Title: GRAPHERNE CONTAINING COMPOSITIONS

Abstract: Compositions comprising graphene sheets, and at least one acid. The compositions may optionally contain a polymer. They may be in the form of inks or coatings. The acids can be organic acids or mineral acids. The pKa in water of the acid is preferably less than 4, or preferably less than 3, or more preferably less than 2.5. The pKa in water may be less than about 2, or less than about 1, or less than about 0. Examples of mineral acids include sulfuric acid, hydrochloric acid, nitric acid, nitrous acid, phosphoric acid, boric acid, hydrobromic acid, perchloric acid, etc. Examples of acids include sulfur-based acids such as sulfonates, aliphatic sulfonic acids, alkyl benzene sulfonic acids, alkyl and aliphatic sulfonic acids, toluenesulfonic acids, and naphthalenesulfonic acids.
GRAPHENE CONTAINING COMPOSITIONS

Reference to Related Applications
The present application claims priority to U.S. Provisional Applications

61/559,715, filed on November 14, 2011, 61/596,216, filed on February 07, 2012,
61/596,220, filed on February 07, 2012, and 61/596,224, filed on February 08, 2012, the
entire contents of which are hereby incorporated by reference.

Field of the Invention
The present invention relates to compositions comprising graphene and at least
one acid.

Statement Regarding Federally Sponsored Research and Development
This invention was made with government support provided by the NSF under
grant numbers IIP-1152700 and IIP-1046880. The government has certain rights in the
invention.

Background
Due to its many excellent properties, graphene is increasingly being used in
myriad practical applications, electrically conductive inks and coatings, polymer
composites, sensors (such as gas sensors biosensors, etc.), electrodes, thermal transfer
applications, energy storage devices (such as batteries and supercapacitors), solar cells,
etc. In some of these cases graphene is used in compositions with other components
(such as polymeric binders, which can, among other advantages, improve the
mechanical properties of the compositions). Despite the success graphene has had in
many such applications, it would be desirable to obtain graphene compositions having
enhanced properties, such as electrical conductivity, thermal conductivity, mechanical
properties, etc.

Summary of the Invention
Disclosed and claimed herein are compositions comprising graphene sheets and
at least one acid. The compositions can further comprise one or more binders. Also
disclosed and claimed herein are inks and coatings comprising compositions comprising
graphene sheets and at least one acid.
Detailed Description of the Invention

The compositions comprise graphene sheets and at least one acid. They may optionally contain at least one polymer.

The compositions may further comprise one or more acid catalysts. The acids can be organic acids or mineral acids. The pKa in water of the acid is preferably less than about 4, or more preferably less than about 3, or yet more preferably less than about 2.5. The pKa in water may be less than about 2, or less than about 1, or less than about 0. The acids may be in a blocked form. In such cases, the pKa is based on the unblocked acid. The acid may be a curing catalyst.

Examples of mineral acids include sulfuric acid, hydrochloric acid, nitric acid, nitrous acid, phosphoric acid, boric acid, hydrobromic acid, perchloric acid, etc.

Examples of acids include sulfur-based acids such as sulfonic acids, polysulfonic acids (such as disulfonic acids), sulfinic acids, including monomeric and polymeric organic sulfonic acids such as aromatic sulfonic acids such as benzenesulfonic acids, alkylbenzene sulfonic acids, alkyl and aliphatic sulfonic acids, toluenesulfonic acids, and naphthalenesulfonic acids. Examples of sulfonic acids include monomeric sulfonic acids, such as p-toluenesulfonic acid, benzenesulfonic acid, cresol sulfonic acid, 4-ethylbenzenesulfonic acid, xylenesulfonic acid, dimethylbenzenesulfonic acid, phenolsulfonic acid, dinonylnaphthalenesulfonic acid (DNNSA), dinonylnaphthalenedisulfonic acid (DNNDSA), dodecylbenzenesulfonic acid (DDBSA), methanesulfonic acid, etc. Examples also include sulfonic acid resins such as poly(styrenesulfonic acid), sulfonated fluoropolymers (such as sulfonated tetrafluoroethylene (e.g., Nafion®)), etc.

The acids may be phosphorus-based acids, such as phosphoric acid and its derivatives, phosphorous acid and its derivatives, organic phosphorous and phosphate-based acids, such as alkyl and dialkyl acid phosphates, etc. Examples include amyl acid phosphate, diethyl acid phosphate, butyl acid phosphate, dibutyl acid phosphate, ethyl acid phosphate, diethyl acid phosphate, octyl acid phosphate, dioctyl acid phosphate, etc. They may be metal salts of phosphorous-based acids, such as metal salts of phosphoric acid and phosphoric acid esters.

In some cases, the acids can be present relative to graphene sheets in a weight ratio of from about 0.1:99.9 to about 75:25, or of from about 0.5:99.5 to about 75:25, or of from about 0.5:99.5 to about 50:50, or of from about 0.5:99.5 to about 25:75, or of
from about 0.5:99.5 to about 15:85, or of from about 0.5:99.5 to about 10:90, or of from about 0.5:99.5 to about 5:95, or of from about 1:99 to about 75:25, or of from about 1:99 to about 50:50, or of from about 1:99 to about 25:75, or of from about 1:99 to about 15:85, or of from about 1:99 to about 10:90, or of from about 1:99 to about 5:95, or of from about 2:98 to about 75:25, or of from about 2:98 to about 50:50, or of from about 2:98 to about 25:75, or of from about 2:98 to about 15:85, or of from about 2:98 to about 10:90, or of from about 2:98 to about 5:95, or of from about 5:95 to about 25:75, or of from about 10:90 to about 75:25, or of from about 10:90 to about 50:50, or of from about 10:90 to about 25:75.

The graphene sheets are graphite sheets preferably having a surface area of from about 100 to about 2630 m²/g. In some embodiments, the graphene sheets primarily, almost completely, or completely comprise fully exfoliated single sheets of graphite (these are approximately ≤ 1 nm thick and are often referred to as "graphene"), while in other embodiments, at least a portion of the graphene sheets may comprise partially exfoliated graphite sheets, in which two or more sheets of graphite have not been exfoliated from each other. The graphene sheets may comprise mixtures of fully and partially exfoliated graphite sheets. Graphene sheets are distinct from carbon nanotubes. Graphene sheets may have a "platey" (e.g. two-dimensional) structure and do not have the needle-like form of carbon nanotubes. The two longest dimensions of the graphene sheets may each be at least about 10 times greater, or at least about 50 times greater, or at least about 100 times greater, or at least about 1000 times greater, or at least about 5000 times greater, or at least about 10,000 times greater than the shortest dimension (i.e. thickness) of the sheets.

Graphene sheets may be made using any suitable method. For example, they may be obtained from graphite, graphite oxide, expandable graphite, expanded graphite, etc.. They may be obtained by the physical exfoliation of graphite, by for example, peeling, grinding, or milling off graphene sheets. They may be made from inorganic precursors, such as silicon carbide. They may be made by chemical vapor deposition (such as by reacting a methane and hydrogen on a metal surface). They may be made by the reduction of an alcohol, such as ethanol, with a metal (such as an alkali metal like sodium) and the subsequent pyrolysis of the alkoxide product (such a method is reported in Nature Nanotechnology (2009), 4 30-33). They may be made by the exfoliation of graphite in dispersions or exfoliation of graphite oxide in dispersions and the subsequently reducing the exfoliated graphite oxide. Graphene sheets may be
made by the exfoliation of expandable graphite, followed by intercalation, and ultrasonication or other means of separating the intercalated sheets (see, for example, *Nature Nanotechnology* (2008), 3, 538-542). They may be made by the intercalation of graphite and the subsequent exfoliation of the product in suspension, thermally, etc.

