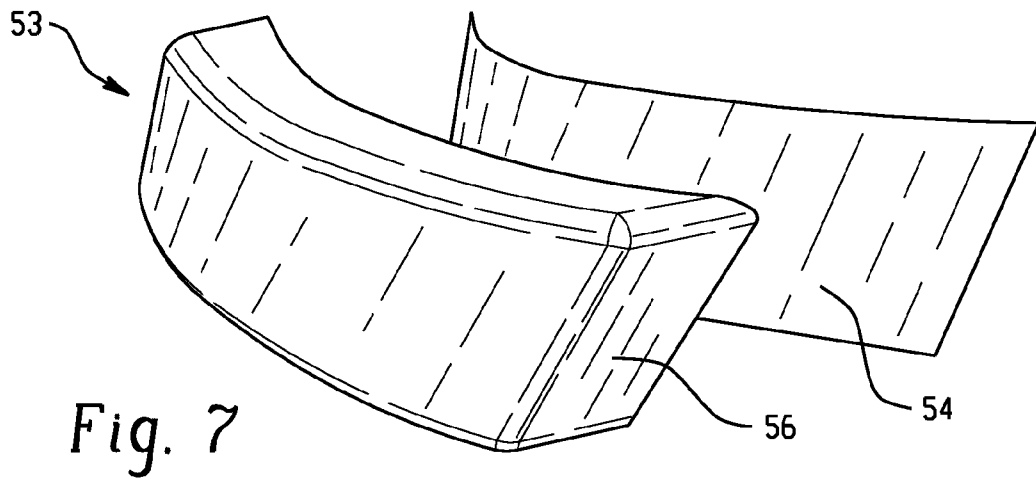


Fig. 5B



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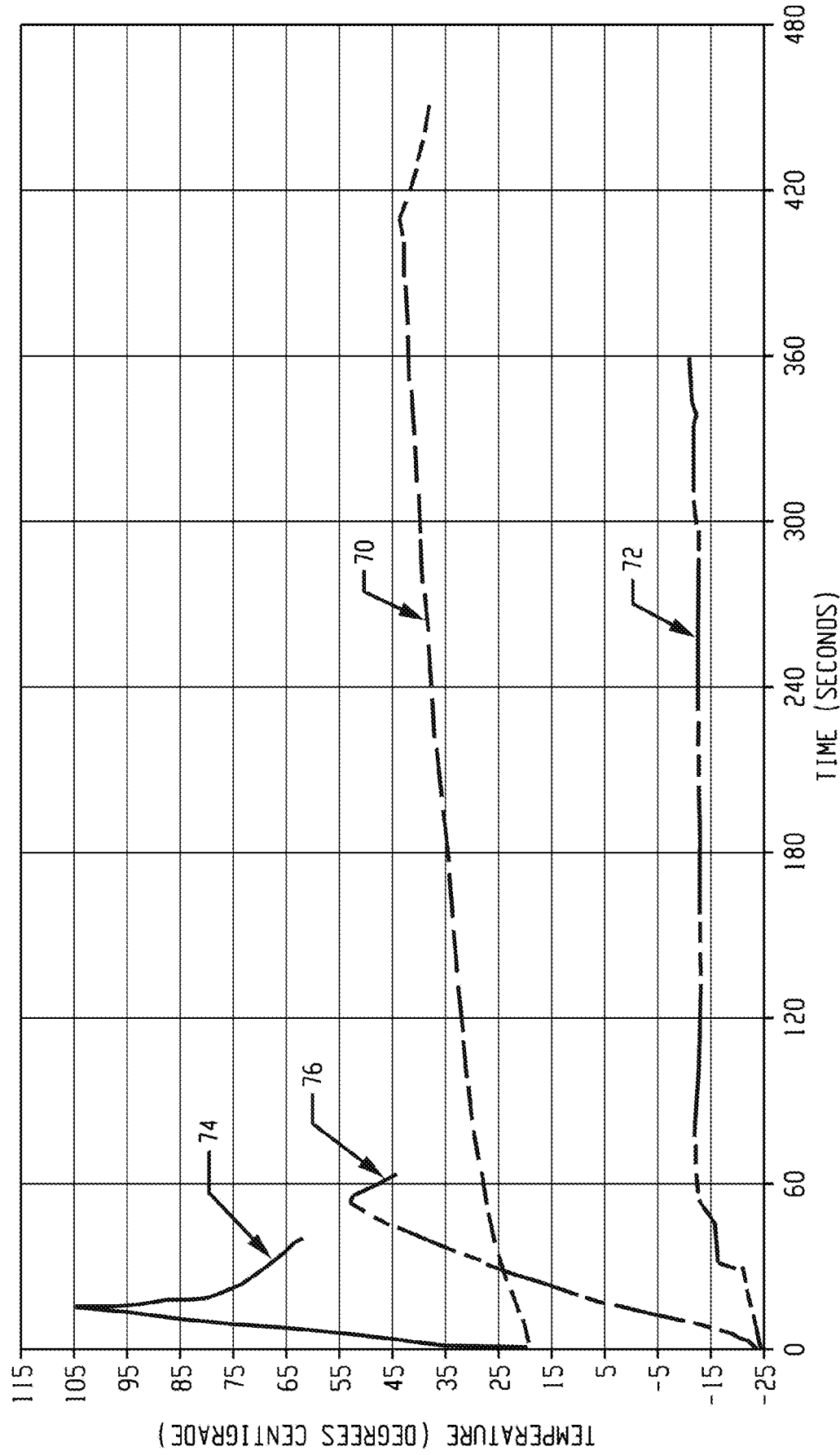


