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(54) **Title:**

POLISHING PAD AND METHOD OF MAKING THE SAME

(57) **Abstract:**

The disclosure is directed to polishing pads with porous polishing layers, methods of making such polishing pads, and methods of using such pads in a polishing process. The polishing pad includes a compliant layer having first and second opposing sides and a porous polishing layer disposed on the first side of the compliant layer. The porous polishing layer includes a crosslinked network comprising a thermally cured component and a radiation cured component, wherein the radiation cured component and the thermally cured component are covalently bonded in the crosslinked network. The porous polishing layer also includes polymer particles dispersed within the crosslinked network, wherein the polymer particles comprise at least one of thermoplastic polymers or thermoset polymers. The porous polishing layer typically also includes closed cell pores dispersed within the crosslinked network.

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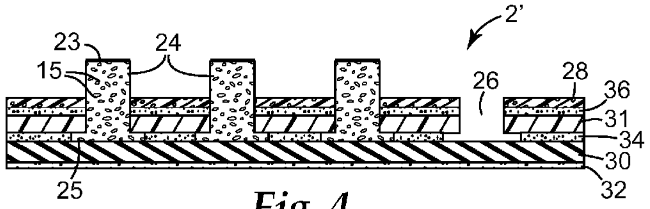

Fig. 4

(57) Abstract: The disclosure is directed to polishing pads with porous polishing layers, methods of making such polishing pads, and methods of using such pads in a polishing process. The polishing pad includes a compliant layer having first and second opposing sides and a porous polishing layer disposed on the first side of the compliant layer. The porous polishing layer includes a crosslinked network comprising a thermally cured component and a radiation cured component, wherein the radiation cured component and the thermally cured component are covalently bonded in the crosslinked network. The porous polishing layer also includes polymer particles dispersed within the crosslinked network, wherein the polymer particles comprise at least one of thermoplastic polymers or thermoset polymers. The porous polishing layer typically also includes closed cell pores dispersed within the crosslinked network.

POLISHING PAD AND METHOD OF MAKING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U. S. Provisional Application Nos. 61/288,982, filed December 22, 2009, and 61/422,442, filed December 13, 2010, the disclosures of which are incorporated by reference herein in their entirety.

BACKGROUND

During the manufacture of semiconductor devices and integrated circuits, silicon wafers are iteratively processed through a series of deposition and etching steps to form overlying material layers and device structures. A polishing technique known as chemical mechanical planarization (CMP) may be used to remove surface irregularities (such as bumps, areas of unequal elevation, troughs, and trenches) remaining after the deposition and etching steps, with the objective of obtaining a smooth wafer surface without scratches or depressions (known as dishing), with high uniformity across the wafer surface.

In a typical CMP polishing process, a substrate such as a wafer is pressed against and relatively moved with respect to a polishing pad in the presence of a working liquid that is typically a slurry of abrasive particles in water and/or an etching chemistry. Various CMP polishing pads for use with abrasive slurries have been disclosed, for example, U.S. Pat. Nos. 5,257,478 (Hyde et al.); 5,921,855 (Osterheld et al.); 6,126,532 (Sevilla et al.); 6,899,598 (Prasad); and 7,267,610 (Elmufdi et al.). Fixed abrasive polishing pads are also known, as exemplified by U.S. Pat. No. 6,908,366 (Gagliardi), in which the abrasive particles are generally fixed to the surface of the pad, often in the form of precisely shaped abrasive composites extending from the pad surface. Recently, a polishing pad having a multiplicity of polishing elements extending from a compressible underlayer was described in Int. App. Publ. No. WO/2006057714 (Bajaj). Although a wide variety of polishing pads are known and used, the art continues to seek new and improved polishing pads for CMP, particularly in CMP processes where larger die diameters are being used, or where higher levels of wafer surface flatness and polishing uniformity are required.

SUMMARY

The present disclosure provides porous polishing pads with a polishing layer having a thermally cured component and a radiation cured component and methods of making such polishing pads. Pores are incorporated into the polishing layer through the use of polymer particles. The pores in the porous polishing pads disclosed herein are closed cell pores that generally have lower pore size non-uniformity and smaller pore size than the pores of conventional thermally cured polishing pads. The control over pore size and distribution may be advantageous, for example, for the polishing performance of the polishing pad.

In one aspect, the present disclosure provides a polishing pad comprising:

a compliant layer having first and second opposing sides; and

a porous polishing layer disposed on the first side of the compliant layer, the porous polishing layer comprising:

a crosslinked network comprising a thermally cured component and a radiation cured component, wherein the radiation cured component and the thermally cured component are covalently bonded in the crosslinked network;

polymer particles dispersed within the crosslinked network,; and

closed cell pores dispersed within the crosslinked network. In some embodiments, the polishing pad further comprises a support layer interposed between the compliant layer and the porous polishing layer.

In another aspect, the present disclosure provides a method of making a polishing pad, the method comprising:

providing a composition comprising a thermally curable resin composition, a radiation curable resin composition, and polymer particles;

forming pores in the composition;

positioning the composition on a support layer; and

forming a porous polishing layer on the support layer by exposing the composition to radiation to at least partially cure the radiation curable resin composition and heating the composition to at least partially cure the thermally curable resin composition. In some embodiments, the method further comprises adhesively bonding a compliant layer to a surface of the support layer opposite the porous polishing layer.

In a further aspect, the present disclosure provides a method of polishing comprising:

contacting a surface of a substrate with the porous polishing layer of the polishing pad according to the present disclosure; and

relatively moving the polishing pad with respect to the substrate to abrade the surface of the substrate.

Exemplary embodiments of polishing pads according to the present disclosure have various features and characteristics that enable their use in a variety of polishing applications. In some embodiments, polishing pads of the present disclosure may be particularly well suited for chemical mechanical planarization (CMP) of wafers used in manufacturing integrated circuits and semiconductor devices. In some embodiments, the polishing pad described in this disclosure may provide some or all of the following advantages.

For example, in some embodiments, a polishing pad according to the present disclosure may act to better retain a working liquid used in the CMP process at the interface between the polishing surface of the pad and the substrate surface being polished, thereby improving the effectiveness of the working liquid in augmenting polishing. In other exemplary embodiments, a polishing pad according to the present disclosure may reduce or eliminate dishing and/or edge erosion of the wafer surface during polishing. In some exemplary embodiments, use of a polishing pad according to the present disclosure in a CMP process may result in improved within wafer polishing uniformity, a flatter polished wafer surface, an increase in edge die yield from the wafer, and improved CMP process operating conditions and consistency. In further embodiments, use of a polishing pad according to the present disclosure may permit processing of larger diameter wafers while maintaining the required degree of surface uniformity to obtain high chip yield, processing of more wafers before conditioning of the pad surface is needed in order to maintain polishing uniformity of the wafer surfaces, or reducing process time and wear on the pad conditioner.

In this disclosure:

"Pore size non-uniformity" refers to the standard deviation of the pore size mean divided by the mean pore size multiplied by 100.

The term "polyurethane" refers to a polymer having more than one urethane linkage (-NH-C(O)-O-), urea linkage (-NH-C(O)-NH- or -NH-C(O)-N(R)-, wherein R can be hydrogen, an aliphatic, cycloaliphatic or aromatic group), biuret, allophanate, uretdione, or isocyanurate linkage in any combination.

The term "(meth)acrylate" refers to acrylates and methacrylates, which can include urethane acrylates, methacrylates and combinations of acrylates and methacrylates.

The term "polymeric" refers to a molecule having a structure that includes the multiple repetition of units derived from molecules of low relative molecule mass. The term "polymeric" includes "oligomeric".

Terms such as "a", "an" and "the" are not intended to refer to only a singular entity, but include the general class of which a specific example may be used for illustration. The terms "a", "an", and "the" are used interchangeably with the term "at least one".

The phrases "at least one of" and "comprises at least one of" followed by a list refers to any one of the items in the list and any combination of two or more items in the list.

All numerical ranges are inclusive of their endpoints and non-integral values between the endpoints unless otherwise stated.

Various aspects and advantages of exemplary embodiments of the disclosure have been summarized. The above Summary is not intended to describe each illustrated embodiment or every implementation of the present disclosure. The Drawings and the Detailed Description that follow more particularly exemplify some embodiments of the disclosure.

BRIEF DESCRIPTION OF DRAWINGS

Exemplary embodiments of the present disclosure are further described with reference to the appended figures, wherein:

FIGS. 1A and 1B are micrographs of a cross-section and top view, respectively, of a porous polishing pad in the prior art;

FIG. 2 is a schematic side view of one embodiment of a polishing pad according to the present disclosure;

FIG. 3 is a side view of a polishing pad having projecting polishing elements according to another embodiment of the present disclosure;

FIG. 4 is a side view of a polishing pad having projecting polishing elements according to yet another embodiment of the present disclosure;

FIGS. 5A and 5B are micrographs of a cross-section and top view, respectively, of the cured composition of Example 2 useful for forming polishing layers according to the present disclosure;

FIGS. 6A and 6B are micrographs of a cross-section and a top view, respectively, of the cured composition of Comparative Example 3;

FIGS. 7A and 7B are micrographs of a cross-section and top view, respectively, of the cured composition of Example 15 useful for forming polishing layers according to the present disclosure; and

FIG. 8 is a micrograph of a cross-section view of the cured composition of Example 11 useful for forming polishing layers according to the present disclosure.

Like reference numerals in the drawings indicate like elements. The drawings herein as not to scale, and in the drawings the components of the polishing pads are sized to emphasize selected features.

DETAILED DESCRIPTION

Typical CMP pads are constructed from thermoset (e.g., polyurethane) materials having pores. The pores can be generated using a variety of methods such as microballoons, soluble fibers, gas entrapment (e.g., in-situ or ex-situ generated), and physical air entrapment. Control of the pore size, pore volume, and pore distribution through the pad can be challenging when using these methods due to temperature gradients created during polymerization, skin/core effects resulting from molding operations, distribution of the fibers, dissolving rate of the soluble fibers, and polishing chemistry.

Some commercially available CMP pads have an open cell pad construction generated during thermal curing of an isocyanate resin. FIG. 1 shows cross-section and top views of a commercially made open cell CMP pad available from PPG Industries, Pittsburgh, PA, under the trade designation "S7". As shown in FIG. 1, the size, shape, and distribution for the pores in this pad is not controlled.

The present disclosure is directed to improved porous polishing pads, in which typically closed cell pores are formed with controlled size and uniformity. Various exemplary embodiments of the disclosure will now be described. Exemplary embodiments of the present disclosure may take on various modifications and alterations without departing from the spirit and scope of the disclosure. Accordingly, it is to be understood that the embodiments of the present invention are not to be limited to the following described exemplary embodiments, but are to be controlled by the limitations set forth in the claims and any equivalents thereof.

Referring now to FIG. 2, the porous polishing pad 2a comprises a compliant layer 10a and a porous polishing layer 12a disposed on one side of (that is, one major surface of) the compliant layer. Interposed between the porous polishing layer 12a and the compliant layer 10a is optional support layer 8a, which is useful for some embodiments of the porous polishing pad and method of the present disclosure. The porous polishing layer comprises a crosslinked network, polymer particles dispersed within the crosslinked network, and closed cell pores dispersed within the crosslinked network. In contrast to polishing pads and methods in which a component of the polishing pad is removed during polishing to form voids (e.g., by erosion or dissolution) the polishing pads according to the present disclosure are porous before the polishing process begins.

Exemplary polymer particles in the polishing layer can include thermoplastic polymer particles, thermoset polymer particles, and mixtures thereof. The term "thermoplastic polymer" refers to a polymeric material that is essentially not crosslinked and essentially does not form a three-dimensional network. The term "thermoset" refers to a polymer that is at least substantially crosslinked wherein said polymer has essentially a three-dimensional network. In some embodiments, the polymer particles can be chosen such that there is minimal sintering of the particles upon heating (i.e., there is minimal plastic flow at the boundary of the polymer particles, and little to no coalescence between the particles of the polymer particles in the polishing pad of the present disclosure). In some embodiments, when the polymer particles of the pad comprises particulate thermoplastic polymer, the polishing pad can be prepared below the melting or sintering point of the particulate thermoplastic polymer. In other embodiments, the polymer particles comprise thermoset polymers.

Polymer particles useful for practicing the present disclosure can be prepared by various methods (e.g., a condensation reaction, a free radical initiated reaction, or combinations thereof). In yet other embodiments, the polymer can include an interpenetrating polymer network formed by stepwise or simultaneous condensation and free radical polymerization reactions. In this disclosure, the term "interpenetrating polymer network" (IPN) refers to a combination of two polymers both in network form, at least one of which is synthesized or crosslinked in the immediate presence of the other. Typically in IPNs, there are no induced covalent bonds between the two polymers. Thus, in addition to mechanical blending and copolymerization, IPNs represent another mechanism by which different polymers can be physically combined.

The polymer particles can be prepared by various methods. In some embodiments, bulk polymers can be cryogenically ground and classified into desired particle size ranges. The shape of the polymer particles can be regular or irregular, and can include the following shapes: sphere, fiber, disk, flake, and combinations or mixtures thereof. In some embodiments, the polymer particles are substantially spherical. The term "substantially spherical" refers to a particle having a sphericity of at least 0.75 (in some embodiments, at least 0.8, 0.85, 0.9, 0.95, 0.96, 0.97, or 0.98). In some embodiments, the polymer particles are fibers. Fibers useful for practicing the present disclosure typically have an aspect ratio (that is, longest dimension over shortest dimension) of at least 1.5:1, for example, at least 2:1, 3:1, 4:1, 5:1, 10:1, 25:1, 50:1, 75:1, 100:1, or more. Fibers useful for practicing the present disclosure may have an aspect ratio in a range from 2:1 to 100:1, 5:1 to 75:1, or 10:1 to 50:1.

In some embodiments, the polymer particles can have an average particle size of at least 5 (in some embodiments, at least 7, 10, 15, 20, 25, 30, 40, or 50) microns. In some embodiments, the polymer particles can have an average particle size of up to 500 (in some embodiments, up to 400, 300, 200, or 100) microns. The particle size generally refers to the diameter of the particle; however, in embodiments when the particles are not spherical (e.g., fibers), the particle size can refer to the largest dimension of the particle. The average particle size of the polymer particles can be determined by conventional methods. For example, the average particle size of the polymer particles can be determined using light scattering techniques, such as a Coulter LS particle size analyzer which is manufactured and commercially available from Beckman Coulter Incorporated. As used herein and in the claims, "particle size" refers to the diameter or largest dimension of the particle based on volume percent as determined by light scattering using a Coulter Counter LS particle size analyzer. In this light scattering technique, the size is determined from a hydrodynamic radius of gyration regardless of the actual shape of the particle. The "average" particle size is the average diameter of the particle based on volume percent. In some embodiments, particularly in embodiments where the particles are fibers, the fibers have a maximum particle size of up to about 600, 500, or 450 microns (30, 35, or 40 U. S. Mesh) as determined by conventional screening techniques. For example, in some embodiments, at least 97, 98, or 99 percent of the fibers pass through a screen having openings of 600, 500, or 400 microns (30, 35, or 40 U.S. Mesh).

