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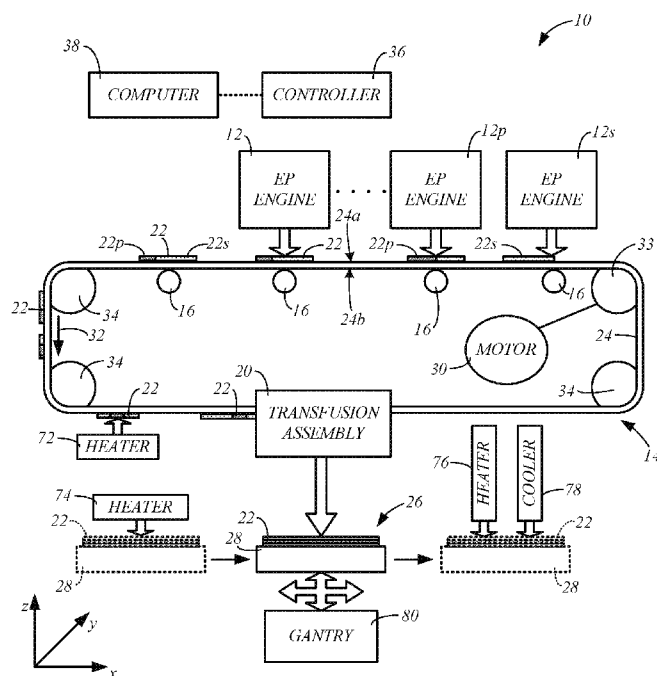


FIG. 1

(57) Abstract: An additive printing composition, the additive printing composition comprising a nylon toner and a magnetic carrier; wherein the magnetic carrier comprises less than 1.0 percent of a polymeric coating. Optionally the magnetic carrier is coated with less than 0.75% of a polymeric coating, less than 0.5% of a polymeric coating, or less than 0.3% of a polymeric coating.

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ADDITIVE MANUFACTURING MATERIALS AND METHODS FOR FORMING POLYAMIDE PARTS

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2023 in the name of Evolve Additive Solutions, Inc., a U.S. national corporation, applicant
for the designation of all countries, and Jerry Pickering, a U.S. Citizen, inventor for the
designation of all countries, and claims priority to U.S. Provisional Patent Application No.
63/326/172 filed March 31, 2022, the contents of which are herein incorporated by reference
in its entirety.

FIELD OF THE INVENTION

Embodiments herein relate to methods and systems for forming three-dimensional
printed parts, in particular printed parts formed of polyamide, and developer for use in 3D
printing.

BACKGROUND

Additive manufacturing systems are used to build 3D parts from digital
representations of the parts using one or more additive manufacturing techniques. Examples
of commercially available additive manufacturing techniques include extrusion-based
techniques, ink jetting, selective laser sintering, powder/binder jetting, electron beam melting,
and stereolithographic processes. For each of these techniques, the digital representation of
the 3D part is initially digitally sliced into multiple horizontal layers. For each sliced layer, a
tool path is then generated, which provides instructions for the particular additive
manufacturing system to form the given layer.

One particularly desirable additive manufacturing method is selective toner
electrophotographic process (STEP) additive manufacturing, which allows for rapid, high-
quality production of 3D parts. STEP manufacturing is performed by applying layers of
thermoplastic material that are carried from an electrophotography (EP) engine by a transfer
medium (e.g., a rotatable belt or drum). The layer of thermoplastic material is then transferred
to a build platform to print the 3D part (or support structure) in a layer-by-layer manner,
where the successive layers are transfused together to produce the 3D part (or support
structure). The layers are placed down in an X-Y plane, with successive layers positioned on
top of one another in a Z-axis perpendicular to the X-Y plane.

A support structure is sometimes built utilizing the same deposition techniques by which the part material is deposited. The supporting layers or structures are often built underneath overhanging portions or in cavities of parts under construction that are not supported by the part material itself. The part material adheres to the support material during fabrication and the support material is subsequently removable from the completed 3D part when the printing process is complete. In typical STEP processes layers of the part material and support material are deposited next to each other in a common X-Y plane. These layers of part and support material are each built on top of one another (layers of part material built on top of other layers of part material; and layers of support material built on top of other layers of support material) along the Z-axis to create a composite part that contains both part material and support material.

Although STEP deposition can produce very high-quality parts, it is still desirable to form even better parts, including production of parts from a wide variety of polymeric materials. Currently, thermoplastic materials made by electrophotography-based additive manufacturing include those made from polymers comprising acrylonitrile, butadiene, and styrene (ABS). However, a need exists for additional thermoplastic materials and methods of using them.

SUMMARY

The present application is directed to an additive printing composition, the additive printing composition comprising a nylon toner and a magnetic carrier, wherein the magnetic carrier comprises less than 1.0 percent of a polymeric coating.

In an embodiment, the magnetic carrier is coated with less than 0.75% of a polymeric coating.

In an embodiment, the magnetic carrier is coated with less than 0.5% of a polymeric coating.

In an embodiment, the magnetic carrier is coated with less than 0.3% of a polymeric coating.

In an embodiment, the magnetic carrier is coated with greater than 0.025% of a polymeric coating.

In an embodiment, the magnetic carrier comprises a hard magnet.

In an embodiment, the hard magnet comprises strontium ferrite.

In an embodiment, the polymeric coating comprises polymethylmethacrylate.

In an embodiment, the nylon is selected from the group consisting of polyamide 6,

polyamide 11, polyamide 1012, polyamide 613, polyamide 66, polyamide 612 and combinations thereof.

In an embodiment, the nylon comprises a charge control agent.

5 In an embodiment, the nylon comprises an infrared absorber, and in an embodiment the infrared adsorber comprises carbon black.

In an embodiment, the nylon toner has a volume D50 of between 12 and 35 μm .

In an embodiment, the nylon toner has a volume D50 of greater than 10 μm .

In an embodiment, the nylon toner has a volume D50 of less than 40 μm .