Graphene sheets may be made from graphite oxide (also known as graphitic acid or graphene oxide). Graphite may be treated with oxidizing and/or intercalating agents and exfoliated. Graphite may also be treated with intercalating agents and electrochemically oxidized and exfoliated. Graphene sheets may be formed by ultrasonically exfoliating suspensions of graphite and/or graphite oxide in a liquid (which may contain surfactants and/or intercalants). Exfoliated graphite oxide dispersions or suspensions can be subsequently reduced to graphene sheets. Graphene sheets may also be formed by mechanical treatment (such as grinding or milling) to exfoliate graphite or graphite oxide (which would subsequently be reduced to graphene sheets).

Reduction of graphite oxide to graphene may be by means of chemical reduction and may be carried out on graphite oxide in a dry form, in a dispersion, etc. Examples of useful chemical reducing agents include, but are not limited to, hydrazines (such as hydrazine, N,N-dimethylhydrazine, etc.), sodium borohydride, citric acid, hydroquinone, isocyanates (such as phenyl isocyanate), hydrogen, hydrogen plasma, etc. A dispersion or suspension of exfoliated graphite oxide in a carrier (such as water, organic solvents, or a mixture of solvents) can be made using any suitable method (such as ultrasonication and/or mechanical grinding or milling) and reduced to graphene sheets.

Graphite oxide may be produced by any method known in the art, such as by a process that involves oxidation of graphite using one or more chemical oxidizing agents and, optionally, intercalating agents such as sulfuric acid. Examples of oxidizing agents include nitric acid, nitrates (such as sodium and potassium nitrates), perchlorates, potassium chlorate, sodium chloride, chromic acid, potassium chromate, sodium chromate, potassium dichromate, sodium dichromate, hydrogen peroxide, sodium and potassium permanganates, phosphoric acid (H₃PO₄), phosphorus pentoxide, bisulfites, etc. Preferred oxidants include KClO₄, HNO₃ and KClO₃; KMnO₄ and/or NaMnO₄; KMnO₄ and NaNO₃; K₂S₂O₈ and P₂O₅ and KMnO₄; KMnO₄ and HNO₃; and HNO₃. Preferred intercalation agents include sulfuric acid. Graphite may also be treated with intercalating agents and electrochemically oxidized. Examples of methods of making graphite oxide include those described by Staudenmaier (*Ber. Stsch. Chem. Ges.* (1898), 31, 1481) and Hummers (*J. Am. Chem. Soc.* (1958), 80, 1339).
One example of a method for the preparation of graphene sheets is to oxidize graphite to graphite oxide, which is then thermally exfoliated to form graphene sheets (also known as thermally exfoliated graphite oxide), as described in US 2007/0092432, the disclosure of which is hereby incorporated herein by reference. The thusly formed graphene sheets may display little or no signature corresponding to graphite or graphite oxide in their X-ray diffraction pattern.

The thermal exfoliation may be carried out in a continuous, semi-continuous batch, etc. process.

Heating can be done in a batch process or a continuous process and can be done under a variety of atmospheres, including inert and reducing atmospheres (such as nitrogen, argon, and/or hydrogen atmospheres). Heating times can range from under a few seconds or several hours or more, depending on the temperatures used and the characteristics desired in the final thermally exfoliated graphite oxide. Heating can be done in any appropriate vessel, such as a fused silica, mineral, metal, carbon (such as graphite), ceramic, etc. vessel. Heating may be done using a flash lamp or with microwave. During heating, the graphite oxide may be contained in an essentially constant location in single batch reaction vessel, or may be transported through one or more vessels during the reaction in a continuous or batch mode. Heating may be done using any suitable means, including the use of furnaces and infrared heaters.

Examples of temperatures at which the thermal exfoliation and/or reduction of graphite oxide can be carried out are at least about 150 °C, at least about 200 °C, at least about 300 °C, at least about 400 °C, at least about 450 °C, at least about 500 °C, at least about 600 °C, at least about 700 °C, at least about 750 °C, at least about 800 °C, at least about 850 °C, at least about 900 °C, at least about 950 °C, at least about 1000 °C, at least about 1100 °C, at least about 1500 °C, at least about 2000 °C, and at least about 2500 °C. Preferred ranges include between about 750 about and 3000 °C, between about 850 and 2500 °C, between about 950 and about 2500 °C, between about 950 and about 1500 °C, between about 750 about and 3100 °C, between about 850 and 2500 °C, or between about 950 and about 2500 °C.

The time of heating can range from less than a second to many minutes. For example, the time of heating can be less than about 0.5 seconds, less than about 1 second, less than about 5 seconds, less than about 10 seconds, less than about 20 seconds, less than about 30 seconds, or less than about 1 min. The time of heating can be at least about 1 minute, at least about 2 minutes, at least about 5 minutes, at least
about 15 minutes, at least about 30 minutes, at least about 45 minutes, at least about 60 minutes, at least about 90 minutes, at least about 120 minutes, at least about 150 minutes, at least about 240 minutes, from about 0.01 seconds to about 240 minutes, from about 0.5 seconds to about 240 minutes, from about 1 second to about 240 minutes, from about 1 minute to about 240 minutes, from about 0.01 seconds to about 60 minutes, from about 0.5 seconds to about 60 minutes, from about 1 second to about 60 minutes, from about 1 minute to about 60 minutes, from about 0.01 seconds to about 10 minutes, from about 0.5 seconds to about 10 minutes, from about 1 second to about 10 minutes, from about 1 minute to about 10 minutes, from about 0.01 seconds to about 1 minute, from about 0.5 seconds to about 1 minute, from about 1 second to about 1 minute, no more than about 600 minutes, no more than about 450 minutes, no more than about 300 minutes, no more than about 180 minutes, no more than about 120 minutes, no more than about 90 minutes, no more than about 60 minutes, no more than about 30 minutes, no more than about 15 minutes, no more than about 10 minutes, no more than about 5 minutes, no more than about 1 minute, no more than about 30 seconds, no more than about 10 seconds, or no more than about 1 second. During the course of heating, the temperature may vary.

Examples of the rate of heating include at least about 120 °C/min, at least about 200 °C/min, at least about 300 °C/min, at least about 400 °C/min, at least about 600 °C/min, at least about 800 °C/min, at least about 1000 °C/min, at least about 1200 °C/min, at least about 1500 °C/min, at least about 1800 °C/min, and at least about 2000 °C/min.

Graphene sheets may be annealed or reduced to graphene sheets having higher carbon to oxygen ratios by heating under reducing atmospheric conditions (e.g., in systems purged with inert gases or hydrogen). Reduction/annealing temperatures are preferably at least about 300 °C, or at least about 350 °C, or at least about 400 °C, or at least about 500 °C, or at least about 600 °C, or at least about 750 °C, or at least about 850 °C, or at least about 950 °C, or at least about 1000 °C. The temperature used may be, for example, between about 750 and 3000 °C, or between about 850 and 2500 °C, or between about 950 and about 2500 °C.

The time of heating can be for example, at least about 1 second, or at least about 10 second, or at least about 1 minute, or at least about 2 minutes, or at least about 5 minutes. In some embodiments, the heating time will be at least about 15 minutes, or about 30 minutes, or about 45 minutes, or about 60 minutes, or about 90 minutes, or
about 120 minutes, or about 150 minutes. During the course of annealing/reduction, the
temperature may vary within these ranges.

The heating may be done under a variety of conditions, including in an inert
atmosphere (such as argon or nitrogen) or a reducing atmosphere, such as hydrogen
(including hydrogen diluted in an inert gas such as argon or nitrogen), or under vacuum.