In some embodiments, the polymer particles have a high degree of uniformity. In some embodiments, the non-uniformity of the size of polymer particles is up to 75 (in some embodiments, up to 70, 65, 60, 65, or 50) percent. Particle size non-uniformity refers to the particle size standard deviation divided by the average particle size multiplied by 100.

In some embodiments, the polymer particles are substantially solid. As used herein, the term "substantially solid" means that the particulate polymer is not hollow, for example, the polymer particles are not in the form of hollow microcapsules. However, in some embodiments, the substantially solid polymer particles can contain entrapped gas bubbles.

Suitable polymer particles include polyvinylchloride, polyvinylfluoride, polyethylene, polypropylene, nylon, polycarbonate, polyester, poly(meth)acrylate, polyether, polyamide, polyurethane, polyepoxide, polystyrene, polyimide (e.g., polyetherimide), polysulfone and mixtures thereof. In some embodiments, the polymer particles can be chosen from poly(meth)acrylate, polyurethane, polyepoxide and mixtures thereof.

In some embodiments, the polymer particles comprise water-soluble particles. Exemplary useful water soluble particles include particles made of saccharides (e.g., polysaccharides such as dextrin, cyclodextrin, starch, mannitol, and lactose), celluloses (e.g., hydroxypropylcelluloses and methylcelluloses), protein, polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylic acid, polyethylene oxide, water-soluble photosensitive resin, sulfonated polyisoprene, sulfonated polyisoprene copolymer, and any combination of these. In some embodiments, the polymer particles comprise a cellulose. In some of these embodiments, the polymer particles comprise methylcellulose. Even though in these embodiments, the polymer particles comprise water-soluble particles, the polymer particles can form pores in the polishing layer when the polishing layer is formed. A working liquid that can dissolve the particles during polishing is not required to form pores.

In some embodiments, the polymer particles comprise a polyurethane, which can be prepared, for example, from a resin comprising at least two isocyanate groups, and/or a capped isocyanate reactant having at least two capped isocyanate groups; and a second resin that has at least two groups that are reactive with isocyanate groups.

In some embodiments, the first and second resins can be mixed together and polymerized or cured to form a bulk polyurethane, which can then be ground (e.g., cryogenically ground), and optionally classified. In some embodiments, the polymer particles can be formed by mixing the first and second resins together, slowly pouring the mixture into heated deionized water under agitation (optionally in the presence of an organic cosolvent and/or surfactant), isolating the formed particulate material (e.g., by filtration), drying the isolated particulate material, and optionally classifying the dried particulate polyurethane. In another embodiment, the isocyanate and hydrogen materials can be mixed together in the presence of an organic solvent (e.g., alcohols, water-insoluble ethers, branched and straight hydrocarbons, ketones, toluene, xylene and mixtures thereof).

In some embodiments, the first resin comprising at least two isocyanate groups can be chosen from isocyanate functional monomers, isocyanate functional prepolymers and combinations thereof. Exemplary suitable isocyanate monomers include aliphatic polyisocyanates; ethylenically unsaturated polyisocyanates; alicyclic polyisocyanates; aromatic polyisocyanates wherein the isocyanate groups are not bonded directly to the aromatic ring, for example, alpha,alpha'-xylene diisocyanate; aromatic polyisocyanates wherein the isocyanate groups are bonded directly to the aromatic ring, for example, benzene diisocyanate; halogenated, alkylated, alkoxylated, nitrated, carbodiimide modified, urea modified, and biuret modified derivatives of these polyisocyanates; and dimerized and trimerized products of these polyisocyanates.

Exemplary aliphatic polyisocyanates include ethylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, nonamethylene diisocyanate, 2,2'-dimethylpentane diisocyanate, 2,2,4-trimethylhexane diisocyanate, decamethylene diisocyanate, 2,4,4,-trimethylhexamethylene diisocyanate, 1,6,1-undecanetriisocyanate, 1,3,6-hexamethylene triisocyanate, 1,8-diisocyanato-4-(isocyanatomethyl)octane, 2,5,7-trimethyl-1,8-diisocyanato-5-(isocyanatomethyl)octane, bis(isocyanatoethyl)-carbonate, bis(isocyanatoethyl)ether, 2-isocyanatopropyl-2,6-diisocyanatohexanoate, lysinediisocyanate methyl ester, lysinetriisocyanate methyl ester and mixtures thereof.

Exemplary suitable ethylenically unsaturated polyisocyanates can include butene diisocyanate and 1,3-butadiene-1,4-diisocyanate. Exemplary suitable alicyclic polyisocyanates include isophorone diisocyanate, cyclohexane diisocyanate, methylcyclohexane diisocyanate, bis(isocyanatomethyl)cyclohexane, bis(isocyanatocyclohexyl)methane, bis(isocyanatocyclohexyl)-2,2-propane, bis(isocyanatocyclohexyl)-1,2-ethane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-5-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-6-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-5-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-6-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-6-(2-isocyanatoethyl)-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-5-(2-isocyanatoethyl)-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-6-(2-isocyanatoethyl)-bicyclo[2.2.1]-heptane and mixtures thereof.

Exemplary aromatic polyisocyanates wherein the isocyanate groups are not bonded directly to the aromatic ring include bis(isocyanatoethyl)benzene, alpha, alpha, alpha', alpha'-tetramethylxylene diisocyanate, 1,3-bis(1-isocyanato-1-methylethyl)benzene, bis(isocyanatobutyl)benzene, bis(isocyanatomethyl)naphthalene, bis(isocyanatomethyl)diphenyl ether, bis(isocyanatoethyl)phthalate, mesitylene triisocyanate, 2,5-di(isocyanatomethyl)furan and mixtures thereof.

Exemplary suitable aromatic polyisocyanates having isocyanate groups bonded directly to the aromatic ring include phenylene diisocyanate, ethylphenylene diisocyanate, isopropylphenylene diisocyanate, dimethylphenylene diisocyanate, diethylphenylene diisocyanate, diisopropylphenylene diisocyanate, trimethylbenzene triisocyanate, benzene triisocyanate, naphthalene diisocyanate, methylnaphthalene diisocyanate, biphenyl diisocyanate, ortho-tolidine diisocyanate, 4,4'-diphenylmethane diisocyanate, bis(3-methyl-4-isocyanatophenyl)methane, bis(isocyanatophenyl)ethylene, 3,3'-dimethoxy-biphenyl-4,4'-diisocyanate, triphenylmethane triisocyanate, polymeric 4,4'-

diphenylmethane diisocyanate, naphthalene triisocyanate, diphenylmethane-2,4,4'-triisocyanate, 4-methyldiphenylmethane-3,5,2',4',6'-pentaisocyanate, diphenylether diisocyanate, bis(isocyanatophenylether)ethyleneglycol, bis(isocyanatophenylether)-1,3-propyleneglycol, benzophenone diisocyanate, carbazole diisocyanate, ethylcarbazole diisocyanate, dichlorocarbazole diisocyanate and mixtures thereof.

In some embodiments, the first resin comprising at least two isocyanate groups is selected from the group consisting of alpha, alpha'-xylene diisocyanate, alpha, alpha, alpha', alpha'-tetramethylxylene diisocyanate, isophorone diisocyanate, bis(isocyanatocyclohexyl)methane, toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, and mixtures thereof.

In some embodiments, the first resin having at least two isocyanate groups can comprise an isocyanate functional polyurethane prepolymer. Isocyanate functional polyurethane prepolymers can be prepared by various conventional techniques. In some embodiments, at least one polyol such as a diol, and at least one isocyanate functional monomer such as a diisocyanate monomer, can be reacted together to form a polyurethane prepolymer having at least two isocyanate groups. Exemplary suitable isocyanate functional monomers include the aforementioned isocyanate functional monomers.

Suitable isocyanate functional polyurethane prepolymers useful for practicing the present disclosure can have molecular weights that vary within a wide range. In some embodiments, the isocyanate functional polyurethane prepolymer can have a number average molecular weight (Mn) of from 500 to 15,000, or from 500 to 5000, as determined, for example, by gel permeation chromatography (GPC) using polystyrene standards.

Exemplary polyols useful for preparing isocyanate functional polyurethane prepolymers include straight or branched chain alkane polyols, such as 1,2-ethanediol, 1,3-propanediol, 1,2-propanediol, 1,4-butanediol, 1,3-butanediol, glycerol, neopentyl glycol, trimethylolethane, trimethylolpropane, di-trimethylolpropane, erythritol, pentaerythritol and di-pentaerythritol; polyalkylene glycols, such as di-, tri- and tetraethylene glycol, and di-, tri- and tetrapropylene glycol; cyclic alkane polyols, such as cyclopentanediol, cyclohexanediol, cyclohexanetriol, cyclohexanedimethanol, hydroxypropylcyclohexanol and cyclohexanediethanol; aromatic polyols, such as dihydroxybenzene, benzenetriol, hydroxybenzyl alcohol and dihydroxytoluene; bisphenols, such as 4,4'-

isopropylidenediphenol (bisphenol A); 4,4'-oxybisphenol, 4,4'-dihydroxybenzophenone, 4,4'-thiobisphenol, phenolphthlalein, bis(4-hydroxyphenyl)methane (bisphenol F), 4,4'-(1,2-ethenediyl)bisphenol and 4,4'-sulfonylbisphenol; halogenated bisphenols, such as 4,4'-isopropylidenebis(2,6-dibromophenol), 4,4'-isopropylidenebis(2,6-dichlorophenol) and 4,4'-isopropylidenebis(2,3,5,6-tetrachlorophenol); alkoxylated bisphenols, such as alkoxylated 4,4'-isopropylidenediphenol having one or more alkoxy groups, such as ethoxy, propoxy, alpha-butoxy and beta-butoxy groups; and biscyclohexanols, which can be prepared by hydrogenating the corresponding bisphenols, such as 4,4'-isopropylidene-biscyclohexanol, 4,4'-oxybiscyclohexanol, 4,4'-thiobiscyclohexanol and bis(4-hydroxycyclohexanol)methane.

Further examples of suitable polyols useful for preparing isocyanate functional polyurethane prepolymers include higher polyalkylene glycols, such as polyethylene glycols having a number average molecular weight (Mn) of from 200 to 2000 grams per mole; hydroxyl-bearing acrylics, such as those formed from the copolymerization of (meth)acrylates and hydroxy functional (meth)acrylates, such as methyl methacrylate and hydroxyethyl methacrylate copolymers; and hydroxy functional polyesters, such as those formed from the reaction of diols, such as butane diol, and diacids or diesters, such as adipic acid or diethyl adipate. In some embodiments, the polyol useful for practicing the present disclosure can have a number average molecular weight (Mn) of from 200 to 2000 grams per mole.

In some embodiments, an isocyanate functional polyurethane prepolymer can be prepared by reacting a diisocyanate such as toluene diisocyanate, with a polyalkylene glycol such as poly(tetrahydrofuran).

In some embodiments, an isocyanate functional polyurethane prepolymer can be prepared in the presence of a catalyst. In some embodiments, the amount of catalyst used can be less than 5 percent by weight, or less than 3 percent by weight, or less than 1 percent by weight, based on the total weight of the polyol and isocyanate functional monomer. In some embodiments, exemplary suitable catalysts include a stannous adduct of an organic acid, such as stannous octoate, dibutyl tin dilaurate, dibutyl tin diacetate, dibutyl tin mercaptide, dibutyl tin dimaleate, dimethyl tin diacetate, dimethyl tin dilaurate, 1,4-diazabicyclo[2.2.2]octane, and mixtures thereof. In other embodiments, the catalyst can be zinc octoate, bismuth, or ferric acetylacetonate. Further exemplary suitable catalysts include tertiary amines such as triethylamine, triisopropylamine and N,N-dimethylbenzylamine.

In some embodiments, for polyurethanes useful for making polymer particles, the first resin having at least two isocyanate groups includes a capped isocyanate compound having at least two capped isocyanate groups. The term "capped isocyanate compound" refers to a monomer or prepolymer having terminal and/or pendent capped isocyanate groups which can be converted to decapped (i.e., free) isocyanate groups and separate or free capping groups. Any of the aforementioned examples of suitable isocyanate compounds can be capped. Exemplary nonfugitive capping groups of the capped isocyanate include 1H-azoles, such as 1H-imidazole, 1H-pyrazole, 3,5-dimethyl-1H-pyrazole, 1H-1,2,3-triazole, 1H-1,2,3-benzotriazole, 1H-1,2,4-triazole, 1H-5-methyl-1,2,4-triazole and 1H-3-amino-1,2,4-triazole; lactams, such as e-caprolactam and 2-pyrolidinone; morpholines such as 3-aminopropyl morpholine; and N-hydroxy phthalimide. Exemplary fugitive capping groups of the capped isocyanate compound include alcohols, such as propanol, isopropanol, butanol, isobutanol, tert-butanol and hexanol; alkylene glycol monoalkyl ethers, such as ethylene glycol monoalkyl ethers (e.g., ethylene glycol monobutyl ether and ethylene glycol monohexyl ether), and propylene glycol monoalkyl ethers (e.g., propylene glycol monomethyl ether); and ketoximes, such as methyl ethyl ketoxime.

While not intending to be bound by any theory, it is believed that the inclusion of capped isocyanate material in the first resin having at least two isocyanate groups can result in the formation of covalent bonds: (a) between at least a portion of the particulate polyurethane particles; and/or (b) between at least a portion of the particulate polyurethane and at least a portion of the crosslinked network. In some embodiments, the capped isocyanate compound can be present in an amount such that the first resin capped isocyanate groups in an amount of at least 5 mole percent, or at least 10 mole percent, or less than 40 mole percent, or less than 50 mole percent, based on the total molar equivalents of free isocyanate and capped isocyanate groups.

The second resin that has at least two groups that are reactive with isocyanate groups can be chosen from a wide variety of materials. In some embodiments, the second resin has functional groups chosen from hydroxyl, mercapto, primary amine, secondary amine and combinations thereof. Exemplary suitable second resins include the aforementioned polyols.