In an embodiment, the nylon toner has a number D50 greater than 8 μm .

10 In an embodiment, the nylon toner has a number D50 greater than 10 μm .

In an embodiment, the nylon toner has a number D50 greater than 15 μm .

In an embodiment, the nylon toner comprises between 7% and 16% of the blend.

In an embodiment, the nylon toner comprises between less than 20 percent of the blend.

15 This summary is an overview of some of the teachings of the present application and is not intended to be an exclusive or exhaustive treatment of the present subject matter. Further details are found in the detailed description and appended claims. Other aspects will be apparent to persons skilled in the art upon reading and understanding the following detailed description and viewing the drawings that form a part thereof, each of which is not to
20 be taken in a limiting sense. The scope herein is defined by the appended claims and their legal equivalents.

DEFINITIONS

25 Unless otherwise specified, the following terms as used herein have the meanings provided below:

The term "copolymer" refers to a polymer having two or more monomer species.

The terms "preferred" and "preferably" refer to embodiments of the invention that may afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances. Furthermore, the recitation of one
30 or more preferred embodiments does not imply that other embodiments are not useful, and is not intended to exclude other embodiments from the inventive scope of the present disclosure.

Reference to "a" chemical compound refers one or more molecules of the chemical compound, rather than being limited to a single molecule of the chemical compound.

Furthermore, the one or more molecules may or may not be identical, so long as they fall under the category of the chemical compound.

The terms "at least one" and "one or more of" an element are used interchangeably, and have the same meaning that includes a single element and a plurality of the elements, and may
5 also be represented by the suffix "(s)" at the end of the element.

Directional orientations such as "above", "below", "top", "bottom", and the like are made with reference to a direction along a printing axis of a 3D part. In the embodiments in which the printing axis is a vertical z-axis, the layer-printing direction is the upward direction along the vertical z-axis. In these embodiments, the terms "above", "below", "top", "bottom",
10 and the like are based on the vertical z-axis. However, in embodiments in which the layers of 3D parts are printed along a different axis, the terms "above", "below", "top", "bottom", and the like are relative to the given axis.

The terms "about" and "substantially" are used herein with respect to measurable values and ranges due to expected variations known to those skilled in the art (e.g., limitations
15 and variabilities in measurements).

The term "providing", such as for "providing a material" and the like, when recited in the claims, is not intended to require any particular delivery or receipt of the provided item. Rather, the term "providing" is merely used to recite items that will be referred to in subsequent elements of the claim(s), for purposes of clarity and ease of readability.

20 The term "selective deposition" refers to an additive manufacturing technique where one or more layers of particles are fused to previously deposited layers utilizing heat and pressure over time where the particles fuse together to form a layer of the part and also fuse to the previously printed layer.

The term "electrostatography" refers to the formation and utilization of latent
25 electrostatic charge patterns to form an image of a layer of a part, a support structure or both on a surface. Electrostatography includes, but is not limited to, electrophotography where optical energy is used to form the latent image, ionography where ions are used to form the latent image and/or electron beam imaging where electrons are used to form the latent image.

The terms "resilient material" and "flowable material" describe distinct materials used
30 in the printing of a 3D part and support. The resilient material has a higher viscosity and/or storage modulus relative to the flowable material.

Unless otherwise specified, pressures referred to herein are based on atmospheric pressure (i.e. one atmosphere).

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic front view of an exemplary electrophotography-based additive manufacturing system for printing 3D parts and support structures from part and support materials, in accordance with embodiments of the present disclosure.

5 FIG. 2 is a schematic front view of a pair of electrophotography engines of the system for developing layers of the part and support materials, in accordance with embodiments of the present disclosure.

10 FIG. 3 is a schematic front view of an alternative electrophotography engine, which includes an intermediary drum or belt, in accordance with embodiments of the present disclosure.

FIG. 4 is a schematic front view of a layer transfusion assembly of the system for performing layer transfusion steps with the developed layers, in accordance with embodiments of the present disclosure.

15 While embodiments are susceptible to various modifications and alternative forms, specifics thereof have been shown by way of example and drawings, and will be described in detail. It should be understood, however, that the scope herein is not limited to the particular embodiments described. On the contrary, the intention is to cover modifications, equivalents, and alternatives falling within the spirit and scope herein.

DETAILED DESCRIPTION

20 Embodiments of the present disclosure relate to a selective deposition-based additive manufacturing system, such as an electrostatography-based additive manufacturing system, to print 3D parts and/or support structures using polyamide (nylon) materials. During a printing operation, electrostatographic engines develop or otherwise image each polyamide layer of the part and support materials using the electrostatographic process. The developed layers are then transferred to a layer transfusion assembly where they are transfused (e.g., using heat and/or pressure over time) to print one or more 3D parts and support structures in a layer-by-layer manner.

30 Thermoplastic materials made by electrophotography-based additive manufacturing include those made from polymers comprising acrylonitrile, butadiene, and styrene (ABS). ABS materials made by additive manufacturing processes are known to possess significantly different physical properties than ABS materials made by injection molding. Polyamides, also known as nylons, are another family of thermoplastic polymers made by 3D-printing. The 3D printed nylons are also known to have decreased physical properties when compared to

injection molding. PA-12 from Arkema has published notched Charpy impact strength values of 6-20 kJ/m² at 23 °C. While PA-12 made by multi-jet fusion additive manufacturing methods has published values of notched Izod impact strength of 3.5-3.6 kJ/m². A reference of 30 grades of Nylon 12 has an average Izod impact strength of 14.8 kJ/m². Thus, there is a need in the art to produce nylon materials from additive manufacturing processes that have higher impact strength, preferably greater than 10 kJ/m², which is much closer to the injection molded values.

The present application is directed to an additive printing composition, the additive printing composition comprising a nylon toner and a magnetic carrier; wherein the magnetic carrier comprises less than 1.0 percent of a polymeric coating.