The heating may be done in any appropriate vessel, such as a fused silica or a mineral
or ceramic vessel or a metal vessel. The materials being heated including any starting
materials and any products or intermediates) may be contained in an essentially
constant location in single batch reaction vessel, or may be transported through one or
more vessels during the reaction in a continuous or batch reaction. Heating may be
done using any suitable means, including the use of furnaces and infrared heaters.

The graphene sheets preferably have a surface area of at least about 100 m²/g
to, or of at least about 200 m²/g, or of at least about 300 m²/g, or of at least about 350 m²/g,
or of at least about 400 m²/g, or of at least about 500 m²/g, or of at least about 600 m²/g., or of
least about 700 m²/g, or of at least about 800 m²/g, or of at least about 900 m²/g, or of least
about 700 m²/g. The surface area may be about 400 to about 1100 m²/g. The
theoretical maximum surface area can be calculated to be 2630 m²/g. The surface area
includes all values and subvalues therebetween, especially including 400, 500, 600, 700,
800, 900, 1000, 1100, 1200, 1300, 1400, 1500, 1600, 1700, 1800, 1900, 2000, 2100,
2200, 2300, 2400, 2500, and 2630 m²/g.

The graphene sheets can have number average aspect ratios of about 100 to
about 100,000, or of about 100 to about 50,000, or of about 100 to about 25,000, or of
about 100 to about 10,000 (where "aspect ratio" is defined as the ratio of the longest
dimension of the sheet to the shortest).

Surface area can be measured using either the nitrogen adsorption/BET method
at 77 K or a methylene blue (MB) dye method in liquid solution.

The dye method is carried out as follows: A known amount of graphene sheets
is added to a flask. At least 1.5 g of MB are then added to the flask per gram of
graphene sheets. Ethanol is added to the flask and the mixture is ultrasonicated for
about fifteen minutes. The ethanol is then evaporated and a known quantity of water is
added to the flask to re-dissolve the free MB. The undissolved material is allowed to
settle, preferably by centrifuging the sample. The concentration of MB in solution is
determined using a UV-vis spectrophotometer by measuring the absorption at \( \lambda_{\text{max}} = 298 \) nm relative to that of standard concentrations.
The difference between the amount of MB that was initially added and the amount present in solution as determined by UV-vis spectrophotometry is assumed to be the amount of MB that has been adsorbed onto the surface of the graphene sheets. The surface area of the graphene sheets are then calculated using a value of 2.54 m² of surface covered per one mg of MB adsorbed.

The graphene sheets may have a bulk density of from about 0.01 to at least about 200 kg/m³. The bulk density includes all values and subvalues therebetween, especially including 0.05, 0.1, 0.5, 1, 5, 10, 15, 20, 25, 30, 35, 50, 75, 100, 125, 150, and 175 kg/m³.

The graphene sheets may be functionalized with, for example, oxygen-containing functional groups (including, for example, hydroxyl, carboxyl, and epoxy groups) and typically have an overall carbon to oxygen molar ratio (C/O ratio), as determined by bulk elemental analysis, of at least about 1:1, or more preferably, at least about 3:2.

Examples of carbon to oxygen ratios include about 3:2 to about 85:15; about 3:2 to about 20:1; about 3:2 to about 30:1; about 3:2 to about 40:1; about 3:2 to about 60:1; about 3:2 to about 80:1; about 3:2 to about 100:1; about 3:2 to about 200:1; about 3:2 to about 500:1; about 3:2 to about 1000:1; about 3:2 to greater than 1000:1; about 1:1 to about 30:1; about 80:1 to about 100:1; about 20:1 to about 100:1; about 20:1 to about 200:1; about 20:1 to about 500:1; about 20:1 to about 1000:1; about 50:1 to about 300:1; about 50:1 to about 500:1; and about 50:1 to about 1000:1. In some embodiments, the carbon to oxygen ratio is at least about 10:1, or at least about 15:1, or at least about 20:1, or at least about 35:1, or at least about 50:1, or at least about 75:1, or at least about 100:1, or at least about 200:1, or at least about 300:1, or at least about 400:1, or at least about 500:1, or at least about 750:1, or at least about 1000:1; or at least about 1500:1, or at least about 2000:1. The carbon to oxygen ratio also includes all values and subvalues between these ranges.

The graphene sheets may contain atomic scale kinks. These kinks may be caused by the presence of lattice defects in, or by chemical functionalization of the twodimensional hexagonal lattice structure of the graphite basal plane.

The compositions may further comprise graphite (including natural, Kish, and synthetic, annealed, pyrolytic, highly oriented pyrolytic, etc. graphites). The ratio by weight of graphite to graphene sheets may be from about 2:98 to about 98:2, or from about 5:95 to about 95:5, or from about 10:90 to about 90:10, or from about 20:80 to about 80:20, or from about 30:70 to 70:30, or from about 40:60 to about 90:10, or from
about 50:50 to about 85:15, or from about 60:40 to about 85:15, or from about 70:30 to about 85:15.

The graphene sheets may comprise two or more graphene powders having different particle size distributions and/or morphologies. The graphite may also comprise two or more graphite powders having different particle size distributions and/or morphologies.

They graphene sheets and acid can be combined with polymers to make composites (including polymer composites), etc. They can be dispersed in one or more solvents with or without a polymer binder. They can be used in thermal transfer applications. They can be used in electrodes, such as those used in solar cells (including dye-sensitized solar cells, organic solar cells, etc.), light-emitting diodes, batteries (such as electrodes for use in rechargeable, lithium ion, lithium polymer, lithium air, etc. batteries), capacitors (including ultracapacitors), etc. Polymer composites can be used in gas barrier applications. Rubber composites can be used in tire applications.

The compositions can be in the form of adhesives.

The compositions may be in the form of inks and coatings. By the terms "ink" and "coating" are meant composition that are in a form that is suitable for application to a substrate as well as the material after it is applied to the substrate, while it is being applied to the substrate, and both before and after any post-application treatments (such as evaporation, cross-linking, curing, etc.). The components of the ink and coating compositions may vary during these stages. The inks and coatings may optionally further comprise a polymeric binder.