In some embodiments, the second resin which can have at least two groups that are reactive with isocyanate groups includes a polyamine. Exemplary polyamines include ethyleneamines such as ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), piperazine, diethylenediamine (DEDA), and 2-amino-1-ethylpiperazine. Further exemplary suitable polyamines include one or more isomers of dialkyl toluenediamine, such as 3,5-dimethyl-2,4-toluenediamine, 3,5-dimethyl-2,6-toluenediamine, 3,5-diethyl-2,4-toluenediamine, 3,5-diethyl-2,6-toluenediamine, 3,5-diisopropyl-2,4-toluenediamine, 3,5-diisopropyl-2,6-toluenediamine and mixtures thereof. In some embodiments, the polyamine can be chosen from methylene dianiline, trimethyleneglycol di(para-aminobenzoate), and amine-terminated oligomers and prepolymers.

In some embodiments, suitable polyamines can be chosen from those based on 4,4'-methylene-bis(dialkylaniline) (e.g., 4,4'-methylene-bis(2,6-dimethylaniline), 4,4'-methylene-bis(2,6-diethylaniline), 4,4'-methylene-bis(2-ethyl-6-methylaniline), 4,4'-methylene-bis(2,6-diisopropylaniline), 4,4'-methylene-bis(2-isopropyl-6-methylaniline), 4,4'-methylene-bis(2,6-diethyl-3-chloroaniline) and mixtures thereof.

In some embodiments, preparation of a particulate polyurethane from a first resin comprising at least two isocyanate groups and a second resin comprising at least two groups that are reactive with an isocyanate can be carried out in the presence of a catalyst. Suitable catalysts include those listed above for the preparation of an isocyanate functional polyurethane prepolymer.

In some embodiments, the molar equivalent ratio of isocyanate groups and optional capped isocyanate groups to isocyanate-reactive groups useful for preparing particulate polyurethanes is from 0.5:1.0 to 1.5:1.0, e.g., from 0.7:1.0 to 1.3:1.0 or from 0.8:1.0 to 1.2:1.0. In some embodiments, a crosslinked polyurethane can be prepared by using less than the stoichiometrically required amount of the second resin such that the urethane or urea linkages will react with remaining isocyanates. In other embodiments, the partial replacement of difunctional by trifunctional compounds will result in more thermally stable chemical crosslinks.

Some useful particulate polyurethanes are commercially available, for example, from Dainichiseika Color & Chemicals Mfg. Co., Ltd. Advanced Polymers Group, Tokyo, Japan, under the trade designation "DAIMIC-BEAZ" in grades "UCN-5350D", "UCN-5150D", and "UCN-5070D"; polyurethane particles available from Negami Chemical Industrial Co., Ltd., Nomi-city, Japan, under the trade designation "ART PEARL"; and aliphatic polyether-based thermoplastic polyurethanes available, for example, from Bayer Corporation under the trade designation "TEXIN".

In some embodiments, suitable polymer particles useful for practicing the present disclosure include particulate polyepoxides. A particulate polyepoxide can be prepared, for example, from a reaction product of a first resin having at least two epoxide groups; and a second resin having at least two groups that are reactive with the epoxide groups of the epoxide.

In some embodiments, the first resin comprising at least two epoxide groups and the second resin can be mixed together and polymerized or cured to form bulk polyepoxide, which then can be ground (e.g., cryogenically ground), and optionally classified. In some embodiments, the particulate polyepoxide can be formed by mixing the epoxide functional and hydrogen functional materials together, slowly pouring the mixture into heated deionized water under agitation, isolating the formed particulate material (e.g., by filtration), drying the isolated particulate material, and optionally classifying the dried particulate polyepoxide.

In some embodiments, suitable epoxide functional materials useful for practicing the present disclosure include epoxide functional monomers, epoxide functional prepolymers and combinations thereof. Exemplary suitable epoxide functional monomers can include aliphatic polyepoxides, such as 1,2,3,4-diepoxybutane, 1,2,7,8-diepoxyoctane; cycloaliphatic polyepoxides, such as 1,2,4,5-diepoxycyclohexane, 1,2,5,6-diepoxycyclooctane, 7-oxa-bicyclo[4.1.0]heptane-3-carboxylic acid 7-oxa-bicyclo[4.1.0]hept-3-ylmethyl ester, 1,2-epoxy-4-oxiranyl-cyclohexane and 2,3-(epoxypropyl)cyclohexane; aromatic polyepoxides, such as bis(4-hydroxyphenyl)methane diglycidyl ether; hydrogenated bisphenol A diepoxide and mixtures thereof. Epoxide functional monomers that may be useful in the present disclosure are typically prepared from the reaction of a polyol and an epihalohydrin, for example, epichlorohydrin. Polyols that may be used to prepare epoxide functional monomers include those recited previously herein with regard to the preparation of the isocyanate functional prepolymer. A useful class of epoxide functional monomers include those prepared from the reaction of a bisphenol and epichlorohydrin (e.g., the reaction of 4,4'-isopropylidenediphenol and epichlorohydrin to make 4,4'-isopropylidenediphenol diglycidyl ether).

In some embodiments, an epoxide functional prepolymer useful for preparing particular epoxides can be prepared by reacting a polymeric polyol and epichlorohydrin. Exemplary suitable polymeric polyols can include polyalkylene glycols, such as polyethylene glycol and polytetrahydrofuran; polyester polyols; polyurethane polyols; poly((meth)acrylate) polyols; and mixtures thereof.

In some embodiments of the present disclosure, the epoxide functional prepolymer can include an epoxy functional poly((meth)acrylate) polymer which can be prepared from a (meth)acrylate monomer and an epoxide functional radically polymerizable monomer (e.g., glycidyl (meth)acrylate). Suitable epoxide functional prepolymers can have a wide range of molecular weight. In some embodiments, the molecular weight of the epoxide functional prepolymer can be from 500 to 15,000 grams per mole, or from 500 to 5000 grams per mole, as determined, for example, by gel permeation chromatography (GPC) using polystyrene standards.

The second resin having at least two groups reactive with epoxides can comprise at least one of hydroxyl, mercapto, carboxylic acid, primary amine, or secondary amine. In some embodiments, the second resin can include polyols recited previously herein. In other embodiments, the second resin can include polyamines recited previously herein. In some embodiments, suitable polyamines can include polyamide prepolymers having at least two amine groups selected from primary amines, secondary amines and combinations thereof. Suitable exemplary polyamide prepolymers can include those available, for example, from Cognis Corporation, Coating & Inks Division, Monheim, Germany, under the trade designation "VERSAMID".

In some embodiments, preparation of a particulate epoxide from a first resin comprising at least two epoxide groups and a second resin comprising at least two groups that are reactive with an epoxide can be carried out in the presence of a catalyst. Exemplary suitable catalysts include tertiary amines such as triethylamine, triisopropylamine, tri-tertiarybutyl amine, tetrafluoroboric acid and N,N-dimethylbenzylamine. In some embodiments, the catalyst can be incorporated into the second resin before it is combined with the epoxide functional material. In some embodiments, the amount of catalyst used can be less than 5 percent by weight, or less than 3 percent by weight, or less than 1 percent by weight, based on the total weight of the combined first and second resins.

The molar equivalents ratio of epoxide groups to epoxide-reactive groups of the reactants used to prepare the particulate crosslinked polyepoxide is typically from 0.5:1.0 to 2.0:1.0, e.g., from 0.7:1.0 to 1.3:1.0 or from 0.8:1.0 to 1.2:1.0.

In some embodiments, the first resin having at least two isocyanate groups or at least two epoxide groups, and/or the second resin can optionally comprise known conventional additives. Examples of such additives include heat stabilizers, antioxidants, mold release agents, static dyes, pigments, flexibilizing additives, such as alkoxylated phenol benzoates and poly(alkylene glycol) dibenzoates, and surfactants, such as ethylene oxide/propylene oxide block copolymeric surfactants. In some embodiments, such additives can be present in an amount totaling up to 10 percent by weight, or up to 5 percent by weight, or up to 3 percent by weight, based on the total weight of the combined first and second resins.

Other polymer particles useful for practicing the present disclosure include thermoplastic poly(meth)acrylates commercially available, for example, from ROHM America, Incorporated, Lawrenceville, Georgia, under the trade designation "ROHADON" and from Negami Chemical Industrial Co., Ltd., under the trade designation "ART PEARL". Yet other polymer particles useful for practicing the present disclosure include cellulose particles commercially available, for example, from Dow Chemical Company, Midland, Michigan, under the trade designation "METHOCEL".

The amount of polymer particles present in the polishing pad according to the present disclosure can vary. Interestingly, it was found that in some embodiments the amount of polymer particles mixed using certain techniques affects the porosity of the resulting polishing layer in an unexpected way. For example, when using a mixer that combines revolution and rotation, it was found that particle levels up to 20 percent by weight provided fewer pores than particle levels up to 15 percent by weight. However, other mixing techniques may provide different results. In some embodiments, the polymer particles are present in an amount of at least 1 percent by weight, or at least 2.5 percent by weight, or at least 5 percent by weight, based on the total weight of the particulate polymer and the crosslinked network. In some embodiments, the polymer particles can be present in an amount of up to 25 percent by weight, or up to 20 percent by weight, or less than 20 percent by weight, based on the total weight of the polymer particles and the crosslinked network.

In some embodiments, including embodiments where the polymer particles are fibers, the polymer particles can be present in an amount of up to 10 percent by weight, or up to 5 percent by weight, or less than 5 percent by weight, based on the total weight of the polymer particles and the crosslinked network. Advantageously, polymer particles in the form of fibers may provide a useful level of porosity even at a level of up to 2 percent by weight, based on the total weight of the polymer particles and the crosslinked network. In some of these embodiments, the polymer particles are water-soluble fibers (e.g., methylcellulose fibers). As shown in the Tables 1 and 2 in the Examples, a higher level of porosity is obtained with methylcellulose fibers than with an equivalent amount by weight of spherical polyurethane particles. A visual comparison between FIG. 8, which is a micrograph of a cross-section view of the cured composition of Example 12, and FIGS. 7A and 7B, which are micrographs of a cross-section and top view, respectively, of the cured composition of Example 15, shows that about the same level of porosity can be obtained with two percent by weight fibers (FIG. 8) as with ten percent by weight particles (FIGS. 7A and 7B).

Incorporating a lower level of particles to obtain the same porosity may be advantageous, for example, for improving uniformity in the particle distribution throughout the crosslinked network and for maintaining hardness at the pad surface during polishing.

Polishing pads according to the present disclosure comprise a polishing layer comprising polymer particles and a crosslinked network comprising a thermally cured component and a radiation cured component. A wide variety of suitable polymers can be useful for forming the crosslinked network. In some embodiments, the thermally cured component comprises at least one of a polyurethane, a polyepoxide, or a urethane-modified polyepoxide.

Typically, the crosslinked network of the present disclosure is formed in the presence of the polymer particles. In some embodiments, a thermally curable resin composition and a radiation curable resin composition can react to form the crosslinked network while the curable compositions are in the presence of the polymer particles.

In some embodiments, the polishing layer disclosed herein can comprise at least 75 percent by weight, or at least 80 percent by weight, or at least 85 percent by weight of the crosslinked network, based on the total weight of the polymer particles and the crosslinked network. In some embodiments, the crosslinked network can be present in the polishing layer in an amount of up to 99 percent by weight, or up to 95 percent by weight, or up to 90 percent by weight, based on the total weight of the polymer particles and the crosslinked network.

The crosslinked network can be prepared by conventional polymerization techniques methods. In some embodiments, the crosslinked network can be formed by condensation reactions, free radical initiated reactions, or combinations thereof. In some embodiments, the thermally cured component can comprise a polyurethane formed by the condensation of a thermally curable resin composition comprising a polyurethane prepolymer with a polyamine. In some embodiments, the radiation cured component can comprise a urethane-polyacrylate or urethane-polymethacrylate formed by the polymerization of a urethane-diacrylate or urethane-dimethacrylate in the presence of a photoinitiator. In some embodiments, the crosslinked network is interpenetrating polymer network formed by stepwise or simultaneous thermal curing and radiation curing polymerizations. In some embodiments, the radiation cured component (in some embodiments a polyacrylate or polymethacrylate) is covalently bonded to the thermally cured component, for example, through urethane or urea linking groups.

Suitable thermally curable resin compositions useful for practicing the present disclosure can include monomers, prepolymers, and mixtures thereof. In some embodiments, the thermally curable resin composition can contain catalysts, crosslinking agents, curing agents, solvents, and other conventional additives that are known in the art.

In some embodiments, the thermally curable resin composition comprises a first resin having at least two isocyanate groups, which may also be capped isocyanate groups, or at least two epoxide groups; and a second resin having at least two groups that are reactive with isocyanates and/or epoxides (e.g., hydroxyl, amino, carboxy, or mercaptan groups).

Exemplary suitable first and second resins that may be used to prepare the thermally cured component can be chosen from the isocyanates (including prepolymers), capped isocyanates, polyols and polyamines described previously herein, respectively, relative to the particulate polyurethanes. Use of capped isocyanates may, for example, delay the onset of gelation when the first and second resins are combined, which may allow for more time for mixing the first and second resins and the polymer particles.

Some isocyanate prepolymers that are useful as the first resin are commercially available, for example, an isocyanate prepolymer available under the trade designation “AIRTHANE PHP-75D” from Air Products and Chemicals, Inc., Allentown, PA. Some diamines that are useful as the second resin are commercially available, for example, oligomeric diamine available under the trade designation “VERSALINK P250” and “VERSALINK P650”from Air Products and Chemicals, Inc.

In some embodiments, the composition comprising a radiation curable resin and a thermally curable resin comprising the first resin having at least two isocyanate groups and the second resin having at least two groups reactive with isocyanate groups can further comprise a catalyst. Exemplary suitable catalysts can include those recited previously herein with regard to the preparation of the particulate polyurethane, (e.g., tertiary amines such as triethylamine and organometallic compounds such as dibutyltin dilaurate). In some embodiments, the catalyst can be incorporated into the second resin before combining the first and second resins. In some embodiments, the catalyst can be present in an amount of less than 5 percent by weight, or less than 3 percent by weight or less than 1 percent by weight, based on the total weight of the combined first and second resins. The molar equivalents ratio of isocyanate groups and optional capped isocyanate groups to isocyanate-reactive groups in the first and second resins, respectively, can be from 0.5:1.0 to 2.0:1.0, or from 0.7:1.0 to 1.3:1.0, or from 0.8:1.0 to 1.2:1.0.