In an embodiment, the magnetic carrier is coated with less than 0.75% of a polymeric coating. In an embodiment, the magnetic carrier is coated with less than 0.5% of a polymeric coating. In an embodiment, the magnetic carrier is coated with less than 0.3% of a polymeric coating. In an embodiment, the magnetic carrier is coated with greater than 0.025% of a polymeric coating.

In an embodiment, the magnetic carrier comprises a hard magnet. In an embodiment, the hard magnet comprises strontium ferrite.

In an embodiment, the polymeric coating comprises polymethylmethacrylate.

In an embodiment, the nylon is selected from the polyamide 6, polyamide 11, polyamide 1012, polyamide 613, polyamide 66, polyamide 612 and combinations thereof.

In an embodiment, the nylon comprises a charge control agent.

In an embodiment, the nylon comprises an infrared absorber. In an embodiment the infrared adsorber comprises carbon black.

In an embodiment, the nylon toner has a volume D50 of between 12 and 35 µm. In an embodiment, the nylon toner has a volume D50 of greater than 10 µm. In an embodiment, the nylon toner has a volume D50 of less than 40 µm. In an embodiment, the nylon toner has a number D50 greater than 8 µm. In an embodiment, the nylon toner has a number D50 greater than 10 µm. In an embodiment, the nylon toner has a number D50 greater than 15 µm. In an embodiment, the nylon toner comprises between 7% and 16% of the blend. In an embodiment, the nylon toner comprises between less than 20 percent of the blend.

One exemplary process for preparing improved nylon compositions is selective thermoplastic electrophotography process (STEP). A challenge for STEP is that nylons are very positive on the triboelectric scale, and a typical process for STEP uses negatively charged particle imaging. The electrophotographic process employs a developer, made with

toner particles and carrier, to form images on a photosensitive member. A developer suitable to use with nylon particle would be of significant benefit in the STEP process.

Example methods and equipment for forming polyamide parts are shown in FIGS. 1 to 4, which show example components of STEP manufacturing systems. FIG. 1 is a simplified diagram of an exemplary electrophotography-based additive manufacturing system 10 configured to perform a selective deposition process to printing 3D parts and associated support structures, in accordance with embodiments of the present disclosure. As shown in FIG. 1, system 10 includes one or more EP engines, generally referred to as 12, such as EP engines 12p and 12s, a transfer assembly 14, biasing mechanisms 16, and a transfusion assembly 20. Examples of suitable components and functional operations for system 10 include those disclosed in Hanson et al., U.S. Patent Nos. 8,879,957 and 8,488,994, and in Comb et al., U.S. Patent Publication Nos. 2013/0186549 and 2013/0186558.

The EP engines 12p and 12s are imaging engines for respectively imaging or otherwise developing layers, generally referred to as 22, of the powder-based part and support materials, where the part and support materials are each preferably engineered for use with the particular architecture of the EP engine 12p or 12s. As discussed below, the developed layers 22 are transferred to a transfer medium (such as belt 24) of the transfer assembly 14, which delivers the layers 22 to the transfusion assembly 20. The transfusion assembly 20 operates to build the 3D part 26, which may include support structures and other features, in a layer-by-layer manner by transfusing the layers 22 together on a build platform 28.

In some embodiments, the transfer medium includes a belt 24, as shown in FIG. 1. Examples of suitable transfer belts for the transfer medium or belt 24 include those disclosed in Comb et al., U.S. Patent Application Publication Nos. 2013/0186549 and 2013/0186558.

In some embodiments, the belt 24 includes front surface 24a and rear surface 24b, where front surface 24a faces the EP engines 12, and the rear surface 24b is in contact with the biasing mechanisms 16.

In some embodiments, the transfer assembly 14 includes one or more drive mechanisms that include, for example, a motor 30 and a drive roller 33, or other suitable drive mechanism, and operate to drive the transfer medium or belt 24 in a feed direction 32. In some embodiments, the transfer assembly 14 includes idler rollers 34 that provide support for the belt 24. The example transfer assembly 14 illustrated in FIG. 1 is highly simplified and may take on other configurations. Additionally, the transfer assembly 14 may include additional components that are not shown in order to simplify the illustration, such as, for

example, components for maintaining a desired tension in the belt 24, a belt cleaner for removing debris from the surface 24a that receives the layers 22, and other components.

The EP engine 12s develops layer or image portions 22s of powder-based support material, and the EP engine 12p develops layer or image portions 22p of powder-based part/build material. In some embodiments, the EP engine 12s is positioned upstream from the EP engine 12p relative to the feed direction 32, as shown in FIG. 1. In alternative embodiments, the arrangement of the EP engines 12p and 12s may be reversed such that the EP engine 12p is upstream from the EP engine 12s relative to the feed direction 32. In further alternative embodiments, system 10 may include three or more EP engines 12 for printing layers of additional materials, as indicated in FIG. 1.

Example system 10 also includes controller 36, which represents one or more processors that are configured to execute instructions, which may be stored locally in memory of the system 10 or in memory that is remote to the system 10, to control components of the system 10 to perform one or more functions described herein. In some embodiments, the controller 36 includes one or more control circuits, microprocessor-based engine control systems, and/or digitally-controlled raster imaging processor systems, and is configured to operate the components of system 10 in a synchronized manner based on printing instructions received from a host computer 38 or a remote location.

In some embodiments, the host computer 38 includes one or more computer-based systems that are configured to communicate with controller 36 to provide the print instructions (and other operating information). For example, the host computer 38 may transfer information to the controller 36 that relates to the sliced layers of the 3D parts and support structures, thereby allowing the system 10 to print the 3D parts 26 and support structures in a layer-by-layer manner. The controller 36 may also use signals from one or more sensors to assist in properly registering the printing of the part or image portion 22p and/or the support structure or image portion 22s with a previously printed corresponding support structure portion 22s or part portion 22p on the belt 24 to form the individual layers 22.