The graphene sheets and acid can be combined with polymers using any suitable method, including melt processing (using, for example, a single or twin-screw extruder, a blender, a kneader, a Banbury mixer, etc.) and solution/dispersion blending. The polymers can be used as binders. When used, the polymers can be thermosets, thermoplastics, non-melt processible polymers, etc. Polymers can also comprise monomers that can be polymerized before, during, or after the application of the coating to the substrate. Polymeric binders can be crosslinked or otherwise cured after the coating has been applied to the substrate. Examples of polymers include, but are not limited to polyolefins (such as polyethylene, linear low density polyethylene (LLDPE), low density polyethylene (LDPE), high density polyethylene, polypropylene, and olefin copolymers), styrene/butadiene rubbers (SBR), styrene/ethylene/butadiene/styrene copolymers (SEBS), butyl rubbers, ethylene/propylene copolymers (EPR),
ethylene/propylene/diene monomer copolymers (EPDM), polystyrene (including high impact polystyrene), polyvinyl acetates), ethylene/vinyl acetate copolymers (EVA), polyvinyl alcohol copolymers (EVOH), polyvinyl butyral (PVB), polyvinyl formal), poly(methyl methacrylate) and other acrylate polymers and copolymers (such as methyl methacrylate polymers, methacrylate copolymers, polymers derived from one or more acrylates, methacrylates, ethyl acrylates, ethyl methacrylates, butyl acrylates, butyl methacrylates, glycidyl acrylates and methacrylates and the like), olefin and styrene copolymers, acrylonitrile/butadiene/styrene (ABS), styrene/acrylonitrile polymers (SAN), styrene/maleic anhydride copolymers, isobutylene/maleic anhydride copolymers, ethylene/acrylic acid copolymers, poly(acrylonitrile), polyvinyl acetate) copolymers, vinyl acetate and vinyl pyrrolidone) and polyvinyl pyrrolidone) copolymers, vinyl acetate and vinyl pyrrolidone copolymers, polycarbonates (PC), polyamides, polyesters, liquid crystalline polymers (LCPs), poly(lactic acid) (PLA), poly(phenylene oxide) (PPO), PPO-polyamide alloys, polysulphone (PSU), polysulfides, polyetherketone (PEK), polyetheretherketone (PEEK), polyimides, polyoxymethylene (POM) homo- and copolymers, polyetherimides, fluorinated ethylene propylene polymers (FEP), polyvinyl fluoride), poly(vinylidene fluoride), poly(vinylidene chloride), polyvinyl chloride) (PVC), polyurethanes (thermoplastic and thermostetting (including crosslinked polyurethanes such as those crosslinked amines, etc.), aramides (such as Kevlar® and Nomex®), polysulfides, polytetrafluoroethylene (PTFE), polysiloxanes (including polydimethylsiloxane, dimethylsiloxane/vinylmethylsiloxane copolymers, vinyl(dimethyl)siloxane terminated poly(dimethylsiloxane), etc.), elastomers, epoxy polymers (including crosslinked epoxy polymers such as those crosslinked with polysulfones, amines, etc.), polyureas, alkyds, cellullosic polymers (such as nitrocellulose, ethyl cellulose, ethyl hydroxyethyl cellulose, carboxymethyl cellulose, cellulose acetate, cellulose acetate propionates, and cellulose acetate butyrates), polyethers (such as poly(ethylene oxide), poly(propylene oxide), poly(propylene glycol), oxide/propylene oxide copolymers, etc.), acrylic latex polymers, polyester acrylate oligomers and polymers, polyester diol diacrylate polymers, UV-curable resins, etc.

Examples of elastomers include, but are not limited to, polyurethanes, copolyetheresters, rubbers (including butyl rubbers and natural rubbers), styrene/butadiene copolymers, styrene/ethylene/butadiene/styrene copolymer (SEBS), polyisoprene, ethylene/propylene copolymers (EPR), ethylene/propylene/diene
monomer copolymers (EPDM), polysiloxanes, and polyethers (such as poly(ethylene oxide), poly(propylene oxide), and their copolymers).

Examples of polyamides include, but are not limited to, aliphatic polyamides (such as polyamide 4,6; polyamide 6,6; polyamide 6; polyamide 11; polyamide 12; polyamide 6,9; polyamide 6,10; polyamide 6,12; polyamide 10,10; polyamide 10,12; and polyamide 12,12), alicyclic polyamides, and aromatic polyamides (such as poly(m-xylene adipamide) (polyamide MXD,6)) and polyterephthalamides such as poly(dodecamethylene terephthalamide) (polyamide 12,T), poly(decamethylene terephthalamide) (polyamide 10,T), poly(nonamethylene terephthalamide) (polyamide 9,T), the polyamide of hexamethyleneterephthalamide and hexamethylene adipamide, the polyamide of hexamethyleneterephthalamide, and 2-methylpentamethyleneterephthalamide), etc. The polyamides may be polymers and copolymers (i.e., polyamides having at least two different repeat units) having melting points between about 120 and 255 °C including aliphatic copolyamides having a melting point of about 230 °C or less, aliphatic copolyamides having a melting point of about 210 °C or less, aliphatic copolyamides having a melting point of about 180 °C or less, etc. Examples of these include those sold under the trade names Macromelt by Henkel and Versamid by Cognis.

Examples of acrylate polymers include those made by the polymerization of one or more acrylic acids (including acrylic acid, methacrylic acid, etc.) and their derivatives, such as esters. Examples include methyl acrylate polymers, methyl methacrylate polymers, and methacrylate copolymers. Examples include polymers derived from one or more acrylates, methacrylates, acrylic acid, methacrylic acid, methyl acrylate, methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, glycidyl acrylate, glycidyl methacrylates, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, hydroxyethyl acrylate, hydroxyethyl (meth)acrylate, acrylonitrile, and the like. The polymers may comprise repeat units derived from other monomers such as olefins (e.g. ethylene, propylene, etc.), vinyl acetates, vinyl alcohols, vinyl pyrrolidones, etc. They may include partially neutralized acrylate polymers and copolymers (such as ionomer resins).

4021, 4026, 4028, 4044, 4059, 4400, 4075, 4060, 4102, etc. Other polymer families include Bynel® polymers (such as Bynel® 2022 supplied by DuPont) and Joncryl® polymers (such as Joncryl® 678 and 682).

Examples of polyesters include, but are not limited to, poly(butylene terephthalate) (PBT), poly(ethylene terephthalate) (PET), poly(1,3-propylene terephthalate) (PPT), poly(ethylene naphthalate) (PEN), poly(cyclohexanedicarboxylate) (PCT), etc.

In some embodiment, the polymer has an acid number of at least about 5, or at least about 10, or at least about 15, or at least about 20.

In some embodiments, the glass transition temperature of at least one polymer is no greater than about 100 °C, 90 °C, or no greater than about 80 °C, or no greater than about 70 °C, or no greater than about 60 °C, or no greater than about 50 °C, or no greater than about 40 °C.

In some cases, when a binder is used, it can be present relative to graphene sheets and graphite, when used, in from about 1 to about 99 weight percent, or from about 1 to about 50 weight percent, or from about 1 to about 30 weight percent, or from about 1 to about 20 weight percent, or from about 5 to about 80 weight percent, or from about 5 to about 60 weight percent, or from about 5 to about 30 weight percent, or from about 15 to about 85 weight percent, or from about 15 to about 60 weight percent, or from about 15 to about 30 weight percent, or from about 25 to about 80 weight percent, or from about 25 to about 50 weight percent, or from about 40 to about 90 weight percent, or from about 50 to about 90 weight percent, or from about 70 to about 95 weight percent, based on the total weight of binder and graphene plus graphite when present.

Examples of solvents into which the graphene sheets and acid can be dispersed include water, distilled or synthetic isoparaffinic hydrocarbons (such as Isopar® and Norpar® (both manufactured by Exxon) and Dowanol® (manufactured by Dow), citrus terpenes and mixtures containing citrus terpenes (such as Purogen, Electron, and Positron (all manufactured by Ecolink)), terpenes and terpene alcohols (including terpineols, including alpha-terpineol), limonene, aliphatic petroleum distillates, alcohols (such as methanol, ethanol, n-propanol, 1-propanol, n-butanol, 1-butanol, sec-butanol,
ie/f-butanol, pentanols, i-amyl alcohol, hexanols, heptanols, octanols, diacetone alcohol, butyl glycol, etc.), ketones (such as acetone, methyl ethyl ketone, cyclohexanone, β-butyl ketone, 2,6,8-trimethyl-4-nonanone etc.), esters (such as methyl acetate, ethyl acetate, n-propyl acetate, β-propyl acetate, n-butyl acetate, i-β-butyl acetate, carbitol acetate, etc.), glycol ethers, ester and alcohols (such as 2-(2-ethoxyethoxy)ethanol, propylene glycol monomethyl ether and other propylene glycol ethers; ethylene glycol monobutyl ether, 2-methoxyethyl ether (diglyme), propylene glycol methyl ether (PGME); and other ethylene glycol ethers; ethylene and propylene glycol ether acetates, diethylene glycol monoethyl ether acetate, 1-methoxy-2-propanol acetate (PGMEA); and hexylene glycol (such as Hexasol™ (supplied by SpecialChem)), dibasic esters (such as dimethyl succinate, dimethyl glutarate, dimethyl adipate), dimethylsulfoxide (DMSO), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU), imides, amides (such as dimethylformamide (DMF), dimethylacetamide, etc.), cyclic amides (such as V-methylpyrrolidone and 2-pyrrolidone), lactones (such as beta-propiolactone, gamma-valerolactone, delta-valerolactone, gamma-butyrolactone, epsilon-caprolactone), cyclic imides (such as imidazolidinones such as N,N′-dimethylimidazolidinone (1,3-dimethyl-2-imidazolidinone)), aromatic solvents and aromatic solvent mixtures (such as toluene, xylenes, mesitylene, cumene, etc.), petroleum distillates, naphthas (such as VM&P naphtha), and and mixtures of two or more of the foregoing and mixtures of one or more of the foregoing with other carriers. Solvents can be low- or non-VOC solvents, non-hazardous air pollution solvents, and non-halogenated solvents.