In some embodiments, the thermally cured component can be prepared by reacting a first resin having at least two epoxide groups; and a second resin having at least two groups reactive with the epoxide groups (e.g., hydroxyl, amino, carboxy, or mercaptan groups). Exemplary suitable first resins having at least two epoxide groups and second resins include any of those epoxides, polyamines, and polyols used to prepare the particulate polyepoxide as discussed previously herein.

In some embodiments, the composition comprising a radiation curable resin and a thermally curable resin comprising the first and second resins used to prepare a polyepoxide themally cured component can further comprise an epoxide ring opening catalyst. Exemplary suitable catalysts for ring-opening of epoxides include any of those described above (e.g., tertiary amines such as tri-tert-butyl amine) and tetrafluoroboric acid). In some embodiments, the catalyst can be added to the second resin before mixing the first and second resins. In some embodiments, the epoxide ring opening catalyst can be present in an amount of less than 5 percent by weight, or less than 3 percent or 1 percent by weight, based on the total weight of the first and second resins. The molar equivalents ratio of epoxide groups to epoxide-reactive groups in the first and second resins, respectively, can be from 0.5:1.0 to 2.0:1.0, or from 0.7:1.0 to 1.3:1.0, or from 0.8:1.0 to 1.2:1.0.

In some embodiments, the thermally curable resins can comprise conventional additives. Exemplary suitable conventional additives include any of those additives as described previously herein with regard to preparation of the particulate polyurethanes and particulate polyepoxides, such as mold release agents, dyes, and flexibilizing agents. In some embodiments, additives can be present in an amount totaling less than 10 percent by weight, or less than 5 percent by weight, or less than 3 percent by weight, based on the total weight of the crosslinked network. The conventional additives can be added, for example, to either the first or second resins.

Porous polishing pads according to the present disclosure comprise a polishing layer having a radiation cured component. The radiation cured component comprises at least one of a polyacrylate, polymethacrylate, poly(vinyl ether), a polyvinyl, or a polyepoxide. In some embodiments, the radiation cured component comprises at least one of a polyacrylate or polymethacrylate. The radiation cured component may be prepared from a radiation curable resin comprising at least two acrylate, methacrylate, vinyl (e.g., vinyl, allyl, or styryl groups), or epoxide groups. In some embodiments, the radiation curable resin comprises at least two acrylate or methacrylate groups.

In some embodiments, the radiation curable resin can comprise a (meth)acrylate-modified polyfunctional isocyanate material having at least two (meth)acrylate-modified isocyanate groups, which can be, for example, the reaction product of a polyurethane prepolymer having terminal and/or pendent isocyanate groups (e.g., those polyurethane prepolymers described above in connection with the preparation of particulate polyurethanes) and an (meth)acrylate having an isocyanate reactive functional group (e.g., a hydroxyl, amino group, or mercapto group).

Exemplary suitable hydroxy or amino functional (meth)acrylates include hydroxyalkyl acrylates and methacrylates (e.g., 2-hydroxyethylacrylate (HEA), 2-hydroxyethylmethylacrylate (HEMA), 2-hydroxypropylacrylate, 3-hydroxypropylacrylate (HPA), 2-hydroxypropyl methacrylate, 3-hydroxypropyl methacrylate, 1,3-dihidroxypropylacrylate, 2,3-dihidroxypropylacrylate and methacrylate, 2-hydroxyethylacrylamide and methacrylamide, 2-hydroxybutyl(meth)acrylate, 4-hydroxybutyl(meth)acrylate, 2-hydroxy-3-phenyloxypropyl(meth)acrylate, 1,4-butanediol mono(meth)acrylate, 2-hydroxy alkyl(meth)acryloyl phosphates, 4-hydroxycyclohexyl(meth)acrylate, 1,6-hexanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolethane di(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate; N-alkyl-N-hydroxyethylacrylamides and methacrylamides, hydroxyethyl-betacarboxyethylacrylate, hydroxyhexyl acrylate, hydroxyoctyl methacrylate, polypropylenegylcol monomethacrylate, propyleneglycol monomethacrylate, caprolactone acrylate, t-butyl aminoethyl methacrylate, and mixtures thereof). Many of these are available from commercial sources, for example, useful hydroxyethylacrylates and hydroxypropylacrylates commercially available from Dow Chemical (Midland, Mich.) and Osaka Organic Chemical Industry Ltd. (Osaka, Japan). Useful hydroxybutyl acrylates are commercially available from Osaka Organic Chemical Industry Ltd. Useful hydroxy polyester acrylates are commercially available under the "TONE MONOMER M-100" trade designation from Dow Chemical Company and "VISCOAT 2308" from Osaka Organic Chemical Industry Ltd. Useful hydroxy polyether acrylates are commercially available under the "ARCOL R-2731" trade designation from Bayer Chemicals (Pittsburgh, Pa.).

The (meth)acrylate groups can be located pendant, terminal, or a combination thereof on the prepolymer. In some embodiments, the prepolymer is end capped with (meth)acrylate groups. The radiation curable resin can be prepared, for example, by reacting a (meth)acrylate having an isocyanate reactive functional group with a polyisocyanate prepolymer, typically in the presence of excess isocyanate. In some embodiments, the (meth)acrylate having an isocyanate reactive functional group is reacted with the isocyanate functional prepolymer in an amount such that from about 10% to about 80%, from about 20% to about 70%, or from about 30% to about 60% of the isocyanate groups on the isocyanate functional prepolymer are reacted with the(meth)acrylate having an isocyanate reactive functional group.

Some (meth)acrylate-modified polyfunctional isocyanate material having at least two (meth)acrylate-modified isocyanate groups are commercially available, for example, an isocyanate urethane acrylate available under the trade designations “DESMOLUX D100”, “DESMOLUX VPLS 2396”, and “DESMOLUX XP2510” from Bayer Materials Science, Pittsburgh, PA.

The composition which includes the radiation curable composition and the thermally curable composition typically also includes a photoinitiator or a combination of photoinitiators. Useful photoinitiators include, e.g., "alpha cleavage type" photoinitiators including, e.g., benzoin, benzoin acetals (e.g., benzyl dimethyl ketal), benzoin ethers (e.g., benzoin ethyl ether, benzoin isopropyl ether, and benzoin isobutyl ether), hydroxy alkyl phenyl ketones (e.g., 1-hydroxycyclohexyl phenyl ketone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, and 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one), benzoyl cyclohexanol, dialkoxy acetophenone derivatives (e.g., 2,2-diethoxyacetophenone), acylphosphine oxides (e.g., bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide, bis(2,6-dimethoxybenzoyl)-(2,4,4-trimethylpentyl)phosphine oxide, and 2,4,4-trimethylbenzoyl diphenylphosphine oxide), methyl thio phenyl morpholino ketones (e.g., 2-methyl-1-4(methylthio) and phenyl-2-morpholino-1-propanone), and morpholino phenyl amino ketones; hydrogen abstracting photoinitiators, which include a photoinitiator and a coinitiator, based on benzophenones, thioxanthones, benzyls, camphorquinones, and ketocoumarins; and combinations thereof. In some embodiments, the photoinitiator is a acylphosphine oxide (e.g., bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide, bis(2,6-dimethoxybenzoyl)-(2,4,4-trimethylpentyl)phosphine oxide, and 2,4,4-trimethylbenzoyl diphenylphosphine oxide).

Exemplary useful commercially available photoinitiators are available under the following trade designations "IRGACURE 369", "IRGACURE 819", "IRGACURE CGI 403", "IRGACURE 651", "IRGACURE 1841", "IRGACURE 29594", "DAROCUR 1173", "DAROCUR 4265", and "CGI1700", all of which are available from Ciba

Specialty Chemicals (Ardsley, N.Y.). The photoinitiator is preferably present in an amount sufficient to provide the desired rate of photopolymerization. The amount will depend, in part, on the light source, the thickness of the layer to be exposed to radiant energy and the extinction coefficient of the photoinitiator at the wavelength. Typically, the photoinitiator component will be present in an amount of at least about 0.01% by weight, at least about 0.1% by weight, at least about 0.2% by weight, up to about 10% by weight, or up to about 5% by weight.

The radiation curable composition and the thermally curable composition can be intimately mixed in the composition for making the porous polishing pad disclosed herein. In some embodiments, the composition comprises at least about 10 (in some embodiments, at least about 15, 20, 25, 30, or 40) weight percent of the radiation curable composition and up to about 85 (in some embodiments, up to about 80, 75, 70, 65, 60, 55, or 50) weight percent of the radiation curable composition, based on the total weight of the composition. In some embodiments, the composition comprises at least about 15 (in some embodiments, at least about 20, 25, 30, 35, 40, 45, 50, 55, of 60) weight percent of the thermally curable composition and up to about 90 (in some embodiments, up to about 85, 80, or 75) weight percent of the thermally curable composition, based on the total weight of the composition.

In some embodiments, the composition comprising a thermally curable resin composition, a radiation curable resin composition, and polymer particles further comprises a surfactant. Similarly, in some embodiments, the porous polishing layer that comprises a crosslinked network comprising a thermally cured component and a radiation cured component, polymer particles dispersed within the crosslinked network, and closed cell pores dispersed within the crosslinked network further comprises a surfactant dispersed within the crosslinked network. Examples of surfactants that may be useful for practicing the present disclosure include anionic surfactants, cationic surfactants, nonionic surfactants, amphoteric surfactants (e.g., zwitterionic surfactants), and combinations thereof. Each of these types of surfactant can include fluorochemical, silicone, and hydrocarbon-based surfactants.

Exemplary useful cationic surfactants include aliphatic ammonium salts. Exemplary useful anionic surfactants include carboxylic acid salts (e.g., fatty acid salts and alkylether carboxylic acid salts), sulfonic acid salts (e.g., alkylbenzenesulfonic acid salts, alkylnaphthalene sulfonic acid salts, and alpha-olefinsulfonic acid salts), sulfuric acid salts (e.g., higher alcohol sulfuric acid ester saltsand alkylether sulfuric acid salts), and phosphoric acid salts (e.g., alkylphosphoric acid salts). Exemplary useful nonionic surfactants include polyoxyethylene alkyl ethers, ether esters (e.g., polyoxyethylene ethers of glycerin esters), esters (e.g., polyethylene glycol fatty acid esters, glycerin esters, sorbitan esters), and silicone glycol copolymers such as those available, for example, for Air Products, Allentown, Pennsylvania, under the trade designation "DABCO". The surfactant may be present in the composition or in the polishing layer, for example, in an amount up to ten percent (in some embodiments, up to 4, 3, or 2 percent) by weight, based on the total weight of the composition or the porous polishing layer. In some embodiments, the surfactant is present in an amount of at least one percent, based on the total weight of the composition or the porous polishing layer.The present disclosure provides a method of making a polishing pad described herein. The method comprises forming pores in the composition comprising the thermally curable resin composition, the radiation curable resin composition, and polymer particles. In some embodiments, forming pores in the composition is carried out by mixing the composition. Mixing can be done with a variety of techniques, for example, using a machine mixer or hand mixing. In some embodiments, the mixing process (and the machine mixer) can include both rotation and revolution. Particle size and loading of the polymer particles can affect the porosity of the resulting polishing layer, as described above.

In some embodiments, the composition comprising the thermally curable resin composition, the radiation curable resin composition, and polymer particles can be mixed together and placed on a support layer. An open mold (e.g., a mold having no top or lid) on top of the support layer can be useful for forming the desired shape of the polishing layer. The mixture can be distributed within the mold by mechanical means to uniformly fill the mold. Suitable mechanical means can include low pressure pressing or the use of compaction rollers.

The method of making the polishing pad disclosed herein also includes forming a polishing layer by exposing the composition to radiation to at least partially cure the radiation curable composition and heating the composition to at least partially cure the thermally curable resin. The radiation is typically ultraviolet radiation (i.e., radiation in the range from about 200 nm to about 400 nm). The amount of radiation necessary to at least partially cure the composition will depend on a variety of factors including, e.g., the angle of exposure to the radiation, the thickness of the composition, the amount of polymerizable groups in the composition, and the type and amount of photoinitiator. Typically, a UV light source with a wavelength from about 200 nm to about 400 nm is directed at the composition that is being transported on a conveyor system that provides a rate of passage past the UV source appropriate for the radiation absorption profile of the composition. Useful sources of UV light include, e.g., extra high pressure mercury lamps, high pressure mercury lamps, medium pressure mercury lamps, low intensity fluorescent lamps, metal halide lamps, microwave powered lamps, xenon lamps, laser beam sources including, e.g., excimer lasers and argon-ion lasers, and combinations thereof. The composition can then can be placed in an oven at, for example, an elevated temperature up to about 180 °C, up to about 150 °C, up to about 135 °C, or up to about 120 °C (e.g., in a range from 80 °C to 120 °C, 80 °C to 110 °C, or 90 °C to 100 °C) for a period of time (for example, from 30 minutes to 24 hours). Exposure to radiation and heating can be carried out in either order or simultaneously. In some embodiments, exposure to radiation is carried out before heating.

The polishing pad of the present disclosure can have one or more work surfaces, wherein "work surface" as used herein refers to a surface of the polishing pad that can come into contact with the surface of the article that is to be polished. In some embodiments, the article to be polished can be a silicon wafer. In some embodiments, the work surface of the polishing pad can have surface features such as channels, grooves, perforations and combinations thereof. These surface features can enhance one or more of the following characteristics: (1) the movement of the polishing slurry between the work surface of the pad and the surface of the article that is being polished; (2) the removal and transport of abraded material away from the surface of the article that is being polished; or (3) the polishing or planarization efficiency of the polishing pad.

Surface features can be incorporated into the work surface of the polishing pad by a variety of methods. In some embodiments, the work surface of the pad can be mechanically modified, for example, by abrading or cutting. In other embodiments, surface features can be incorporated into the work surface of the pad during the molding process, for example, by providing at least one interior surface of the mold with raised features that can be imprinted into the work surface of the pad during its formation.

Surface features can be distributed in the form of random or uniform patterns across the work surface of the polishing pad. Exemplary surface feature patterns can include spirals, circles, squares, cross-hatches and waffle-like patterns.

In some embodiments, the polishing pad according to or made according to the present disclosure comprises separate polishing elements protruding from the support layer. Referring now to FIG. 3, an embodiment of a polishing pad 2 is shown, comprising a plurality of polishing elements 4, each of the polishing elements 4 being affixed to an optional support layer 8. The polishing pad 2 further comprises a compliant layer 10. Typically, the polishing layer comprising the separate polishing elements is a continuous layer although this is not shown in FIG. 3. Between the separate polishing elements, the film can have a thickness, for example, of up to 0.01, 0.02, or 0.03 mm. In other embodiments, the polishing layer comprising separate polishing elements may have discontinuities, for example, in the film between the separate polishing elements. Since the polishing elements 4 are affixed to the support layer in the illustrated embodiment with a thin film layer (not shown) between polishing elements 4, lateral movement of the polishing elements 4 with respect to one or more of the other polishing elements 4 is restricted, but the polishing elements 4 typically remain independently moveable in an axis normal to a polishing surface 14 of each polishing element 4. As shown, each of the polishing elements 4 generally have a plurality of pores 15 distributed substantially throughout the entire polishing element 4.