The components of system 10 may be retained by one or more frame structures (not shown for simplicity). Additionally, the components of system 10 may be retained within an enclosable housing (not shown for simplicity) that prevents components of the system 10 from being exposed to ambient light during operation.

FIG. 2 is a schematic front view of the EP engines 12p and 12s of the system 10, in accordance with example embodiments of the present disclosure. In the illustrated

embodiment, the EP engines 12p and 12s may include the same components, such as a photoconductor drum 42 having a conductive drum body 44 and a photoconductive surface 46. The conductive drum body 44 is an electrically-conductive drum (e.g., fabricated from copper, aluminum, tin, or the like) that is electrically grounded and configured to rotate
5 around a shaft 48. The shaft 48 is correspondingly connected to a drive motor 50, which is configured to rotate the shaft 48 (and the photoconductor drum 42) in the direction of arrow 52 at a constant rate.

The photoconductive surface 46 can be a thin film extending around the circumferential surface of the conductive drum body 44, and is preferably derived from one
10 or more photoconductive materials, such as amorphous silicon, selenium, zinc oxide, organic materials, and the like. As discussed below, the surface 46 is configured to receive latent-charged images of the sliced layers of a 3D part or support structure (or negative images), and to attract charged particles of the part or support material to the charged or discharged image areas, thereby creating the layers of the 3D part or support structure.

As further shown, each of the example EP engines 12p and 12s also includes a charge inducer 54, an imager 56, a development station 58, a cleaning station 60, and a discharge device 62, each of which may be in signal communication with the controller 36. The charge inducer 54, the imager 56, the development station 58, the cleaning station 60, and the discharge device 62 accordingly define an image-forming assembly for the surface 46 while
15 the drive motor 50 and the shaft 48 rotate the photoconductor drum 42 in the direction 52.

Each of the EP engines 12 uses the powder-based material (e.g., polymeric or thermoplastic toner, such as polyamide particles), generally referred to herein by reference character 66, to develop or form the layers 22. In some embodiments, the image-forming assembly for the surface 46 of the EP engine 12s is used to form support layers 22s (e.g.,
25 image portions) of powder-based support material 66s, where a supply of the support material 66s may be retained by the development station 58 (of the EP engine 12s) along with carrier particles formed of strontium ferrite as described below. Similarly, the image-forming assembly for the surface 46 of the EP engine 12p is used to form part layers 22p (e.g., image portion) of powder-based part material 66p, where a supply of the part material 66p may be
30 retained by the development station 58 (of the EP engine 12p) along with carrier particles. Additional EP engines 12 may be included that utilize other support or part materials 66.

The charge inducer 54 is configured to generate a uniform electrostatic charge on the surface 46 as the surface 46 rotates in the direction 52 past the charge inducer 54. Suitable

devices for the charge inducer 54 include corotrons, scorotrons, charging rollers, and other electrostatic charging devices.

Each imager 56 is a digitally-controlled, pixel-wise light exposure apparatus configured to selectively emit electromagnetic radiation toward the uniform electrostatic charge on the surface 46 as the surface 46 rotates in the direction 52 the past imager 56. The selective exposure of the electromagnetic radiation to the surface 46 is directed by the controller 36, and causes discrete pixel-wise locations of the electrostatic charge to be removed (i.e., discharged to ground), thereby forming latent image charge patterns on the surface 46.

Suitable devices for the imager 56 include scanning laser (e.g., gas or solid-state lasers) light sources, light emitting diode (LED) array exposure devices, and other exposure device conventionally used in 2D electrophotography systems. In alternative embodiments, suitable devices for the charge inducer 54 and the imager 56 include ion-deposition systems configured to selectively directly deposit charged ions or electrons to the surface 46 to form the latent image charge pattern.

Each development station 58 is an electrostatic and magnetic development station or cartridge that retains the supply of the part material 66p or the support material 66s, along with hard magnetic carrier particles customized for use with polyamide toner. The development stations 58 may function in a similar manner to single or dual component development systems and toner cartridges used in 2D electrophotography systems. For example, each development station 58 may include an enclosure for retaining the part material 66p or the support material 66s and hard magnet (typically strontium ferrite) carrier particles. When agitated, the carrier particles generate triboelectric charges to attract the powders of the part material 66p or the support material 66s, which charges the attracted polyamide powders to a desired sign and magnitude, as discussed below.

Each development station 58 may also include one or more devices for transferring the charged polyamide part or the support material 66p or 66s to the surface 46, such as conveyors, brushes, paddle wheels, rollers, and/or magnetic brushes. For instance, as the surface 46 (containing the latent charged image) rotates from the imager 56 to the development station 58 in the direction 52, the charged part material 66p or the support material 66s is attracted to the appropriately charged regions of the latent image on the surface 46, utilizing either charged area development or discharged area development (depending on the electrophotography mode being utilized). This creates successive layers 22p or 22s as the photoconductor drum continues to rotate in the direction 52, where the

successive layers 22p or 22s correspond to the successive sliced layers of the digital representation of the 3D part or support structure.

The successive layers 22p or 22s are then rotated with the surface 46 in the direction 52 to a transfer region in which layers 22p (polyamide part material) or 22s (support material) are successively transferred from the photoconductor drum 42 to the belt 24 or other transfer medium, as discussed below. While illustrated as a direct engagement between the photoconductor drum 42 and the belt 24, in some preferred embodiments, the EP engines 12p and 12s may also include intermediary transfer drums and/or belts, as discussed further below.

After a given layer 22p or 22s is transferred from the photoconductor drum 42 to the belt 24 (or an intermediary transfer drum or belt), the drive motor 50 and the shaft 48 continue to rotate the photoconductor drum 42 in the direction 52 such that the region of the surface 46 that previously held the layer 22p or 22s passes the cleaning station 60. The cleaning station 60 is a station configured to remove any residual, non-transferred portions of part or support material 66p or 66s. Suitable devices for the cleaning station 60 include blade cleaners, brush cleaners, electrostatic cleaners, vacuum-based cleaners, and combinations thereof.