The compositions can contain additives such as dispersion aids (including surfactants, emulsifiers, and wetting aids), adhesion promoters, thickening agents (including clays), defoamers and antifoamers, biocides, additional fillers, flow enhancers, stabilizers, crosslinking and curing agents, conductive additives, etc.

Examples of dispersing aids include glycol ethers (such as poly(ethylene oxide), block copolymers derived from ethylene oxide and propylene oxide (such as those sold under the trade name Pluronic® by BASF), acetylenic diols (such as 2,5,8,11-tetramethyl-6-dodecen-5,8-diol ethoxylate and others sold by Air Products under the trade names Surfynol® and Dynol®), salts of carboxylic acids (including alkali metal and ammonium salts), and polysiloxanes.
Examples of grinding aids include stearates (such as Al, Ca, Mg, and Zn stearates) and acetylenic diols (such as those sold by Air Products under the trade names Surfynol® and Dynol®).

Examples of adhesion promoters include titanium chelates and other titanium compounds such as titanium phosphate complexes (including butyl titanium phosphate), titanate esters, diisopropoxy titanium bis(ethyl-3-oxobutanoate), isopropoxy titanium acetylacetonate, and others sold by Johnson-Matthey Catalysts under the trade name Vertec.

Examples of thickening agents include glycol ethers (such as poly(ethylene oxide), block copolymers derived from ethylene oxide and propylene oxide (such as those sold under the trade name Pluronic® by BASF), long-chain carboxylate salts (such as aluminum, calcium, zinc, etc. salts of stearates, oleates, palmitates, etc.), aluminosilicates (such as those sold under the Minex® name by Unimin Specialty Minerals and Aerosil® 9200 by Evonik Degussa), fumed silica, natural and synthetic zeolites, etc.

The compositions may optionally comprise at least one "multi-chain lipid", by which term is meant a naturally-occurring or synthetic lipid having a polar head group and at least two nonpolar tail groups connected thereto. Examples of polar head groups include oxygen-, sulfur-, and halogen-containing, phosphates, amides, ammonium groups, amino acids (including a-amino acids), saccharides, polysaccharides, esters (Including glyceryl esters), zwitterionic groups, etc.

The tail groups may be the same or different. Examples of tail groups include alkanes, alkenes, alkynes, aromatic compounds, etc. They may be hydrocarbons, functionalized hydrocarbons, etc. The tail groups may be saturated or unsaturated. They may be linear or branched. The tail groups may be derived from fatty acids, such as oleic acid, palmitic acid, stearic acid, arachidic acid, erucic acid, arachidonic acid, linoleic acid, linolenic acid, oleic acid, etc.

Examples of multi-chain lipids include, but are not limited to, lecithin and other phospholipids (such as phosphatidylcholine, phosphoglycerides (including phosphatidylserine, phosphatidylinositol, phosphatidylethanolamine (cephalin), and phosphatidylglycerol) and sphingomyelin); glycolipids (such as glucosyl-cerebroside); saccharolipids; sphingolipids (such as ceramides, di- and triglycerides, phosphosphingolipids, and glycosphingolipids); etc. They may be amphoteric, including zwitterionic.
Compositions may optionally contain electrically and/or thermally conductive components, such as metals (including metal alloys), conductive metal oxides, conductive carbons, polymers, metal-coated materials, etc. These components can take a variety of forms, including particles, powders, flakes, foils, needles, etc.

Examples of metals include, but are not limited to silver, copper, aluminum, platinum, palladium, nickel, chromium, gold, zinc, tin, iron, gold, lead, steel, stainless steel, rhodium, titanium, tungsten, magnesium, brass, bronze, colloidal metals, etc. Examples of metal oxides include antimony tin oxide and indium tin oxide and materials such as fillers coated with metal oxides. Metal and metal-oxide coated materials include, but are not limited to metal coated carbon and graphite fibers, metal coated glass fibers, metal coated glass beads, metal coated ceramic materials (such as beads), etc. These materials can be coated with a variety of metals, including nickel.

Examples of electrically conductive polymers include, but are not limited to, polyacetylene, polyethylene dioxythiophene (PEDOT), poly(styrenesulfonate) (PSS), PEDOT:PSS copolymers, polythiophene and polythiophenes, poly(3-alkylthiophenes), poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT), poly(phenylenevinylene), polypyrrole, polycarbazole, polyazulene, polyazepine, polyfluorenes, polynaphthalene, polypyrrole, poly(phenylene sulfide), polycarbozoles, polyindoles, polyphenylenes, copolymers of one or more of the foregoing, etc., and their derivatives and copolymers. The conductive polymers may be doped or undoped. They may be doped with boron, phosphorous, iodine, etc.

Examples of conductive carbons include, but are not limited to, graphite (including natural, Kish, and synthetic, annealed, pyrolytic, highly oriented pyrolytic, etc. graphites), graphitized carbon, carbon black, mesoporous carbon, carbon fibers and fibrils, carbon whiskers, vapor-grown carbon nanofibers, metal coated carbon fibers, carbon nanotubes (including single- and multi-walled nanotubes), fullerenes, activated carbon, carbon fibers, expanded graphite, expandable graphite, graphite oxide, hollow carbon spheres, carbon foams, etc.

Inks and coatings can be formed by blending the graphene sheets and acid with at least one solvent and/or binder, and, optionally, other additives. Blending can be done using one or more of the preceding methods. The compositions may be made using any suitable method, including wet or dry methods and batch, semi-continuous, and continuous methods. Dispersions, suspensions, solutions, etc. of graphene sheets
and one or more aliphatic compounds (including inks and coatings formulations) can be made or processed (e.g., milled/ground, blended, dispersed, suspended, etc.) by using suitable mixing, dispersing, and/or compounding techniques.

For example, components of the compositions, such as one or more of the graphene sheets, acids, graphite (if used), binders, carriers, and/or other components may be processed (e.g., milled/ground, blended, etc. by using suitable mixing, dispersing, and/or compounding techniques and apparatus, including ultrasonic devices, high-shear mixers, ball mills, attrition equipment, sandmills, two-roll mills, three-roll mills, cryogenic grinding crushers, extruders, kneaders, double planetary mixers, triple planetary mixers, high pressure homogenizers, horizontal and vertical wet grinding mills, etc.) Processing (including grinding) technologies can be wet or dry and can be continuous or discontinuous. Suitable materials for use as grinding media include metals, carbon steel, stainless steel, ceramics, stabilized ceramic media (such as cerium yttrium stabilized zirconium oxide), PTFE, glass, tungsten carbide, etc. Methods such as these can be used to change the particle size and/or morphology of the graphite, graphene sheets, other components, and blends or two or more components.