In the embodiment illustrated by FIG. 3, the polishing elements 4 are shown affixed to a first major side of the support layer 10, for example, by direct bonding to the support layer 8. The polishing elements 4 may be molded and cured directly on the support layer 8. In other embodiments, the polishing elements 4 may be attached to the support layer 8 or directly to the compliant layer 10 using an adhesive. In these embodiments, the porous polishing layer is typically a discontinuous layer. In the particular embodiment illustrated by FIG. 3, an optional pressure sensitive adhesive layer 12, which may be used to secure the polishing pad 2 to a polishing platen (not shown in FIG. 3) of a CMP polishing apparatus (not shown in FIG. 3), is shown adjacent to the compliant layer 10, opposite the support layer 8.

Referring to FIG. 4, another exemplary embodiment of a polishing pad 2' is shown, the polishing pad 2' comprising a compliant layer 30 having a first major side and a second major side opposite the first major side; a plurality of polishing elements 24, each polishing element 24 having a land region 25 for affixing each polishing element 24 to the first major side of the compliant layer 30; and an optional guide plate 31 having a first major surface and a second major surface opposite the first major surface, the guide plate 31 positioned to arrange the plurality of polishing elements 24 on the first major side of compliant layer 30 with the first major surface of guide plate 31 distal from the compliant layer 30.

As illustrated by FIG. 4, each polishing element 24 extends from the first major surface of the guide plate 31 along a first direction substantially normal to the first major side. In the particular embodiment illustrated by FIG. 4, each of the porous polishing elements 24 is also shown as having a plurality of pores 15 distributed substantially throughout the entire polishing element 24. Additionally, in the particular embodiment illustrated by FIG. 4, three polishing elements 24 are shown, and all of the polishing elements 24 are shown as porous polishing elements including both a porous polishing surface 23 and pores 15 distributed substantially throughout the entire polishing element 24. However, it will be understood that any number of polishing elements 24 may be used, and the number of porous polishing elements may be selected to be as few as one polishing element, to as many as all of the polishing elements, or any number in between.

An optional polishing composition distribution layer 28 is additionally illustrated by FIG. 4. During a polishing process, the optional polishing composition distribution layer 28 aids distribution of the working liquid and/or polishing slurry to the individual polishing elements 24. A plurality of apertures 26 may also be provided extending through at least the guide plate 31 and the optional polishing composition distribution layer 28 as illustrated by FIG. 4. In some embodiments, guide plate 31 may also serve as a polishing composition distribution layer.

As illustrated by FIG. 4, in some embodiments, each polishing element 24 has a land region 25, and each polishing element 24 is affixed to the first major side of the compliant layer 30 by engagement of the corresponding land region 25 to the second major surface of the guide plate 31. At least a portion of each polishing element 24 extends into a corresponding aperture 26, and each polishing element 24 also passes through the corresponding aperture 26 and extends outwardly from the first major surface of the guide plate 31. Thus, the plurality of apertures 26 of guide plate 31 serves to guide the lateral arrangement of polishing elements 24 on the support layer 30, while also engaging with each land region 25 to affix each the corresponding polishing element 24 to the support layer 30.

Consequently, during a polishing process, the polishing elements 24 are free to independently undergo displacement in a direction substantially normal to the first major side of support layer 30, while still remaining affixed to the compliant layer 30 by the guide plate 31. In some embodiments, this may permit use of non-compliant polishing elements, for example, porous polishing elements having pores distributed substantially at or near only the polishing surface.

In the particular embodiment illustrated by FIG. 4, the polishing elements 24 are additionally affixed to a first major side of the compliant layer 30 using an optional adhesive layer 34 positioned at an interface between the compliant layer 30 and the guide plate 31. However, other bonding methods may be used, including direct bonding of the polishing elements 24 to the compliant layer 30 using, for example, heat and pressure.

In a related exemplary embodiment not illustrated in FIG. 4, the plurality of apertures may be arranged as an array of apertures, wherein at least a portion of the apertures 26 comprise a main bore and an undercut region of guide plate 31, and the undercut region forms a shoulder that engages with the corresponding polishing element land region 25, thereby retaining the polishing element 24 without requiring an adhesive between the polishing element 24 and the compliant layer 30.

Furthermore, a second optional adhesive layer 36 may be used affix the optional polishing composition distribution layer 28 to a first major surface of the guide plate 31, as illustrated by FIG. 4. In addition, in the particular embodiment illustrated by FIG. 4, an optional pressure sensitive adhesive layer 32, which may be used to secure the polishing pad 2' to a polishing platen (not shown in FIG. 4) of a CMP polishing apparatus (not shown in FIG. 4), is shown adjacent to the support layer 30, opposite the guide plate 31.

A guide plate and/or distribution layer may also be used in connection with the embodiment shown in FIG. 3, in which the porous polishing elements 4 do not have land regions. The support layer 8 may be eliminated in the presence of a guide plate, and the porous polishing elements may be affixed to the compliant layer 10, for example, using adhesive.

The cross-sectional shape of the polishing elements 4 and 24, taken through a polishing element 4 and 24 in a direction generally parallel to the polishing surface 14 and 23, may vary widely depending on the intended application. Although FIGS. 3 and 4 show generally cylindrical polishing element 4 and 24 having a generally circular cross section, other cross-sectional shapes are possible and may be desirable in some embodiments. For example, circular, elliptical, triangular, square, rectangular, hexagonal, and trapezoidal cross-sectional shapes may be useful.

For cylindrical polishing elements 4 and 24 having a circular cross section, the cross-sectional diameter of the polishing element 4 and 24 in a direction generally parallel to the polishing surface 14 and 23 may be from about 50 μm to about 20 mm, in some embodiments the cross-sectional diameter is from about 1 mm to about 15 mm, and in other embodiments the cross-sectional diameter is from about 5 mm to about 15 mm (or even about 5 mm to about 10 mm). For non-cylindrical polishing elements having a non-circular cross section, a characteristic dimension may be used to characterize the polishing element size in terms of a specified height, width, and length. In some exemplary embodiments, the characteristic dimension may be selected to be from about 0.1 mm to about 30 mm.

In other exemplary embodiments, the cross-sectional area of each polishing element 4 and 24 in a direction generally parallel to the polishing surface 14 and 23, may be from about 1 mm^2 to about 1,000 mm^2, in other embodiments from about 10 mm^2 to about 500 mm^2, and in yet other embodiments, from about 20 mm^2 to about 250 mm^2.

The polishing elements (4 in FIG. 3, 24 in FIG. 4) may be distributed on a major side of the compliant layer (10 in FIG. 3, 30 in FIG. 4) in a wide variety of patterns, depending on the intended application, and the patterns may be regular or irregular. The polishing elements may reside on substantially the entire surface of the compliant layer, or there may be regions of the support layer that include no polishing elements. In some embodiments, the polishing elements have an average surface coverage of the compliant layer from about 30 to about 95 percent of the total area of the major surface of the compliant layer, as determined by the number of polishing elements, the cross-sectional area of each polishing element, and the cross-sectional area of the polishing pad.

The cross-sectional area of the polishing pad in a direction generally parallel to a major surface of the polishing pad may, in some exemplary embodiments, range from about 100 cm^2 to about 300,000 cm^2, in other embodiments from about 1,000 cm^2 to about 100,000 cm^2, and in yet other embodiments, from about 2,000 cm^2 to about 50,000 cm^2.

Before the first use of the polishing pad (2 in FIG. 3, 2' in FIG. 4) in a polishing operation, in some exemplary embodiments, each polishing element (4 in FIG. 3, 24 in FIG. 4) extends along the first direction substantially normal to the first major side of the compliant layer (10 in FIG. 3, 30 in FIG. 4). In other exemplary embodiments, each polishing element extends along the first direction at least about 0.25 mm above a plane including the guide plate (31 in FIG. 4). In further exemplary embodiments, each polishing element extends along the first direction at least about 0.25 mm above a plane including the support layer (10 in FIG. 3). In additional exemplary embodiments, the height of the polishing surface (14 in FIG. 3, 23 in FIG. 4) above the base or bottom of the polishing element (2 in FIG. 3, 2' in FIG. 4) may be 0.25 mm, 0.5 mm, 1.5 mm, 2.0 mm, 2.5 mm, 3.0 mm, 5.0 mm, 10 mm or more, depending on the polishing composition used and the material selected for the polishing elements.

Referring again to FIG. 4, the depth and spacing of the apertures 26 throughout the polishing composition distribution layer (28 and guide plate 31 may be varied as necessary for a specific CMP process. The polishing elements 24 are each maintained in planar orientation with respect to one another and the polishing composition distribution layer 28 and guide plate 31, and project above the surface of the polishing composition distribution layer 28 and guide plate 31.

In some exemplary embodiments, the volume created by the extension of the polishing elements (4 in FIG. 3, 24 in FIG. 4) above the guide plate 31 and any polishing composition distribution layer (28 in FIG. 4) or support layer (8 in FIG. 3) may provide room for distribution of a polishing composition on the surface of the polishing composition distribution layer (28 in FIG. 4) or support layer (8 in FIG. 3). The polishing elements (4 in FIG. 3, 24 in FIG. 4) protrude above the polishing composition distribution layer (28 in FIG. 4) or support layer (8 in FIG. 3) by an amount that depends at least in part on the material characteristics of the polishing elements and the desired flow of polishing composition (working liquid and or abrasive slurry) over the surface of the polishing composition distribution layer (28 in FIG. 4) or support layer (8 in FIG. 3).

The guide plate useful for some embodiments can be made of a wide variety of materials, such as polymers, copolymers, polymer blends, polymer composites, or combinations thereof. A non-conducting and liquid impermeable polymeric material is generally preferred, and polycarbonates have been found to be particularly useful.

The optional polishing composition distribution layer useful for some embodiments may also be made of a wide variety of polymeric materials. The polishing composition distribution layer may, in some embodiments, comprise at least one hydrophilic polymer. Preferred hydrophilic polymers include polyurethanes, polyacrylates, polyvinyl alcohols, polyoxymethylenes, and combinations thereof. The polymeric materials are preferably porous, more preferably comprising a foam to provide a positive pressure directed toward to substrate during polishing operations when the polishing composition distribution layer is compressed. Porous or foamed materials with open or closed cells may be preferred in some embodiments. In some particular embodiments, the polishing composition distribution layer has between about 10 and about 90 percent porosity. In an alternative embodiment, the polishing composition layer may comprise a hydrogel material, such as, for example a hydrophilic urethane, that can absorb water, preferably in a range of about 5 to about 60 percent by weight to provide a lubricious surface during polishing operations.

In some exemplary embodiments, the polishing composition distribution layer may substantially uniformly distribute a polishing composition across the surface of the substrate undergoing polishing, which may provide more uniform polishing. The polishing composition distribution layer may optionally include flow resistant elements such as baffles, grooves (not shown in the figures), pores, and the like, to regulate the flow rate of the polishing composition during polishing. In further exemplary embodiments, the polishing composition distribution layer can include various layers of different materials to achieve desired polishing composition flow rates at varying depths from the polishing surface.

In some exemplary embodiments, one or more of the polishing elements may include an open core region or cavity defined within the polishing element, although such an arrangement is not required. In some embodiments, as described in Int. Pat. Appl. Pub. No. WO 2006/055720 (Torgerson et al.), the core of the polishing element can include sensors to detect pressure, conductivity, capacitance, eddy currents, and the like.

In some embodiments of the polishing pad and/or the method of making the polishing pad disclosed herein, the support layer comprises a flexible and compliant material. The support layer is typically a film that provides a surface onto which the composition comprising the thermally curable resin composition and the radiation curable resin composition can be cured. In some exemplary embodiments wherein the porous polishing layer includes polishing elements, the polishing elements, at least a portion of which comprise porous polishing elements, may be formed with the support layer as a unitary sheet of polishing elements affixed to the support layer.

The support layer also serves to protect the compliant layer from water or other fluid in the polishing composition while the polishing pad is in use. The support layer is generally fluid impermeable (although permeable materials may be used in combination with an optional barrier to prevent or inhibit fluid penetration through the support layer. In some exemplary embodiments, the support layer comprises a polymeric material selected from silicone, natural rubber, styrene-butadiene rubber, neoprene, polyurethane, polyolefin, and combinations thereof. The support layer may further comprise a wide variety of additional materials, such as fillers, particulates, fibers, reinforcing agents, and the like. In some embodiments, the support layer is transparent.

Support layers can be made, for example, by extrusion of a material (e.g., silicone, natural rubber, styrene-butadiene rubber, neoprene, polyurethane, polyolefin, and combinations thereof) into a film. In some embodiments, the material is a polyurethane available, for example, from Lubrizol Advanced Materials, Inc., Cleveland, OH, under the trade designation "ESTANE 58887-NAT02" or from Dow Chemical, Midland, MI, under the trade designation "PELLETHANE" for example "PELLETHANE 2102-65D". Commercially available films that are useful as support layers include polyurethane films available, for example, from Stevens Urethane, Easthampton, Massachusetts, under the trade designations "ST-1882", "ST-1035", "SS-3331", "SS-1495L", and "ST-1880".

In some embodiments of the polishing pad and/or the method of making the polishing pad disclosed herein, the compliant layer comprises a flexible and compliant material, such as a compliant rubber or polymer. The compliant layer is generally compressible to provide a positive pressure directed toward the polishing surface and can, for example, help provide uniformity of contact between the polishing pad and the surface of the substrate that is being polished. In some exemplary embodiments, the compliant layer is made of a compressible polymeric material (e.g., a foamed polymeric material made, for example, of natural rubber, synthetic rubber, or thermoplastic elastomer). Closed cell porous materials may be useful. In some embodiments, the compliant layer comprises a polyurethane and may be, for example, a foamed polyurethane or polyurethane impregnated felt. The thickness of the compliant layer can be, for example, in a range from 0.2 to 3 mm. In some exemplary embodiments wherein the polishing layer includes polishing elements, the polishing elements, at least a portion of which comprise porous polishing elements, may be formed with the compliant layer as a unitary sheet of polishing elements affixed to the compliant layer, which may be a porous compliant layer.