Fig. 10

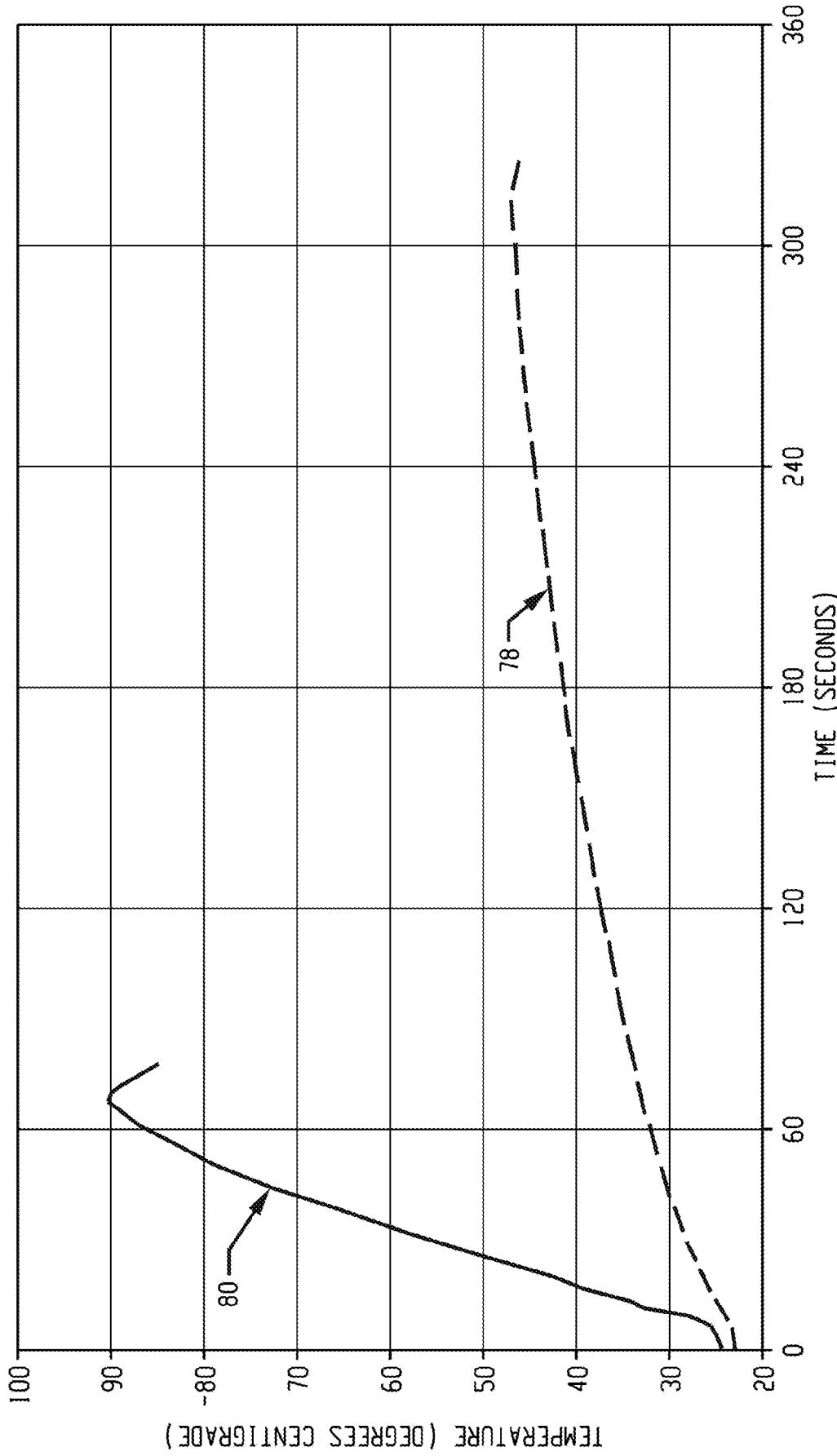


Fig. 11

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2015/060010

A. CLASSIFICATION OF SUBJECT MATTER INV. C09K5/14 H01B1/22 B29C45/14 B29C43/00 B29C43/18 C08J5/00 ADD. 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) C09K H01B B29K B29C C08J Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 10 2010 040826 A1 (LEIBNIZ INST POLYMERFORSCHUNG [DE]) 15 March 2012 (2012-03-15) [0028]; example 1 -----	1-20
☐ 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 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 1 March 2016		Date of mailing of the international search report 11/03/2016
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Pellegrini, Paolo

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2015/060010

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 102010040826 A1	15-03-2012	NONE	