After passing the cleaning station 60, the surface 46 continues to rotate in the direction 52 such that the cleaned regions of the surface 46 pass the discharge device 62 to remove any residual electrostatic charge on the surface 46, prior to starting the next cycle. Suitable devices for the discharge device 62 include optical systems, high-voltage alternating-current corotrons and/or scorotrons, one or more rotating dielectric rollers having conductive cores with applied high-voltage alternating-current, and combinations thereof.

The biasing mechanisms 16 are configured to induce electrical potentials through the belt 24 to electrostatically attract the layers 22p and 22s from the EP engines 12p and 12s to the belt 24. Because the layers 22p and 22s are each only a single layer increment in thickness at this point in the process, electrostatic attraction is suitable for transferring the layers 22p and 22s from the EP engines 12p and 12s to the belt 24.

The controller 36 preferably rotates the photoconductor drums of the EP engines 12p and 12s at the same rotational rates that are synchronized with the line speed of the belt 24 and/or with any intermediary transfer drums or belts. This allows the system 10 to develop and transfer the layers 22p and 22s in coordination with each other from separate developer images. In particular, as shown, each part layer 22p may be transferred to the belt 24 with proper registration with each support layer 22s to produce a combined part and support

material layer or combined image layer, which is generally designated as layer 22. As can be appreciated, some of the layers 22 transferred to the layer transfusion assembly 20 may only include support material 66s or may only include part material 66p, depending on the particular support structure and 3D part geometries and layer slicing.

5 In an alternative embodiment, the part layers 22p and the support layers 22s may optionally be developed and transferred along the belt 24 separately, such as with alternating layers 22p and 22s. These successive, alternating layers 22p and 22s may then be transferred to layer transfusion assembly 20, where they may be transfused separately to form the layer 22 and print or build the 3D part 26 and support structure.

10 In a further alternative embodiment, one or both of the EP engines 12p and 12s may also include one or more intermediary transfer drums and/or belts between the photoconductor drum 42 and the belt or transfer medium or belt 24. For example, as shown in FIG. 3, the EP engine 12p may also include an intermediary drum 42a that rotates in the direction 52a that opposes the direction 52, in which drum 42 is rotated, under the rotational
15 power of motor 50a. The intermediary drum 42a engages with the photoconductor drum 42 to receive the developed layers 22p of polyamide from the photoconductor drum 42, and then carries the received developed layers 22p and transfers them to the belt 24.

The EP engine 12s may include the same arrangement of an intermediary drum 42a for carrying the developed layers 22s from the photoconductor drum 42 to the belt 24. The
20 use of such intermediary transfer drums or belts for the EP engines 12p and 12s can be beneficial for thermally isolating the photoconductor drum 42 from the belt 24, if desired.

FIG. 4 illustrates an embodiment of the layer transfusion assembly 20. As shown, the exemplary transfusion assembly 20 includes the build platform 28, a nip roller 70, and pre-transfusion heaters 72 and 74. In some embodiments, the transfusion assembly includes, an
25 optional post-transfusion heater 76, and/or a cooler (e.g., air jets 78 or other cooling units), as shown in FIGS. 1 and 4. The build platform 28 is a platform assembly or platen of system 10 that is configured to receive the heated combined layers 22 (or separate layers 22p and 22s) for printing the part 26, which includes a 3D part 26p formed of the part layers 22p, and support structure 26s formed of the support layers 22s, in a layer-by-layer manner. In some
30 embodiments, the build platform 28 may include removable film substrates (not shown) for receiving the printed layers 22, where the removable film substrates may be restrained against build platform using any suitable technique (e.g., vacuum drawing).

The build platform 28 is supported by a gantry 84 or other suitable mechanism, which can be configured to move the build platform 28 along the z-axis and the x-axis (and,

optionally, also the y-axis), as illustrated schematically in FIG. 1 (the y-axis being into and out of the page in FIG. 1, with the z-, x- and y-axes being mutually orthogonal, following the right-hand rule). The layers are put down generally parallel to an x-y plane, and the layers stack on top of one another along the z-axis. The gantry 84 may produce cyclical movement patterns relative to the nip roller 70 and other components, as illustrated by broken line 86 in FIG. 4. The particular movement pattern of the gantry 84 can follow essentially any desired path suitable for a given application. The gantry 84 may be operated by a motor 88 based on commands from the controller 36, where the motor 88 may be an electrical motor, a hydraulic system, a pneumatic system, or the like.

In one embodiment, the gantry 84 can include an integrated mechanism that precisely controls movement of the build platform 28 in the z- and x-axis directions (and optionally the y-axis direction). In alternate embodiments, the gantry 84 can include multiple, operatively-coupled mechanisms that each control movement of the build platform 28 in one or more directions, for instance, with a first mechanism that produces movement along both the z-axis and the x-axis and a second mechanism that produces movement along only the y-axis. The use of multiple mechanisms can allow the gantry 84 to have different movement resolution along different axes. Moreover, the use of multiple mechanisms can allow an additional mechanism to be added to an existing mechanism operable along fewer than three axes.

In the illustrated embodiment, the build platform 28 can be heatable with heating element 90 (e.g., an electric heater). The heating element 90 is configured to heat and maintain the build platform 28 at an elevated temperature that is greater than room temperature (25°C), such as at a desired average part temperature of 3D part 26p and/or support structure 26s, as discussed in Comb et al., U.S. Patent Application Publication Nos. 2013/0186549 and 2013/0186558. This allows the build platform 28 to assist in maintaining 3D part 26p and/or support structure 26s at this average part temperature.

The nip roller 70 is an example heatable element or heatable layer transfusion element, which is configured to rotate around a fixed axis with the movement of the belt 24. In particular, the nip roller 70 may roll against the rear surface 22s in the direction of arrow 92 while the belt 24 rotates in the feed direction 32. In the shown embodiment, the nip roller 70 is heatable with a heating element 94 (e.g., an electric heater). The heating element 94 is configured to heat and maintain nip roller 70 at an elevated temperature that is greater than room temperature (25°C), such as at a desired transfer temperature for the layers 22.