In some exemplary embodiments, the compliant layer comprises a polymeric material selected from silicone, natural rubber, styrene-butadiene rubber, neoprene, polyolefin, polyurethane, and combinations thereof. The support layer may further comprise a wide variety of additional materials, such as fillers, particulates, fibers, reinforcing agents, and the like. In some embodiments, the compliant layer is fluid impermeable (although permeable materials may be used in combination with the support layer described above).

Suitable commercially available compliant layers include, for example, microcellular polyurethanes available under the trade designation "PORON" from Rogers Corp., Rogers, CT, for example, having product descriptions 4701-60-20062-04, 4701-50-20062-04, 4701-40-20062-04. Other suitable compliant layers include polyurethane impregnated polyester felts available, for example, from Rodel, Incorporated, Newark, DE, under the trade designation "SUBA IV" as well as bonded rubber sheets available from Rubberite Cypress Sponge Rubber Products, Inc., Santa Ana, CA, under the trade designation "BONDTEX".

In some embodiments of the polishing pad and/or the method of making the polishing pad disclosed herein, the polishing pad may include a window extending through the pad in the direction normal to the polishing surface, or may use transparent layers and/or transparent polishing elements, to allow for optical endpointing of a polishing process, as described in Int. Pat. Appl. Pub. No. WO 2009/140622 (Bajaj et al.).

The term “transparent layer” as used above is intended to include a layer that comprises a transparent region, which may be made of a material that is the same or different from the remainder of the layer. In some exemplary embodiments, at least one of a polishing element, the support layer, the compliant layer, or a region of the polishing layer or support layer, may be transparent, or may be made transparent by applying heat and/or pressure to the material. In some embodiments, a transparent material may be cast in place in an opening suitably positioned in a layer (e.g., using a mold) to create a transparent region (e.g., in the polishing layer, support layer, or compliant layer). In some embodiments, the polishing layer is cured in the presence of a pre-formed window to create a transparent region in the polishing layer. In some embodiments, the entire support layer and/or compliant layer may be made of a material that is or may be made transparent to energy in the range of wavelength(s) of interest utilized by an endpoint detection apparatus. Suitable transparent materials for a transparent element, layer or region include, for example, transparent polyurethanes.

Furthermore, as used above, the term "transparent" is intended to include an element, layer, and or region that is substantially transparent to energy in the range of wavelength(s) of interest utilized by an endpoint detection apparatus. In some exemplary embodiments, the endpoint detection apparatus uses one or more source of electromagnetic energy to emit radiation in the form of ultraviolet light, visible light, infrared light, microwaves, radio waves, combinations thereof, and the like. In some embodiments, the term "transparent" means that at least about 25% (e.g., at least about 35%, at least about 50%, at least about 60%, at least about 70%, at least about 80%, at least about 90%, at least about 95%) of energy at a wavelength of interest that impinges upon the transparent element, layer or region is transmitted therethrough.

In some exemplary embodiments, the support layer is transparent. In some embodiments, the polishing layer is transparent. In some exemplary embodiments, including embodiments illustrated in FIG. 3 above, at least one polishing element is transparent. In some embodiments, the support layer is transparent, at least a portion of the polishing layer (e.g., a polishing element) is transparent, and there is a hole in the compliant layer aligned with the transparent portion of the polishing layer.

In additional exemplary embodiments, including embodiments illustrated in FIG. 4 above, at least one polishing element is transparent, and the adhesive layer and the compliant layer are also transparent. In further exemplary embodiments, the compliant layer, the guide plate, the polishing composition distribution layer, at least one polishing element, or a combination thereof is transparent.

The present disclosure is further directed to a method of using a polishing pad as described above in a polishing process, the method including contacting a surface of a substrate with the porous polishing layer of the polishing pad according to the present disclosure and relatively moving the polishing pad with respect to the substrate to abrade the surface of the substrate. In some embodiments, the porous polishing layer of the polishing pad comprises a plurality of polishing elements, at least some of which are porous. In some exemplary embodiments, a working liquid may be provided to an interface between the polishing pad surface and the substrate surface. Suitable working liquids include, for example, those described in U.S. Patent Nos. 6,238,592 (Hardy et al) and 6,491,843 (Srinivasan et al.) and in Int. Pat. Appl. Pub. No. WO 2002/33736 (Her et al.).

In some embodiments, the polishing layer in the polishing pad of the present disclosure and/or prepared according to the method of the present disclosure can have an average pore size of at least 5 microns, at least 10 microns, or at least 15 microns. In some embodiments, the polishing pad can have an average pore size of up to 100, 75, 50, 45, or 40 microns. For example, the average pore size can be in a range from 5 to 100, 5 to 75, 5 to 50, 5 to 40, or 5 to 30 microns. In some embodiments (e.g., embodiments in which at least one of a surfactant is included or the polymer particles are fibers), the polishing pad can have an average pore size of up to 30, 25, or 20 microns. The pore size generally refers to the diameter of the pore. However, in embodiments in which the pores are non-spherical, the pore size can refer to the largest dimension of the pore. In some embodiments, the pore size non-uniformity is in a range from 40 to 75 percent or in a range from 40 to 60 percent. In some embodiments, the pore size non-uniformity is up to 75, 70, 65, 60, 55, or 50 percent. In contrast, comparative compositions comprising thermally curable compositions can have a pore size non-uniformity that is greater than 80, 90 or 100%. In some embodiments, the polishing layer in the polishing pad according to the present disclosure can have a porosity in a range from 5 to 60 percent or in a range from 5 to 55, 10 to 50, or 10 to 40 percent.

The difference between the control of pore size in the polishing layer according to the present disclosure and in a comparative thermally curable composition is illustrated in

FIGS. 5A, 5B, 6A, and 6B. FIGS. 5A and 5B are micrographs of a cross-section and top view, respectively, of the cured composition described in Example 2 in the Examples below. In contrast, FIGS. 6A and 6B are micrographs of a cross-section and a top view, respectively of the cured composition of Comparative Example 3. Both Example 2 and Comparative Example 3 were prepared using ten percent by weight polymer particles and mixed the same way. However, Example 2 was cured both by radiation curing and by thermal curing, and Comparative Example 3 was cured by thermal curing only. The micrographs illustrate that the pores in Example 2 are better controlled than the pores of Comparative Example 3. The data in Table 1 in the following Examples also supports that there is a lower size range, lower pore size non-uniformity, and higher hardness in Example 2 than in Comparative Example 3

Without wanting to be bound by theory, it is believed that control over the pore size and pore size non-uniformity may be related to the hardness of the polishing layer. In some embodiments, the porous polishing layer has a hardness of at least 40, 45, or 50 Shore D. The hardness can be measured, for example, according to Test Method 2, described in the Examples below. In contrast, comparative compositions comprising thermally curable compositions may have a hardness of less than 40 Shore D.

Surfactants are useful in the compositions and porous polishing layers disclosed herein, for example, for typically reducing the pore size and the pore size range and enhancing the pore distribution even more than with the dual cure method in the absence of surfactant. In other words, the addition of a surfactant can help provide better control on the pore size distribution and the size, density, and shape of the pores, which in turn can have a positive impact on key metrics of uniform performance (e.g., removal rate and within wafer uniformity). The micrographs in FIGS. 7A and 7B, which are micrographs of a cross-section and top view, respectively, of the cured composition described in Example 15 in the Examples below, illustrate that the addition of a surfactant can have a positive impact on the pore size range and pore distribution. For example, there is a lower pore size range in Example 15 than there is in Example 2, which has the same number of polymer particles and is prepared in the same way but has no surfactant.

Selected Embodiments of the Disclosure

In a first embodiments, the present disclosure provides a polishing pad comprising:

a compliant layer having first and second opposing sides; and

a porous polishing layer disposed on the first side of the compliant layer, the porous polishing layer comprising:

a crosslinked network comprising a thermally cured component and a radiation cured component, wherein the radiation cured component and the thermally cured component are covalently bonded in the crosslinked network;

polymer particles dispersed within the crosslinked network; and

closed cell pores dispersed within the crosslinked network.

In a second embodiment, the present disclosure provides the polishing pad according to the first embodiment, further comprising a support layer interposed between the compliant layer and the porous polishing layer.

In a third embodiment, the present disclosure provides the polishing pad according to the first or second embodiment, wherein the thermally cured component comprises at least one of a polyurethane or a polyepoxide, and wherein the radiation cured component comprises at least one of a polyacrylate, a polymethacrylate, a poly(vinyl ether), a polyvinyl, or a polyepoxide.

In a fourth embodiment, the present disclosure provides the polishing pad according to the first or second embodiment, wherein thermally cured component and the polymer particles each independently comprise a polyurethane.

In a fifth embodiment, the present disclosure provides the polishing pad according to any one of the first to fourth embodiments, wherein the polymer particles are covalently bonded to at least one of the thermally cured component or the radiation cured component in the crosslinked network.

In a sixth embodiment, the present disclosure provides the polishing pad according to any one of the first to fifth embodiments, wherein the radiation cured component comprises at least one of a polyacrylate or a polymethacrylate.

In a seventh embodiment, the present disclosure provides the polishing pad according to the sixth embodiment, wherein the polyacrylate or polymethacrylate is covalently bonded to the thermally cured component through urethane or urea linking groups.

In a eighth embodiment, the present disclosure provides the polishing pad according to any preceding embodiment, wherein the porous polishing layer has a hardness of at least 40 Shore D as measured by Test Method 2.

In a ninth embodiment, the present disclosure provides the polishing pad according to any preceding embodiment, wherein the polymer particles have a mean particle size in a range from 5 micrometers to 500 micrometers.

In a tenth embodiment, the present disclosure provides the polishing pad according to any preceding embodiment, wherein the polymer particles are substantially spherical.

In an eleventh embodiment, the present disclosure provides the polishing pad according to any preceding embodiment, wherein the polymeric particles are fibers.

In a twelfth embodiment, the present disclosure provides the polishing pad according to any preceding embodiment, wherein the polymer particles are present up to 20 percent by weight, based on the total weight of the porous polishing layer.

In a thirteenth embodiment, the present disclosure provides the polishing pad according to any preceding embodiment, wherein the pores have a pore size non-uniformity up to 75 percent.

In a fourteenth embodiment, the present disclosure provides the polishing pad according to any preceding embodiment, wherein the pores have an average pore size in a range from 5 microns to 100 microns.

In a fifteenth embodiment, the present disclosure provides the polishing pad according to any preceding embodiment, wherein the polishing layer comprises separate polishing elements protruding from the support layer or compliant layer.

In a sixteenth embodiment, the present disclosure provides the polishing pad according to the fifteenth embodiment, wherein polishing elements each have an end distal from the support layer, and wherein the distal end is movable in an axis normal to a polishing surface of the polishing elements.

In a seventeenth embodiment, the present disclosure provides the polishing pad according to the fifteenth or sixteenth embodiment, further comprising a guide plate having a plurality of openings therein, the separate polishing elements each protruding through one of the plurality of openings.

In an eighteenth embodiment, the present disclosure provides the polishing pad according to any one of the fifteenth to seventeenth embodiment, wherein the polishing elements are affixed to the compliant layer with adhesive.

In a nineteenth embodiment, the present disclosure provides the polishing pad according to any preceding embodiment, wherein the compliant layer comprises at least one of silicone, natural rubber, styrene-butadiene rubber, neoprene, polyolefin, or polyurethane.

In a twentieth embodiment, the present disclosure provides the polishing pad according to any preceding embodiment, wherein at least a portion of the polishing pad is transparent.

In a twenty-first embodiment, the present disclosure provides the polishing pad according to any preceding embodiment, wherein the polymer particles are soluble in water.

In a twenty-second embodiment, the present disclosure provides the polishing pad according to any preceding embodiment, wherein the porous polishing layer further comprises a surfactant in the crosslinked network.

In a twenty-third embodiment, the present disclosure provides a method of making a polishing pad, the method comprising:

providing a composition comprising a thermally curable resin composition, a radiation curable resin composition, and polymer particles;

forming pores in the composition;

positioning the composition on a support layer; and

forming a porous polishing layer on the support layer by exposing the composition to radiation to at least partially cure the radiation curable resin composition and heating the composition to at least partially cure the thermally curable resin composition.

In a twenty-fourth embodiment, the present disclosure provides a method according to the twenty-third embodiment, further comprising adhesively bonding a compliant layer to a surface of the support layer opposite the porous polishing layer.

In a twenty-fifth embodiment, the present disclosure provides the method according to the twenty-third or twenty-fourth embodiment, wherein the thermally curable resin composition comprises a first resin having at least two isocyanate groups or at least two epoxide groups and at least a second resin having at least two hydroxyl, amino, carboxy, or mercaptan groups, and wherein the radiation curable composition comprises at least two acrylate, methacrylate, vinyl, or epoxide groups.

In a twenty-sixth embodiment, the present disclosure provides the method according to the twenty-fifth embodiment, wherein the first resin has at least two isocyanate groups, wherein the second resin has at least two hydroxyl groups or at least two amino groups, wherein the radiation curable composition comprises at least two acrylate or methacrylate groups, and wherein the radiation curable composition further comprises at least one of an isocyanate group or a hydroxyl group.

In a twenty-seventh embodiment, the present disclosure provides the method according to the twenty-sixth embodiment, wherein the radiation curable composition is an aliphatic, isocyanate-functional urethane acrylate or methacrylate.

In a twenty-eighth embodiment, the present disclosure provides the method according to any one of the twenty-third to twenty-seventh embodiments, further comprising positioning an open mold in the composition on the support layer before the porous polishing layer is formed.

In a twenty-ninth embodiment, the present disclosure provides the method according to any one of the twenty-third to twenty-eighth embodiments, wherein the pores are closed cell pores.

In a thirtieth embodiment, the present disclosure provides the method according to any one of the twenty-third to twenty-ninth embodiments, wherein the composition further comprises a surfactant.

In a thirty-first embodiment, the present disclosure provides the method according to any one of the twenty-third to thirtieth embodiments, wherein the porous polishing layer has a hardness of at least 40 Shore D as measured by Test Method 2.

In a thirty-second embodiment, the present disclosure provides the method according to any one of the twenty-third to thirty-first embodiments, wherein the polymer particles have an average particle size in a range from 5 micrometers to 500 micrometers.

In a thirty-third embodiment, the present disclosure provides the method according to any one of the twenty-third to thirty-second embodiments, wherein the polymer particles are substantially spherical.

In a thirty-fourth embodiment, the present disclosure provides the method according to any one of the twenty-third to thirty-third embodiments, wherein the polymer particles are fibers.

In a thirty-fifth embodiment, the present disclosure provides the method according to any one of the twenty-third to thirty-fourth embodiment, wherein the polymer particles are soluble in water.