Components may be processed together or separately and may go through multiple processing (including mixing/blending) stages, each involving one or more components (including blends).

There is no particular limitation to the way in which the graphene sheets, graphite (if used), and other components are processed and combined. For example, graphene sheets and/or graphite may be processed into given particle size distributions and/or morphologies separately and then combined for further processing with or without the presence of additional components. Unprocessed graphene sheets and/or graphite may be combined with processed graphene sheets and/or graphite and further processed with or without the presence of additional components. Processed and/or unprocessed graphene sheets and/or processed and/or unprocessed graphite may be combined with other components, such as one or more binders and then combined with processed and/or unprocessed graphene sheets and/or processed and/or unprocessed graphite.

Two or more combinations of processed and/or unprocessed graphene sheets and/or processed and/or unprocessed graphite that have been combined with other components may be further combined or processed.

In one embodiment, if a multi-chain lipid is used, it can be added to graphene sheets (and/or graphite if present) before processing.
After blending and/or grinding steps, additional components may be added to the compositions, including, but not limited to, thickeners, viscosity modifiers, binders, etc. The compositions may also be diluted by the addition of more carrier.

Inks and coatings can be applied to a wide variety of substrates, including, but not limited to, flexible and/or stretchable materials, silicones and other elastomers and other polymeric materials, metals (such as aluminum, copper, steel, stainless steel, etc.), adhesives, heat-sealable materials (such as cellulose, biaxially oriented polypropylene (BOPP), poly(lactic acid), polyurethanes, etc.), fabrics (including cloths) and textiles (such as cotton, wool, polyesters, rayon, etc.), clothing, glasses and other minerals, ceramics, silicon surfaces, wood, paper, cardboard, paperboard, cellulose-based materials, glassine, labels, silicon and other semiconductors, laminates, corrugated materials, concrete, bricks, and other building materials, etc. Substrates can in the form of films, papers, wafers, larger three-dimensional objects, etc.

The substrates may have been treated with other coatings (such as paints) or similar materials before the inks and coatings are applied. Examples include substrates (such as PET) coated with indium tin oxide, antimony tin oxide, etc. They may be woven, nonwoven, in mesh form; etc. They may be woven, nonwoven, in mesh form; etc.

The substrates may be paper-based materials generally (including paper, paperboard, cardboard, glassine, etc.). Paper-based materials can be surface treated. Examples of surface treatments include coatings such as polymeric coatings, which can include PET, polyethylene, polypropylene, acetates, nitrocellulose, etc. Coatings may be adhesives. Paper-based materials may be sized.

Examples of polymeric materials include, but are not limited to, those comprising thermoplastics and thermosets, including elastomers and rubbers (including thermoplastics and thermosets), silicones, fluorinated polysiloxanes, natural rubber, butyl rubber, chlorosulfonated polyethylene, chlorinated polyethylene, styrene/butadiene copolymers (SBR), styrene/ethylene/butadiene/styrene copolymers (SEBS), styrene/ethylene/butadiene/styrene copolymers grafted with maleic anhydride, styrene/isoprene/styrene copolymers (SIS), polyisoprene, nitrile rubbers, hydrogenated nitrile rubbers, neoprene, ethylene/propylene copolymers (EPR), ethylene/propylene/diene copolymers (EPDM), ethylene/vinyl acetate copolymer (EVA), hexafluoropropylene/vinylidene fluoride/tetrafluoroethylene copolymers, tetrafluoroethylene/propylene copolymers, fluorelastomers, polyesters (such as
poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene naphthalate),
liquid crystalline polyesters, poly(lactic acid), etc.; polystyrene; polyamides (including
polyterephthalamides); polyimides (such as Kapton®); aramids (such as Kevlar® and
Nomex®); fluropolymers (such as fluorinated ethylene propylene (FEP),
polytetrafluoroethylene (PTFE), polyvinyl fluoride), poly(vinylidene fluoride), etc.);
polyetherimides; poly(vinyl chloride); poly(vinylidene chloride); polyurethanes (such as
thermoplastic polyurethanes (TPU); spandex, cellulosic polymers (such as nitrocellulose,
cellulose acetate, etc.); styrene/acrylonitriles polymers (SAN);
acrylonitrile/butadiene/styrene polymers (ABS); polycarbonates; polyacrylates;
poly(methyl methacrylate); ethylene/vinyl acetate copolymers; thermoset epoxies and
polyurethanes; polyolefins (such as polyethylene (including low density polyethylene,
high density polyethylene, ultrahigh molecular weight polyethylene, etc.), polypropylene
(such as biaxially-oriented polypropylene, etc.); Mylar; etc. They may be non-woven
materials, such as DuPont Tyvek®. They may be adhesive or adhesive-backed
materials (such as adhesive-backed papers or paper substitutes). They may be mineral-
based paper substitutes such as Teslin® from PPG Industries. The substrate may be a
transparent or translucent or optical material, such as glass, quartz, polymer (such as
polycarbonate or poly(methyl)acrylates (such as poly(methyl methacrylate).

The inks and coatings may be applied to the substrate using any suitable
method, including, but not limited to, painting, pouring, spin casting, solution casting, dip
coating, powder coating, by syringe or pipette, spray coating, curtain coating, lamination,
co-extrusion, electrospray deposition, ink-jet printing, spin coating, thermal transfer
(including laser transfer) methods, doctor blade printing, screen printing, rotary screen
printing, gravure printing, lithographic printing, intaglio printing, digital printing, capillary
printing, offset printing, electrohydrodynamic (EHD) printing (a method of which is
described in WO 2007/053621, which is hereby incorporated herein by reference),
microprinting, pad printing, tampon printing, stencil printing, wire rod coating, drawing,
flexographic printing, stamping, xerography, microcontact printing, dip pen
nanolithography, laser printing, via pen or similar means, etc. The compositions can be
applied in multiple layers.

After they have been applied to a substrate, the inks and coatings may be cured
using any suitable technique, including drying and oven-drying (in air or another inert or
reactive atmosphere), UV curing, IR curing, drying, crosslinking, thermal curing, laser
curing, IR curing, microwave curing or drying, sintering, and the like.
The cured inks and coatings can have a variety of thicknesses. For example, they can optionally have a thickness of at least about 2 nm, or at least about 5 nm. In various embodiments, the coatings can optionally have a thickness of about 2 nm to 20 mm, about 5 nm to 1 mm, about 2 nm to about 100 nm, about 2 nm to about 200 nm, about 2 nm to about 500 nm, about 2 nm to about 1 micrometer, about 5 nm to about 200 nm, about 5 nm to about 500 nm, about 5 nm to about 1 micrometer, about 5 nm to about 50 micrometers, about 5 nm to about 200 micrometers, about 10 nm to about 200 nm, about 50 nm to about 500 nm, about 50 nm to about 1 micrometer, about 100 nm to about 10 micrometers, about 1 micrometer to about 2 mm, about 1 micrometer to about 1 mm, about 1 micrometer to about 500 micrometers, about 1 micrometer to about 200 micrometers, about 1 micrometer to about 100 micrometers, about 50 micrometers to about 1 mm, about 100 micrometers to about 2 mm, about 100 micrometers to about 1 mm, about 100 micrometers to about 750 micrometers, about 100 micrometers to about 500 micrometers, about 500 micrometers to about 2 mm, or about 500 micrometers to about 1 mm.

When applied to a substrate, the inks and coatings can have a variety of forms. They can be present as a film or lines, patterns, letters, numbers, circuitry, logos, identification tags, and other shapes and forms. The inks and coatings may be covered in whole or in part with additional material, such as overcoatings, varnishes, polymers, fabrics, etc.