The pre-transfusion heater 72 includes one or more heating devices (e.g., an infrared heater and/or a heated air jet) that are configured to heat the layers 22 on the belt 24 to a selected temperature of the layer 22, such as up to a fusion temperature of the part material 66p and the support material 66s, prior to reaching nip roller 70. Each layer 22 desirably passes by (or through) the heater 72 for a sufficient residence time to heat the layer 22 to the intended transfer temperature. The pre-transfusion heater 74 may function in the same manner as the heater 72, and heats the top surfaces of the 3D part 26p and support structure 26s on the build platform 28 to an elevated temperature, and in one embodiment to supply heat to the layer upon contact.

The part and support materials 66p and 66s of the layers 22p and 22s may be heated together with the heater 72 to substantially the same temperature, and the part and support materials 66p and 66s at the top surfaces of the 3D part 26p and support structure 26s may be heated together with heater 74 to substantially the same temperature. This allows the part layers 22p and the support layers 22s to be transfused together to the top surfaces of the 3D part 26p and the support structure 26s in a single transfusion step as the combined layer 22. As discussed below, a gap can be placed between the support layers 22s and part layers 22p, and under heat and pressure part and support material are pressed together in a manner such as to produce an improved interface with reduced surface roughness.

An optional post-transfusion heater 76 may be provided downstream from nip roller 70 and upstream from air jets 78, and configured to heat the transfused layers 22 to an elevated temperature in a single post-fuse step.

As mentioned above, in some embodiments, prior to building the part 26 on the build platform 28, the build platform 28 and the nip roller 70 may be heated to their selected temperatures. For example, the build platform 28 may be heated to the average part temperature (e.g., bulk temperature) of 3D part 26p and support structure 26s. In comparison, the nip roller 70 may be heated to a desired transfer temperature or nip entrance temperature for the layers 22.

As further shown in FIG. 4, during operation, the gantry 84 may move the build platform 28 (with 3D part 26p and support structure 26s) in a reciprocating pattern 86. In particular, the gantry 84 may move the build platform 28 along the x-axis below, along, or through the heater 74. The heater 74 heats the top surfaces of 3D part 26p and support structure 26s to an elevated temperature, such as the transfer temperatures of the part and support materials. As discussed in Comb et al., U.S. Patent Application Publication Nos. 2013/0186549 and 2013/0186558, the heaters 72 and 74 may heat the layers 22 and the top

surfaces of 3D part 26p and support structure 26s to about the same temperatures to provide a consistent transfusion interface temperature. Alternatively, the heaters 72 and 74 may heat layers 22 and the top surfaces of 3D part 26p and support structure 26s to different temperatures to attain a desired transfusion interface temperature.

5 The continued rotation of the belt 24 and the movement of the build platform 28 align or register the heated layer 22 (e.g., combined image layer) with the heated top surfaces of 3D part 26p and support structure 26s with proper registration along the x-axis. The gantry 84 may continue to move the build platform 28 along the x-axis, at a rate that is synchronized with the rotational rate of the belt 24 in the feed direction 32 (i.e., the same directions and
10 speed). This causes the rear surface 24b of the belt 24 to rotate around the nip roller 70 to nip the belt 24 and the heated layer 22 against the top surfaces of 3D part 26p and support structure 26s. This presses the heated layer 22 between the heated top surfaces of 3D part 26p and support structure 26s at the location of the nip roller 70, which at least partially transfuses the heated layer 22 to the top layers of 3D part 26p and support structure 26s.

15 As the transfused layer 22 passes the nip of the nip roller 70, the belt 24 wraps around the nip roller 70 to separate and disengage from the build platform 28. This assists in releasing the transfused layer 22 from the belt 24, allowing the transfused layer 22 to remain adhered to 3D part 26p and support structure 26s. Maintaining the transfusion interface temperature at a transfer temperature that is higher than its glass transition temperature, but
20 lower than its fusion temperature, allows the heated layer 22 to be hot enough to adhere to the 3D part 26p and support structure 26s, while also being cool enough to readily release from the belt 24. Additionally, the close melt rheologies of the part and support materials allow them to be transfused in the same step. The temperature and pressures can be selected, as is discussed below, to promote flow of part material and support material into a gap between the
25 two materials. Often the rheologies are preferably close, they can be transfused with glass transition temperatures that are significantly different from one another in some constructions. This flow into the gap, typically accompanied by an upward movement of the part and support material, results in a smoother interface between the part and support, plus a smoother surface for the part after removal of the support.

30 After release, the gantry 84 continues to move the build platform 28 along the x-axis to the post-transfusion heater 76. At optional post-transfusion heater 76, the top-most layers of 3D part 26p and the support structure 26s (including the transfused layer 22) may then be heated to at least the fusion temperature of the thermoplastic-based powder in a post-fuse or heat-setting step. This optionally heats the material of the transfused layer 22 to a highly

fusible state such that polymer molecules of the transfused layer 22 quickly interdiffuse (also referred to as reptate) to achieve a high level of interfacial entanglement with 3D part 26p and support structure 26s.

5 Additionally, as the gantry 84 continues to move the build platform 28 along the x-axis past the post-transfusion heater 76 to the air jets 78, the air jets 78 blow cooling air towards the top layers of 3D part 26p and support structure 26s. This actively cools the transfused layer 22 down to the average part temperature, as discussed in Comb et al., U.S. Patent Application Publication Nos. 2013/0186549 and 2013/0186558.