In a thirty-sixth embodiment, the present disclosure provides the method according to any one of the twenty-third to thirty-fifth embodiments, wherein the polymer particles are present up to 20 percent by weight, based on the total weight of the porous polishing layer.

In a thirty-seventh embodiment, the present disclosure provides the method according to any one of the twenty-third to thirty-sixth embodiments, wherein the pores have a pore size non-uniformity up to 75 percent.

In a thirty-eighth embodiment, the present disclosure provides the method according to any one of the twenty-third to thirty-seventh embodiments, wherein the pores have an average pore size in a range from 5 microns to 100 microns.

In a thirty-ninth embodiment, the present disclosure provides the method according to any one of the twenty-third to thirty-eighth embodiments, wherein the polishing layer comprises separate polishing elements affixed to and protruding from the support layer.

In a fortieth embodiment, the present disclosure provides the method according to the thirty-ninth embodiment, wherein the separate polishing elements each have an affixed end and an end distal from the support layer, and wherein the distal end is movable in an axis normal to a polishing surface of the polishing elements.

In a forty-first embodiment, the present disclosure provides the method according to any one of the twenty-third to thirty-eighth embodiments, wherein the polishing layer comprises separate polishing elements protruding from the compliant layer, wherein polishing elements each have an end distal from the support layer, and wherein the distal end is movable in an axis normal to a polishing surface of the polishing elements.

In a forty-second embodiment, the present disclosure provides the method according to any one of the the thirty-ninth to forty-first embodiments, further comprising a guide plate having a plurality of openings therein, the discrete polishing elements each protruding through one of the plurality of openings.

In a forty-third embodiment, the present disclosure provides the method according to any one of the twenty-third to forty-second embodiments, wherein the support layer comprises at least one of silicone, natural rubber, styrene-butadiene rubber, neoprene, polyolefin, or polyurethane.

In a forty-fourth embodiment, the present disclosure provides the method according to any one of the twenty-third to forty-third embodiments, wherein at least a portion of the polishing pad is transparent.

In a forty-fifth embodiment, the present disclosure provides a method of polishing comprising:

contacting a surface of a substrate with the porous polishing layer of the polishing pad according to any one of the first to twenty-second embodiments; and

relatively moving the polishing pad with respect to the substrate to abrade the surface of the substrate.

In a forty-sixth embodiment, the present disclosure provides the method of the forty-fifth embodiment, further comprising providing a working liquid to an interface between the porous polishing layer and the substrate surface.

Exemplary polishing pads according to the present disclosure will now be illustrated with reference to the following non-limiting examples.

EXAMPLES

Materials	
Abbreviation or Trade Name	Description
D100	An isocyanate urethane acrylate available under the trade designation "Desmolux D100" from Bayer Materials Science, Pittsburgh, PA.
PHP-75D	An isocyanate prepolymer available under the trade designation "Airthane PHP-75D" from Air Products and Chemicals, Inc., Allentown, PA.
P250	An oligomeric diamine available under the trade designation "Versalink P250" from Air Products and Chemicals, Inc.
P650	An oligomeric diamine available under the trade designation "Versalink P650" from Air Products and Chemicals, Inc.
M1	A mixture of 690 g of P250 and 430 g P-650.
5350D	Polyurethane particles, 35 micron size, available under the trade designation "DAIMIC-BEAZ UCN-5350D" from Dainichiseika Color & Chemicals Mfg. Co., Ltd. Advanced Polymers Group, Tokyo, Japan.
5150D	Polyurethane particles, 15 micron size, available under the trade designation "DAIMIC-BEAZ UCN-5150D" from Dainichiseika Color & Chemicals Mfg. Co., Ltd. Advanced Polymers Group.
5070D	Polyurethane particles, 7 micron size, available under the trade designation "DAIMIC-BEAZ UCN-5070D" from Dainichiseika Color & Chemicals Mfg. Co., Ltd. Advanced Polymers Group.
TPO-L	2,4,6-trimethylbenzoylphenylphosphinic acid ethyl ester available under the trade designation "Lucirin TPO-L" available from BASF, Florham Park, New Jersey.
ST-1880	An aromatic polyurethane film available under the trade designation "ST-1880" from Stevens Urethane, Easthampton, Massachusetts.
A15LV	Methylcellulose available under the trade designation METHOCEL A15 Premium LV from Dow Chemical Company, Midland, Michigan
DC5604	A silicone glycol copolymer surfactant available under the trade designation "DABCO DC5604" from Air Products Chemicals, Inc., Allentown, Pennsylvania

Test Method 1: FESEM

Scanning electron micrographs of the article (top view and cross section view) were obtained using a Hitachi S-4500 FESEM available from Hitachi High-Technologies Corporation, Tokyo, Japan, following conventional procedures. Cross sections of the articles were obtained by cutting with a sharp razor blade. Samples were subsequently sputter coated with Au/Pd using conventional techniques before SEM examination. Images of both the cross sections and top of the article were obtained.

Test Method: 2: Durometer

Durometer measurements were taken using a Model 1500 Shore D durometer available from Rex Gauge Company, Inc., Buffalo Grove, Illinois. Values reported in Table 1 are the average of five measurements, each measurement made on a different polishing feature of the example.

Test Method 3: Pore Size Determination via Optical Microscopy.

The pore size mean, pore size standard deviation (Std. Dev.), pore size range (the maximum size pore observed minus the minimum size pore observed), pore size non-uniformity (the pore size Std. Dev. divided by the mean pore size multiplied by 100) and the porosity (measured area of the image consisting of pores divided by the entire area of the image multiplied by 100) were determined using image analysis of optical images obtained using a MM-40 Nikon measuring microscope available from Nikon Instruments, Inc. Elgin, IL, in combination with Image-pro plus analysis software available from Media Cybernetics, Bethesda, MD.

Prior to optical imaging, samples were prepared in the following manner. Three polishing features were cut from an article and sealed in a Phenolic ring form, 2.5 cm outside diameter x 2.2 cm inside diameter, available from Buehler Ltd., 41, Lake Bluff, Illinois, using a potting compound obtained from 3M Company, St. Paul, Minnesota, under the trade designation "3M SCOTCH-WELD Epoxy Potting Compound/Adhesive DP270 CLEAR". The features embedded in the epoxy were fine polished using an Ecomet 3 grinder-polisher, available from Buehler Ltd., using a six step process at a down force 4.25 psi (29.3 kPa), and a head and platen speed of 120 rpm for all six steps. In all cases, the indicated sand paper or polishing pad was mounted to the platen of the Ecomet 3 by use of a pressure sensitive adhesive (psa).

Step 1: 8 inch diameter, 240 grit disc obtained from 3M Company under the trade designation "3M WETORDRY PSA Disc 21366", the grinding time was 3 min with water as a grinding fluid.

Step 2: 8 inch diameter, 600 Grit disc obtained from Buehler Ltd., under the trade designation "CARBIMET 8” PSA Disc 30-5118-600-100, the grinding time was 6 min with water as the grinding fluid.

Step 3: 8” diameter pad obtained from Buehler Ltd. under the trade designation "TEXMET 1500 Polishing Pad", 40-8618, the polishing time was 6 min with 15 μm grade polycrystalline diamond suspension 90-30035, available from Allied High Tech Products, Inc., Rancho Dominguez, California, as the polishing fluid.

Step 4: 8 inch diameter pad obtained from Buehler Ltd. under the trade designation "TEXMET 1500 Polishing Pad", 40-8618, the polishing time was 6 min with 6 μm grade polycrystalline diamond suspension 90-30025, available from Allied High Tech Products, Inc., as the polishing fluid.

Step 5: 8 inch diameter pad obtained from Buehler Ltd. under the trade designation "TEXMET 1500 Polishing Pad", 40-8618, the polishing time was 6 min with 3 μm grade polycrystalline diamond suspension 90-30020, available from Allied High Tech Products, Inc., as the polishing fluid.

Step 6: 8 inch diameter pad obtained from Buehler Ltd. under the trade designation "TEXMET 1500 Polishing Pad", 40-8618, the polishing time was 6 min with 1 μm grade polycrystalline diamond suspension 90-30015, available from Allied High Tech Products, Inc., as the polishing fluid.

After polishing, the polished surface of the features was then coated with carbon using a sputtering coater available from Denton Vacuum, LLC, Moorestown, NJ, using conventional techniques. Optical imaging was subsequently conducted.

Example 1

Example 1 was prepared by placing 0.28 g 5350D, 2.15 g M1, 1.83 g PHP-75D, 1.27 g D100 and 0.06 g TPO-L in a 50 mL plastic beaker. The components were mixed together by placing the beaker in an Awatori-Rentaro AR-500 Thinky Mixer (from Thinky Corporation, Tokyo, Japan) and running the AR-500 in a two step process. The first step was conducted at a rotation of 1000 rpm and a revolution of 1000 rpm for 5 minutes. The second step immediately followed the first and was conducted at a rotation of 30 rpm and a revolution of 2000 rpm for 15 seconds, forming a resin mixture. The resin mixture was poured into a teflon coated, Ni plated, aluminum mold formed from an aluminum plate having a length of 19.5 cm and width of 9.2 cm. The mold consisted of a square array of tapered, cylindrical cavities. The cavities had a diameter of 7.8 mm at the top of the cavity, a 6.5 mm diameter at the bottom of the cavity and a depth of 1.8 mm. The center to center distance between cavities was about 11.7 mm. A piece of polyurethane film, ST-1880, was used as a backing. The backing was cut to size, about 12 cm x 10 cm, and placed over the region of the mold containing the resin mixture. A quartz plate, 28 cm length x 17 cm width x 3.5 mm thickness was placed on top of the polyurethane backing, forcing the resin into the cavities and creating a thin land region, about 0.5 mm thick, of resin mixture between the cavities.

The resin mixture was UV cured by passing the mold, resin mixture, backing and quartz plate under two ultraviolet light lamps ('V' bulb, available from Fusion Systems Inc., Gaithersburg, Maryland) that operated at about 157.5 Watts/cm (400 Watts/inch). The mold passed under the lights at a speed of about 2.4 meters/minute (8 feet/minute) with the radiation passing through the quartz plate and polyurethane backing to reach the resin mixture. The mold, partially cured resin mixture and polyurethane backing was then transferred to an air flow through oven having a set temperature of 100°C for two hours to thermally cure the resin mixture. The cured article was removed from the mold by gently pulling on the polyurethane backing, forming an article having structured polishing features, Example 1.

Example 2

Example 2 was prepared identically to Example 1 except the composition of the resin mixture was 0.58 g 5350D, 2.15 g M1, 1.83 g PHP-75D, 1.27 g D100 and 0.06 g TPO-L.

Example 3

Example 3 was prepared identically to Example 1 except the curing was conducted in the reverse order, the thermal cure first followed by the UV cure.

Example 4

Example 4 was prepared identically to Example 2 except the curing was conducted in the reverse order, the thermal cure first followed by the UV cure.

Comparative Example C1

Comparative Example C1 was prepared identically to Example 1 except the 5350D was omitted from the composition of the resin mixture.

Comparative Example C2

Comparative Example C2 was prepared identically to Comparative Example C1 except the composition of the resin mixture was 0.31 g 5350D, 2.15 g M1, and 3.65 g PHP-75D and only the thermal cure at 100°C for two hours was used, the UV curing step being omitted.

Comparative Example C3

Comparative Example C3 was prepared identically to Comparative Example C2 except the composition of the resin mixture was 0.65 g 5350D, 2.15 g M1, and 3.65 g PHP-75D.

Example 5

Example 5 was prepared by placing 9.49 g 5350D, 35.00 g M1, 29.69 g PHP-75D, 20.63 g D100 and 1.03 g TPO-L in a 500 ml plastic beaker. The components were mixed together by placing the beaker in the Awatori-Rentaro AR-500 Thinky Mixer and running the AR-500 in a two step process. The first step was conducted at a rotation of 1000 rpm and a revolution of 1000 rpm for 5 minutes. The second step immediately followed the first and was conducted at a rotation of 30 rpm and a revolution of 2000 rpm for 15 s forming a resin mixture.

Using a knife coater having a width of about 21 inch (53 cm), and a gap of 60 mil (1.52 mm), an approximate 28 cm x 28 cm coating of the resin mixture was prepared on a 26 μm thick backing formed by extrusion of a thermoplastic polyurethane (TPU), ESTANE 58887-NAT02 (available from Lubrizol Advanced Materials, Inc., Cleveland, OH) into film form at 182°C onto a paper release liner.

The coated resin mixture and backing were placed on a 12 inch x 12 inch (30.5 cm x 30.5 cm) by 0.25 inch (6.35 mm) thick aluminum plate. Thirty-six magnets, 0.375 inch (9.6 mm) in diameter by 0.125 inch (3.2 mm) thick were fitted into recesses in the back of the aluminum plate. The 36 recesses were in a square array with center to center distances between recesses of about 5 cm. The diameter and depth of the recesses were 9.8 mm and 4.3 mm, respectively. A teflon coated metal screen, about 41 cm x 30 cm and about 1.6 mm in thickness, having a hexagonal array of circular holes each about 6.2 mm in diameter and a center to center distance of about 8 mm was placed on top of the resin mixture coating. The magnetic attraction between the screen and the magnets in the aluminum plate caused the screen to be forced through the resin mixture coating, leaving a thin land region of the coating between the metal screen and backing. The UV curing of the coating was conducted identically to that of Example 1, except the quartz plate was not used. Thermal cure followed, using the identical procedure as that described in Example 1.

After removing from the oven, the metal screen was removed from the cured resin, forming a textured pad surface adhered to the original paper backed polyurethane backing. The paper was removed exposing the opposite side of the polyurethane backing. Using a 127 μm thick transfer adhesive, 3M Adhesive Transfer Tape 9672 (from 3M Company), the polyurethane backing of the textured pad surface was hand laminated to an approximate 30 cm x 30 cm by 0.0625 inch (1.59 mm) thick piece of polyurethane foam, Rogers "PORON" urethane foam, part # 4701-50-20062-04 (from American Flexible Products, Inc., Chaska, Minnesota). A 23 cm diameter pad with an 18 mm diameter center hole was die cut from the laminate forming a pad having structured polishing features of the present invention, Example 5.

Comparative Example C4

Comparative Example C4 was prepared identically to Example 5, except the composition of the resin mixture was 10.48 g 5350D, 35.00 g M1, and 59.38 g PHP-75D and only the thermal cure at 100°C for two hours was used, the UV curing step being omitted.