The inks and coatings can be applied to the same substrate in varying thicknesses at different points and can be used to build up three-dimensional structures on the substrate.

The inks and coatings can be used for the passivation of surfaces, such as metal (e.g. steel, aluminum, etc.) surfaces, including exterior structures such as bridges and buildings. Examples of other uses of the inks and coatings include: UV radiation resistant coatings, abrasion resistant coatings, coatings having permeation resistance to liquids (such as hydrocarbon, alcohols, water, etc.) and/or gases, electrically conductive coatings, static dissipative coatings, and blast and impact resistant coatings. They can be used to make fabrics having electrical conductivity. The inks and coatings can be used in solar cell applications; solar energy capture applications; signage, flat panel displays; flexible displays, including light-emitting diode, organic light-emitting diode, and polymer light-emitting diode displays; backplanes and frontplanes for displays; and lighting, including electroluminescent and OLED lighting. The displays may be used as
components of portable electronic devices, such as computers, cellular telephones, games, GPS receivers, personal digital assistants, music players, games, calculators, artificial "paper" and reading devices, etc.

They may be used in packaging and/or to make labels. They may be used in inventory control and anti-counterfeiting applications (such as for pharmaceuticals), including package labels. They may be used to make smart packaging and labels (such as for marketing and advertisement, information gathering, inventory control, information display, etc.). They may be used to form a Faraday cage in packaging, such as for electronic components.

The inks and coatings can be used on electrical and electronic devices and components, such as housings etc., to provide EMI shielding properties. They may be used in microdevices (such as microelectromechanical systems (MEMS) devices) including to provide antistatic coatings.

They may be used in the manufacture of housings, antennas, and other components of portable electronic devices, such as computers, cellular telephones, games, navigation systems, personal digital assistants, music players, games, calculators, radios, artificial "paper" and reading devices, etc.

The inks and coatings can be used to form thermally conductive channels on substrates or to form membranes having desired flow properties and porosities. Such materials could have highly variable and tunable porosities and porosity gradients can be formed. The inks and coatings can be used to form articles having anisotropic thermal and/or electrical conductivities. The coatings can be used to form three-dimensional printed prototypes.

The inks and coatings can be used to make printed electronic devices (also referred to as "printed electronics") that may be in the form of complete devices, parts or sub elements of devices, electronic components, etc.

Printed electronics may be prepared by applying the inks and coatings to the substrate in a pattern comprising an electrically conductive pathway designed to achieve the desired electronic device. The pathway may be solid, mostly solid, in a liquid or gel form, etc.

The printed electronic devices may take on a wide variety of forms and be used in a large array of applications. They may contain multiple layers of electronic components (e.g. circuits) and/or substrates. All or part of the printed layer(s) may be covered or coated with another material such as a cover coat, varnish, cover layer, cover
films, dielectric coatings, electrolytes and other electrically conductive materials, etc. There may also be one or more materials between the substrate and printed circuits. Layers may include semiconductors, metal foils, dielectric materials, etc.

The printed electronics may further comprise additional components, such as processors, memory chips, other microchips, batteries, resistors, diodes, capacitors, transistors, etc.

Other applications include, but are not limited to: passive and active devices and components; electrical and electronic circuitry, integrated circuits; flexible printed circuit boards; transistors; field-effect transistors; microelectromechanical systems (MEMS) devices; microwave circuits; antennas; diffraction gratings; indicators; chipless tags (e.g. for theft deterrence from stores, libraries, etc.); security and theft deterrence devices for retail, library, and other settings; key pads; smart cards; sensors (including gas and biosensors); liquid crystalline displays (LCDs); signage; lighting; flat panel displays; flexible displays, including light-emitting diode, organic light-emitting diode, and polymer light-emitting diode displays; backplanes and frontplanes for displays; electroluminescent and OLED lighting; photovoltaic devices, including backplanes; product identifying chips and devices; membrane switches, batteries, including thin film batteries; electrodes; indicators; printed circuits in portable electronic devices (for example, cellular telephones, computers, personal digital assistants, global positioning system devices, music players, games, calculators, etc.); electronic connections made through hinges or other movable/bendable junctions in electronic devices such as cellular telephones, portable computers, folding keyboards, etc.; wearable electronics; and circuits in vehicles, medical devices, diagnostic devices, instruments, etc.

The electronic devices may be radiofrequency identification (RFID) devices and/or components thereof and/or radiofrequency communication device. Examples include, but are not limited to, RFID tags, chips, and antennas. The RFID devices may be ultrahigh frequency RFID devices, which typically operate at frequencies in the range of about 868 to about 928 MHz. Examples of uses for RFID tags are for tracking shipping containers, products in stores, products in transit, and parts used in manufacturing processes; passports; barcode replacement applications; inventory control applications; pet identification; livestock control; contactless smart cards; automobile key fobs; etc.

The electronic devices may also be elastomeric (such as silicone) contact pads and keyboards. Such devices can be used in portable electronic devices, such as calculators, cellular telephones, GPS devices, keyboards, music players, games, etc.
They may also be used in myriad other electronic applications, such as remote controls, touch screens, automotive buttons and switches, etc.

The compositions, including those in the form of polymer composites, dispersions, inks and coatings, etc. can be electrically and/or thermally conductive. In some embodiments, the composition can have a conductivity of at least about 10⁻⁰ S/m, or about 10⁻¹ S/m, or about 10⁻² S/m, or about 10⁻³ S/m, or about 10⁻⁴ S/m, or about 10⁻⁵ S/m to about 10⁻⁶ S/m. In other embodiments of the invention, the coating has conductivities of at least about 0.001 S/m, or at least about 0.01 S/m, or at least about 0.1 S/m, or at least about 1 S/m, or at least about 10 S/m, or at least about 100 S/m, or at least about 1000 S/m, or at least about 10,000 S/m, or at least about 20,000 S/m, or at least about 30,000 S/m, or at least about 40,000 S/m, or at least about 50,000 S/m, or at least about 60,000 S/m, or at least about 75,000 S/m, or at least about 10⁵ S/m, or at least about 10⁶ S/m.

In some embodiments, the surface resistivity of the composition (including polymer composites, cured inks and coatings, etc.) may be no greater than about 10⁰ S/m, or no greater than about 5000 Ω/square/mil, or no greater than about 10,000 Ω/square/mil or no greater than about 700 Ω/square/mil, or no greater than about 500 Ω/square/mil, or no greater than about 350 Ω/square/mil, or no greater than about 200 Ω/square/mil, or no greater than about 150 Ω/square/mil, or no greater than about 100 Ω/square/mil, or no greater than about 75 Ω/square/mil, or no greater than about 50 Ω/square/mil, or no greater than about 30 Ω/square/mil, or no greater than about 20 Ω/square/mil, or no greater than about 10 Ω/square/mil, or no greater than about 5 Ω/square/mil, or no greater than about 1 Ω/square/mil, or no greater than about 0.1 Ω/square/mil, or no greater than about 0.01 Ω/square/mil, or no greater than about 0.001 Ω/square/mil.