10 To assist in keeping the 3D part 26p formed of polyamide and support structure 26s at the average part temperature, in some embodiments, the heater 74 and/or the heater 76 may operate to heat only the top-most layers of 3D part 26p and support structure 26s. For example, in embodiments in which heaters 72, 74, and 76 are configured to emit infrared radiation, the 3D part 26p and support structure 26s may include heat absorbers and/or other colorants configured to restrict penetration of the infrared wavelengths to within the top-most
15 layers. Alternatively, the heaters 72, 74, and 76 may be configured to blow heated air across the top surfaces of 3D part 26p and support structure 26s. In either case, limiting the thermal penetration into 3D part 26p and support structure 26s allows the top-most layers to be sufficiently transfused, while also reducing the amount of cooling required to keep 3D part 26p and support structure 26s at the average part temperature. However generally sufficient
20 thermal penetration is desired to promote flow of part material and support material into gaps positioned at the interface between the part and support material.

The gantry 84 may then actuate the build platform 28 downward and move the build platform 28 back along the x-axis to a starting position along the x-axis, following the reciprocating rectangular pattern 86. The build platform 28 desirably reaches the starting
25 position for proper registration with the next layer 22. In some embodiments, the gantry 84 may also actuate the build platform 28 and 3D part 26p/support structure 26s upward for proper registration with the next layer 22. The same process may then be repeated for each remaining layer 22 of 3D part 26p and support structure 26s.

30 After the transfusion operation is completed, the resulting 3D part 26p and support structure 26s may be removed from system 10 and undergo one or more post-printing operations. For example, support structure 26s may be sacrificially removed from 3D part 26p using an aqueous-based solution, such as an aqueous alkali solution. Under this technique, support structure 26s may at least partially dissolve in the solution, separating it from 3D part 26p in a hands-free manner.

In comparison, part materials are chemically resistant to aqueous alkali solutions. This allows the use of an aqueous alkali solution to be employed for removing the sacrificial support structure 26s without degrading the shape or quality of 3D part 26p. Examples of suitable systems and techniques for removing support structure 26s in this manner include those disclosed in Swanson et al., U.S. Patent No. 8,459,280; Hopkins et al., U.S. Patent No. 8,246,888; and Dunn et al., U.S. Patent Application Publication No. 2011/0186081; each of which are incorporated by reference to the extent that they do not conflict with the present disclosure.

Furthermore, after support structure 26s is removed, 3D part 26p may undergo one or more additional post-printing processes, such as surface treatment processes. Examples of suitable surface treatment processes include those disclosed in Priedeman et al., U.S. Patent No. 8,123,999; and in Zinniel, U.S. Patent No. 8,765,045.

For use in electrophotography-based additive manufacturing systems the part material preferably has a controlled average particle size and a narrow particle size distribution, as described below in the Particle Sizes and Particle Size Distributions standard. For example, preferred D50 particles sizes include those up to about 100 micrometers if desired, more preferably from about 10 micrometers to about 30 micrometers, more preferably from about 10 micrometers to about 20 micrometers, and even more preferably from about 10 micrometers to about 15 micrometers.

Particle sizes and particle size distributions are measured using a particle size analyzer commercially available under the tradename "COULTER MULTISIZER II ANALYZER" from Beckman Coulter, Inc., Brea, Calif. The particle sizes are measured on a volumetric-basis based on the D50 particles size, D10 particle size, and D90 particles size parameters. For example, a D50 particle size of 10.0 micrometers for a sample of particles means that 50% of the particles in the sample are larger than 10.0 micrometers, and 50% of the particles in the sample are smaller than 10.0 micrometers. Similarly, a D10 particle size of 9.0 micrometers for a sample of particles means that 10% of the particles in the sample are smaller than 9.0 micrometers. Moreover, a D90 particle size of 12.0 micrometers for a sample of particles means that 90% of the particles in the sample are smaller than 12.0 micrometers.

Particle size distributions are determined based on the D90/D50 distributions and the D50/D10 distributions. For example, a D50 particle size of 10.0 micrometers, a D10 particle size of 9.0 micrometers, and a D90 particle size of 12.0 micrometers provides a D90/D50 distribution of 1.2, and a D50/D10 distribution of 1.1.

As mentioned above, the geometric standard deviation σ_g preferably meets the criteria

pursuant to the above-shown Equation 1, where the D90/D50 distributions and D50/D10 distributions are preferably the same value or close to the same value. The “closeness of the D90/D50 distributions and D50/D10 distributions are determined by the ratio of the distributions. For example, a D90/D50 distribution of 1.2 and a D50/D10 distribution of 1.1 provides a ratio of $1.2/1.1=1.09$, or about a 9% difference.

Examples

The following materials were used for example purposes to identify appropriate carrier particles for use in polyamide (nylon) developers to make polyamide printed parts:

Rilsan Clear G850 (Arkema) is a nylon 11 or polyamide 11 material. Rilsan Clear G850 has a notched Charpy Impact strength = 7.5 kJ/m^2 from an injection molded sample.

Ultrasint PA6-LM (BASF) is a nylon 6 or polyamide 6 material.

Regal 330 (Cabot) is a low structure carbon black

Bontron E84 (Knowde) is a charge control agent.

Material Example 1

Ultrasint PA6-LM nylon 6 was obtained from BASF and sieved to remove particles greater than $38 \mu\text{m}$. The resulting powder was nominally $22 \mu\text{m}$ particle size, with a volume D50 of $21.6 \mu\text{m}$ and a number D50 of $5.3 \mu\text{m}$ as measured using a coulter counter.

Material Example 2-5

The nylon powder of Material Example 1 was combined with $22 \mu\text{m}$ strontium ferrite carrier powder and blended to make a developer with 10% concentration by weight of nylon powder. This process was repeated to generate a series of developers with varying PMMA coating levels on the strontium ferrite carrier, the strontium ferrite carrier coated with 0.3% PMMA, 0.1% PMMA, 0.025% PMMA, and 0% PMMA. The developers were evaluated for initial charge, steady state charge, and dusting and the results are shown in table “Carrier Material Table A”.