Using Test Methods 2 and 3; durometer, pore size mean, pore size Std. Dev., pore size range, pore size non-uniformity and porosity of Examples 1-5 and Comparative Examples C1-C4 were measured. Results are shown in Table 1, below.

Table 1. Durometer, Pore Size and Porosity Data

Example	Durometer	Pore Size Mean (μm)	Pore Size Std. Dev. (μm)	Pore Size Range (μm)	Pore Size Non-Uniformity (%)	Porosity (%)
1	55	31.5	18.2	84.4	57.8	21.3
2	55	32.5	17.8	76.6	54.7	11.2
3	60	30.8	21.9	97.4	71.1	12.1
4	60	26.2	14.0	90.3	53.3	18.4
5	50	33.7	15.7	93.7	46.6	37.3
C1*	60	-	-	-	-	-
C2	35	37.1	40.1	189.1	107.9	21.1
C3	35	37.7	31.9	161.0	84.8	23.1
C4	35	42.1	37.1	190.3	88.0	26.6

* No pore size data was measurable, as comparative example C1 had no pores.

Example 6

Example 6 was prepared identically to Example 1 except the composition of the resin mixture was 0.28 g 5150D, 2.15 g M1, 1.83 g PHP-75D, 1.27 g D100 and 0.06 g TPO-L.

Illustrative Example I-1

Illustrative Example I-1 was prepared identically to Example 1 except the composition of the resin mixture was 0.28 g 5070D, 2.15 g M1, 1.83 g PHP-75D, 1.27 g D100 and 0.06 g TPO-L.

Example 7

Example 7 was prepared identically to Example 1 except the amount of 5350D was 0.05 g.

Example 8

Example 8 was prepared identically to Example 1 except the amount of 5350D was 0.14 g.

Example 9

Example 9 was prepared identically to Example 1 except the amount of 5350D was 0.93 g.

Illustrative Example I-2

Illustrative Example I-2 was prepared identically to Example 1 except the amount of 5350D was 1.31 g.

FESEM (Test Method 1) results of Examples 6-9 indicated that they had an acceptable level of porosity. FESEM (Test Method 1) results of Illustrative Examples I-1 and I-2 indicated that they had a low level of porosity.

Example 10

Example 10 was prepared identically to Example 5 except for the following changes. The composition of the resin mixture was 0.62 g A15LV, 23 g P-250, 15.83 g PHP-75D, 22 g D100, 1.1g TPO-L and 0.68 g DC5604. The components were place and mixed in a 500 ml plastic container.

The resin mixture was UV cured by passing the screen with resin mixture and TPU backing under two ultraviolet light lamps ('V' bulb, available from Fusion Systems Inc.) that operated at about 157.5 Watts/cm (400 Watts/inch). The resin mixture passed under the lights at a speed of about 2.4 meters/minute (8 feet/minute) with the radiation passing through the resin mixture. Then a fluoropolymer coated polyester film release liner obtained from 3M Company under the trade designation "3M SCOTCHPAK 1022 Release Liner" was put on top of the screen and partially cured resin mixture. The assembly was then flipped over such that the polyurethane backing was on top and the fluoropolymer coated polyester film/screen/partially cured resin mixture at the bottom. The whole assembly was run through the same UV curing process for the second time with a quartz plate on top of the backing. After the second UV cure was finished, the quartz plate and the fluoropolymer coated polyester film were removed and the screen/partially cured resin mixture/backing assembly was transferred to an air flow through oven having a set temperature of 100°C for two hours to thermally cure the resin mixture. After cooling to room temperature, a 23 cm diameter pad with an 18 mm diameter center hole was fabricated, as described in Example 5, yielding Example 10.

Example 11

Example 11 was prepared identically to Example 10 except that the weight of A15LV was 1.25 g.

Example 12

Example 12 was prepared identically to Example 10 except that the weight of A15LV was 3.20 g.

Example 13

Example 13 was prepared identically to Example 10 except that the weight of A15LV was 6.76 g.

Example 14

Example 14 was prepared by placing 6.88 g A15LV, 127.78 g P-250, 6.11 g TPO-L and 3.51 g DC5604 in a 650 ml plastic container. The components were mixed together by placing the container in the Awatori-Rentaro AR-500 Thinky Mixer and running the AR-500 at a rotation of 1000 rpm and a revolution of 1000 rpm for 4 minutes. The container was removed from the mixer and 87.29 g PHP-75D and 122.22 g D100 were added to the container. The mixture went through a two step mixing process. The first step was conducted at a rotation of 1000 rpm and a revolution of 1000 rpm for 4 minutes. The second step immediately followed the first and was conducted at a rotation of 30 rpm and a revolution of 2000 rpm for 15 second forming a resin mixture.

Using a knife coater having a width of about 21 inch (53 cm), and a gap of 60 mil (1.52 mm), an approximate 21 in x 23 in (53.3 cm x 58.4) coating of the resin mixture was prepared on a 4 mil (102 μm) thick backing formed by extrusion of the TPU, "ESTANE 58309-022", into film form at 210°C onto a conventional 4 mil polyester release liner.

The coated resin mixture and backing were placed on a 24 inch x 24 inch (61.0 cm x 61.0 cm) by 0.25 inch (6.35 mm) thick aluminum plate. 113 magnets, 0.375 inch (9.6 mm) in diameter by 0.125 inch (3.2 mm) thick were fitted into recesses in the back of the aluminum plate. The recesses were in a linear array consisting of 15 rows. Eight of the rows had 8 recesses per row while 7 of the rows had seven recesses per row. The spacing between rows was 4 mm while the spacing between recesses within a row was 7.5 mm. The first row of recesses (near an edge of the plate) had eight recesses; the second row had seven recesses. This alternating pattern continued until the fifteenth row having eight recesses. The recesses for the even numbered rows were positioned such that they were centered between the recesses of the corresponding adjacent rows. The diameter and depth of the recesses were 9.8 mm and 4.3 mm, respectively. A tape capable of handling high temperature was used to secure the magnets in the recesses. A teflon coated metal screen, about 24 in x 24 in (61.0 cm x 61.0 cm) and about 1.6 mm in thickness, having a hexagonal array of circular holes each about 6.2 mm in diameter and a center to center distance of about 8 mm was placed on top of the resin mixture coating. The magnetic attraction between the screen and the magnets in the aluminum plate caused the screen to be forced through the resin mixture coating, leaving a thin land region of the coating between the metal screen and backing.

The resin mixture was cured following the identical curing procedure of Example 10. After removing from the oven, the metal screen was removed from the cured resin, forming a textured pad surface adhered to the original polyester backed polyurethane TPU backing. Using a 127 µm thick transfer adhesive, "3M ADHESIVE TRANSFER TAPE 9672" (from 3M Company), the polyester release liner of the textured pad surface was hand laminated to an approximate 21 in x 23 in (53.3 cm x 58.4) by 0.0787 inch (2 mm) thick piece of polyurethane foam. A 20.0 in (50.8 cm) diameter pad was die cut from the laminate forming a pad having structured polishing features of the present invention, Example 14.

Comparative Example C5

Comparative Example C5 was prepared identically to Example 10 except the A15LV was omitted from the composition of the resin mixture.

Comparative Example C6

Comparative Example C6 was prepared identically to Example 10, except the composition of the resin mixture was 1.44 g A15LV, 23 g P-250, 47.50 g PHP-75D and

0.68 g DC5604, and only the thermal cure at 100°C for two hours was used, the UV curing step being omitted.

Comparative Example C7

Comparative Example C7 was prepared identically to Comparative Example C6 except the A15LV was omitted from the composition of the resin mixture.

Example 15

Example 15 was prepared identically to Example 5 except that the composition of the resin mixture was 7.58 g 5350D, 28.00 g M1, 23.75 g PHP-75D, 16.50 g D100, 0.83 g TPO-L and 0.77g DC5604.

Comparative Example C8

Comparative Example C8 was prepared identically to Example 15, except the composition of the resin mixture was 8.39 g 5350D, 28.00 g M1, 47.50 g PHP-75D and 3.5g DC5604, and only the thermal cure at 100°C for two hours was used, the UV curing step being omitted.

Using Test Methods 2 and 3; durometer, pore size mean, pore size Std. Dev., pore size range, pore size non-uniformity and porosity of Examples 10-15 and Comparative Examples C5-C8 were measured. Results are shown in Table 2, below.

Table 2. Durometer, Pore Size and Porosity Data

Example	Durometer	Pore Size Mean (µm)	Pore Size Std. Dev. (µm)	Pore Size Range (µm)	Pore Size Non-Uniformity (%)	Porosity (%)
10	60	16.2	10.6	63.2	65.6	16.9
11	60	16.0	10.7	61.6	67.2	21.3
12	55	14.0	11.8	57.7	83.8	33.9
13	45	14.9	13.3	81.42	89.5	46.5
14	60	16.2	12.2	62.7	75.5	18.9
15	50	17.2	9.6	51.6	55.9	27.0
C5	65	26.5	25.0	68.9	94.4	0.33
C6	30	18.8	21.0	128.9	111.7	33.3
C7	30	44.5	34.1	105.5	76.6	4.7
C8	30	15.9	16.7	121.7	105.2	22.5

Reference throughout this specification to “one embodiment”, “some embodiments”, “one or more embodiments” or “an embodiment”, whether or not including the term “exemplary” preceding the term “embodiment”, means that a particular feature, structure, material, or characteristic described in connection with the embodiment is included in at least one embodiment of the some exemplary embodiments of the present disclosure. Thus, the appearances of the phrases such as “in one or more embodiments”, “in some embodiments”, “in one embodiment” or “in an embodiment” in various places throughout this specification are not necessarily referring to the same embodiment of the some exemplary embodiments of the present disclosure. Furthermore, the particular features, structures, materials, or characteristics may be combined in any suitable manner in one or more embodiments.

While the specification has described in detail some exemplary embodiments, it will be appreciated that those skilled in the art, upon attaining an understanding of the foregoing, may readily conceive of alterations to, variations of, and equivalents to these embodiments. Accordingly, it should be understood that this disclosure is not to be unduly limited to the illustrative embodiments set forth hereinabove. In particular, as used herein, the recitation of numerical ranges by endpoints is intended to include all numbers subsumed within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5). In addition, all numbers used herein are assumed to be modified by the term 'about'.

Furthermore, all publications and patents referenced herein are incorporated by reference in their entirety to the same extent as if each individual publication or patent was specifically and individually indicated to be incorporated by reference.

Various exemplary embodiments have been described. These and other embodiments are within the scope of the following claims.

What is claimed is:

1. A polishing pad comprising:
   a compliant layer having first and second opposing sides; and
   a porous polishing layer disposed on the first side of the compliant layer, the porous polishing layer comprising:
      a crosslinked network comprising a thermally cured component and a radiation cured component, wherein the radiation cured component and the thermally cured component are covalently bonded in the crosslinked network;
      polymer particles dispersed within the crosslinked network; and
      closed cell pores dispersed within the crosslinked network.

2. The polishing pad according to claim 1, further comprising a support layer interposed between the compliant layer and the porous polishing layer.

3. The polishing pad according to claim 1 or 2, wherein the thermally cured component comprises at least one of a polyurethane or a polyepoxide, and wherein the radiation cured component comprises at least one of a polyacrylate, a polymethacrylate, a poly(vinyl ether), a polyvinyl, or a polyepoxide.

4. The polishing pad according to claim 1 or 2, wherein thermally cured component and the polymer particles each independently comprise a polyurethane, and wherein the radiation cured component comprises at least one of a polyacrylate or a polymethacrylate.

5. The polishing pad according to any one of claims 1 to 4, wherein the polymer particles are covalently bonded to at least one of the thermally cured component or the radiation cured component in the crosslinked network.

6. The polishing pad according to claim 4, wherein the polyacrylate or polymethacrylate is covalently bonded to the thermally cured component through urethane or urea linking groups.

7. A method of making a polishing pad, the method comprising:

providing a composition comprising a thermally curable resin composition, a radiation curable resin composition, and polymer particles;

forming pores in the composition;

positioning the composition on a support layer; and

forming a porous polishing layer on the support layer by exposing the composition to radiation to at least partially cure the radiation curable resin composition and heating the composition to at least partially cure the thermally curable resin composition.

8. The method according to claim 7, further comprising adhesively bonding a compliant layer to a surface of the support layer opposite the porous polishing layer.

9. The method according to claim 7 or 8, wherein the thermally curable resin composition comprises a first resin having at least two isocyanate groups or at least two epoxide groups and at least a second resin having at least two hydroxyl, amino, carboxy, or mercaptan groups, and wherein the radiation curable composition comprises at least two acrylate, methacrylate, vinyl, or epoxide groups.

10. The method according to claim 9, wherein the first resin has at least two isocyanate groups, wherein the second resin has at least two hydroxyl groups or at least two amino groups, wherein the radiation curable composition comprises at least two acrylate or methacrylate groups, and wherein the radiation curable composition further comprises at least one of an isocyanate group or a hydroxyl group.

11. The method according to any one of claims 7 to 10, wherein the composition further comprises a surfactant.

12. The method according to any one of claims 7 to 11, wherein the pores are closed cell pores.

13. The polishing pad or method according to any preceding claim, wherein the porous polishing layer has a hardness of at least 40 Shore D as measured by Test Method 2.

14. The polishing pad or method according to any preceding claim, wherein the polymer particles have an average particle size in a range from 5 micrometers to 500 micrometers.

15. The polishing pad or method according to any preceding claim, wherein the polymer particles are substantially spherical.

16. The polishing pad or method according to any preceding claim, wherein the polymeric particles are fibers.

17. The polishing pad or method according to any preceding claim, wherein the polymer particles are present up to 20 percent by weight, based on the total weight of the porous polishing layer.

18. The polishing pad or method according to any preceding claim, wherein the pores have a pore size non-uniformity up to 75 percent.

19. The polishing pad or method according to any preceding claim, wherein the pores have an average pore size in a range from 5 microns to 100 microns.

20. The polishing pad or method according to any preceding claim, wherein the polishing layer comprises separated polishing elements protruding from the support layer or the compliant layer.

21. The polishing pad or method according to any preceding claim, wherein at least one of the support layer or compliant layer comprises at least one of silicone, natural rubber, styrene-butadiene rubber, neoprene, polyolefin, or polyurethane.

22. The polishing pad or method according to any preceding claim, wherein at least a portion of the polishing pad is transparent.

23. A method of polishing comprising:

contacting a surface of a substrate with the porous polishing layer of the polishing pad according to any one of claims 1 to 6 or any one of claims 13 to 22 as dependent on any one of claims 1 to 6; and

relatively moving the polishing pad with respect to the substrate to abrade the surface of the substrate.