In some embodiments, the composition can have a thermal conductivity of about 0.1 to about 50 W/nvK, or of about 0.5 to about 30 W/nvK, or of about 0.1 to about 0.5 W/nvK, or of about 0.1 to about 1 W/nvK, or of about 0.1 to about 5 W/nvK, or of about 0.5 to about 2 W/nvK, or of about 1 to about 5 W/nvK, or of about 0.1 to about 0.5 W/nvK, or of about 0.1 to about 50 W/nvK, or of about 1 to about 30 W/nvK, or of about 1 to about 20 W/nvK, or of about 1 to about 10 W/nvK, or of about 1 to about 5 W/nvK, or of about 2 to about 25 W/nvK, or of about 5 to about 25 W/nvK, or of about 5 to about 7 W/nvK, or of about 1.5 to about 7 W/nvK, or of about 3 W/nvK, or of about 3 to about 15 W/nvK, or of about 5 W/nvK, or of about 7 W/nvK, or of about 10 W/nvK, or of about 15 W/nvK.
Examples

Comparative Example 1 and Examples 1-7

The ink formulations of Examples 1-7 and Comparative Examples 1 and 2 are prepared by mixing graphene sheets, graphite, methyl methacrylate copolymer, isopropyl alcohol, n-butyl acetate, /V-methyl pyrrolidone, and gamma-butyrolactone. p-Toluenesulfonic acid (TsOH) is added to each formulation in the amounts shown in Table 1 (given as the weight percent of p-toluenesulfonic acid relative to the total weight of binder and acid).

Comparative Example 2 and Example 7

In the case of Comparative Example 2, pigment (graphene sheets and graphite) is dispersed in a solvent system of hexanol and /V-methylpyrrolidone to form a coating. In the case of Example 7, pigment (graphene sheets and graphite) and p-toluenesulfonic acid are combined in a solvent system of hexanol and /V-methylpyrrolidone to form a coating. The non-volatile components comprise about 2.5 weight percent of the coatings. The solid components are present relative to each other by weight in the amounts given in Table 2.

Comparative Example 3 and Example 8

In the case of Comparative Example 3, pigment (graphene sheets and graphite) is dispersed in a solvent system of hexanol and /V-methylpyrrolidone to form a coating. In the case of Example 8, pigment (graphene sheets and graphite) and p-toluenesulfonic acid are combined in a solvent system of hexanol and /V-methylpyrrolidone to form a coating. The non-volatile components comprise about 10 weight percent of the coatings. The solid components are present relative to each other by weight in the amounts given in Table 2.

Printing and measurements

The coatings are applied to PET films using a #28 wire rod. Each coating is applied in two layers and is cured at 130 °C between coats and after the second coat. The surface resistivities of the resulting cured prints are measured using a four point probe. The results are given in Tables 1-3.

The adhesion (pull) of the prints is measured by firmly applying a piece of 3M Scotch® #810 tape to the surface of a print and rapidly pulling the tape off the surface.
using a yanking motion perpendicular to the surface of the prints. The adhesion of the print is graded on a scale of 1 to 5 (where one is the best) based on the appearance of the tape after pulling. Samples having almost no ink transferred to the tape are given a grade of 1. Samples where the tape is completely dark after being pulled from the print are given a grade of 5. The results are given in Table 3.

The adhesion (peel) of the prints is measured by firmly applying a piece of 3M Scotch® #810 tape to the surface of a print and gently pulling it off in a direction parallel to the surface of the print. The surface resistivity of the print is measured before the tape is applied and again after the tape is pulled off. The percent increase in resistivity after the tape pull is given in Table 2.

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. Ex. 1</td>
</tr>
<tr>
<td>Example 1</td>
</tr>
<tr>
<td>Example 2</td>
</tr>
<tr>
<td>Example 3</td>
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<tr>
<td>Example 4</td>
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<tr>
<td>Example 5</td>
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<td>Example 6</td>
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Table 2

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Comp. Ex. 2</th>
<th>Ex. 7</th>
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</thead>
<tbody>
<tr>
<td>Pigment</td>
<td>100</td>
<td>94.1</td>
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<tr>
<td>TsOH</td>
<td>--</td>
<td>5.9</td>
</tr>
<tr>
<td>Surface resistivity (Ohm/sq)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adhesion (peel) (surface resistivity increase (percentage))</td>
<td>10</td>
<td>8</td>
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<tr>
<td></td>
<td>150</td>
<td>150</td>
</tr>
</tbody>
</table>

Ingredient quantities are in weight percentages based on the total weight of the given ingredients.

Table 3

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Comp Ex. 3</th>
<th>Ex. 8</th>
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<tbody>
<tr>
<td>Pigment</td>
<td>82</td>
<td>74.2</td>
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<tr>
<td>Binder</td>
<td>18</td>
<td>16.3</td>
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<tr>
<td>Catalyst</td>
<td>--</td>
<td>9.5</td>
</tr>
<tr>
<td>Surface resistivity (Ohm/sq)</td>
<td>17</td>
<td>13</td>
</tr>
<tr>
<td>Adhesion (pull)</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

Ingredient quantities are in weight percentages based on the total weight of the given ingredients.
Claims

1. A composition, comprising graphene sheets and at least one acid.

2. The composition of claim 1, further comprising at least one polymer.

3. The composition of claim 1, wherein the polymer is selected from polyvinyl butyral, polyvinyl formal, and polyacrylates.

4. The composition of claim 1, wherein the acid is a sulfonic acid.

5. The composition of claim 1, wherein the acid is p-toluenesulfonic acid.

6. The composition of claim 1, wherein the graphene sheets have a surface area of at least about 300 m²/g.

7. The composition of claim 1, wherein the graphene sheets have a surface area of at least about 400 m²/g.

8. The composition of claim 1, wherein the graphene sheets have a carbon to oxygen molar ratio of at least about 25:1.

9. The composition of claim 1, wherein the graphene sheets have a carbon to oxygen molar ratio of at least about 75:1.

10. The composition of claim 1, further comprising graphite.

11. An ink or coating, comprising a composition comprising graphene sheets and at least one acid.

12. The ink or coating of claim 11, further comprising at least one polymer.
13. The ink or coating of claim 12, wherein the polymer is selected from polyvinyl butyral, polyvinyl formal, and polyacrylates.

14. The ink or coating of claim 11, wherein the acid is a sulfonic acid.

15. The ink or coating of claim 11, wherein the acid is p-toluene sulfonic acid.

16. The ink or coating of claim 11, wherein the graphene sheets have a surface area of at least about 300 m$^2$/g.

17. The ink or coating of claim 11, wherein the graphene sheets have a surface area of at least about 400 m$^2$/g.

18. The ink or coating of claim 11, wherein the graphene sheets have a carbon to oxygen molar ratio of at least about 25:1.

19. The ink or coating of claim 11, wherein the graphene sheets have a carbon to oxygen molar ratio of at least about 75:1.

20. An article coated with the ink or coating of claim 11.
### INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

**IPC(8) -**

C01B 31/04 (2013.01)

**USPC -**

423/448

According to International Patent Classification (IPC) or to both national classification and IPC.

### B. FIELD SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - C01B 31/04 (2013.01);

USPC - 423/448

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Patents and NPL (classification, keyword; search terms below).

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

PubWest (USPTO, EPO, JPO, WIPO), GoogleScholar (PL, NPL), FreePatentsOnline (USPTO, EPO, JPO, WIPO, NPL);

search terms: graphene, acid, sulfuric, hydrochloric, nitric, nitrous, phosphoric, boric, hydrobromic, perchloric, catalyst, toluenesulfonic, ink, coat, graphite

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 20110186786 A1 (SCHIEFFER et al.) 4 August 2011 (04.08.2011), para [0005], [0006], [0009], [0026], [0029], [0030], [0039], [0047], [0051], [0070]</td>
<td>1-3, 6-13, 16-20</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C.

- **T** - later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- **X** - document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- **Y** - document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- **&** - document member of the same patent family

**Date of the actual completion of the international search**

25 January 2013 (25.01.2013)

**Date of mailing of the international search report**

28 FEB 2013

**Name and mailing address of the ISA/US**

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

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

Facsimile No. 571-273-3201

**Authorized officer:**

Lee W. Young

PCT Helpdesk: 571-272-4200

PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)