Carrier Material Table A

Example Developer	PMMA level	initial charge		equilibrium charge		ad-mix charge		Add-mix Dust
		% Transferred	Q/m	% Transferred	Q/m	% Transferred	Q/m	
M.Ex.2	0.3%	95%	-0.6	8%	0.0	31%	-1.2	5.3%
M.Ex.3	0.1%	92%	-1.2	25%	0.0	80%	-0.9	29.1%

M.Ex.4	0.025%	95%	-5.6	103%	-2.1	97%	-5.2	21.4%
M.Ex.5	0.0 %	85%	-8.8	88%	-9.3	74%	-6.6	3.9%

Material Example 6

The nylon 6 powder from example 1 was used to prepare a powder fraction with a narrow distribution with minimal material below 10 μm in size such that the volume D50 was 20.9 μm and the number D50 was 13.9 μm .

Material Example 7-9

The nylon powder, or toner, of Material Example 6 was combined with 22 μm strontium ferrite carrier powder and blended to make a developer with 10% concentration of nylon powder. This process was repeated to generate a series of developers with varying PMMA coating level with strontium ferrite coated with 0.1% PMMA, 0.025% PMMA, and 0% PMMA on the strontium ferrite carrier. The developers were evaluated for initial charge, steady state charge and add-mix dust and the result are shown in table “Material Table B”.

Carrier Material Table B

	PMMA level	initial charge		equilibrium charge		Ad-mix charge		Add-mix Dust
		% Transferred	Q/m	% Transferred	Q/m	% Transferred	Q/m	
M.Ex.7	0.1%	94%	-0.6	88%	-1.2	104%	-2.5	16.8%
M.Ex.8	0.025%	99%	-1.1	102%	-2.7	87%	-3.8	7.9%
M.Ex.9	0.0%	97%	-1.6	100%	-3.7	78%	-4.1	2.1%

The results of Carrier Material Table A show that charge to mass and transfer increases as the PMMA coating is lowered below 0.3%, but can start to increase as the coating goes to 0. Carrier Material Table B shows the same trend but with lower dust. The desired combination of performance with good charge, high transfer, and low dust is the developer with the fines removed and the carrier with between 0.025% and 0.0% PMMA coating. Higher PMMA coatings (above 0.1%) have relatively little charge and high dust or poor transfer. Developer without a PMMA coating can be acceptable but is not the preferred composition. Notably, good charge and low dust is accomplished without the addition of surface treatments as is common in electrophotography. An advantage of using little or no surface treatment is a purer material and better mechanical properties for the finished part.

Material Example 10

An amorphous Nylon 11 was obtained from Arkema(G850) and compounded with 1% carbon black (Regal330) and 1% of a charge control agent (Bontron E-84). This compound was micronized into a powder and screened to remove any particles greater than 38 μm . The powder has a volume D50 of 19 μm and a number D50 of 2.8 μm .

Material Example 11-14

The nylon powder of Material Example 10 was combined with 22 μm strontium ferrite carrier powder and blended to make a developer with 10% concentration of nylon powder. This process was repeated to generate a series of developers with varying PMMA coating levels with strontium ferrite coated with 0.3% PMMA, 0.1% PMMA, 0.025% PMMA, and 0% PMMA on the strontium ferrite. The developers were evaluated for initial charge, steady state charge and add-mix dust and the result are shown in table “Material Example Table C”.

Carrier Material Example Table C

	PMMA level	initial charge		equilibrium charge		Ad-mix charge		Add-mix Dust
		% Transferred	Q/m	% Transferred	Q/m	% Transferred	Q/m	
M.Ex.11	0.3%	16%	0.0	67%	-5.6	96%	-3.5	9.6%
M.Ex.12	0.1%	58%	-1.9	91%	-10.1	96%	-6.8	2.6%
M.Ex.13	0.025%	76%	-4.2	53%	-13.3	69%	-10.5	1.0%
M.Ex.14	0%	78%	-4.9	46%	-14.0	63%	-10.3	1.4%

Material Example 15

Nylon 11 powder from Material Example 8 was classified to prepare a powder fraction with a narrow distribution with minimal material below 10 μm in size such that the volume D50 was 20.4 μm and the number D50 was 15 μm .

Material Example 16-19

The nylon powder, or toner, of Material Example 15 was combined with 22 μm strontium ferrite powder and blended to make a developer with 10% concentration of nylon

powder. This process was repeated to generate a series of developers with varying PMMA coating level with strontium ferrite coated with 0.3% PMMA, 0.1% PMMA, 0.025% PMMA, and 0% PMMA on the strontium ferrite. The developers were evaluated for initial charge, steady state charge and add-mix dust and the result are shown in table “Material Example

5 Table D”.

Carrier Material Example Table D

	PMMA level	initial charge		equilibrium charge		Add-mix charge		Add-mix Dust
		% Transferred	Q/m	% Transferred	Q/m	% Transferred	Q/m	
M.Ex.16	0.3%	61%	0.0	88%	-1.8	91%	-2.1	3.8%
M.Ex.17	0.1%	71%	-0.7	82%	-6.5	92%	-8.8	1.1%
M.Ex.18	0.025%	74%	-8.9	22%	-15.0	8%	-13.0	0.8%
M.Ex.19	0%	69%	-9.5	5%	-33.3	4%	-20.0	0.8%

In Carrier Material Table D the classified powder shows lower dust and higher charge compared to powder without the fines removed, but as the PMMA coating goes below 0.1% the high charge lowers the transfer percentage.

A desirable combination of performance with good charge, high transfer, and low dust is the developer with the fines removed and the carrier with between 0.1% and 0.025% PMMA coating. Higher PMMA coatings (above 0.3%) have very little charge and high dust. No PMMA coating leads to very high charge that will limit the amount of material that can be transferred in a single layer. This good charge, transfer, and low dust is accomplished without the addition of surface treatments as is common in electrophotography. The advantage of little or no surface treatment is a purer material and better mechanical properties. The addition of a charge agent to this formulation increase the overall charge relative to the materials of material examples 1 to 9.

Aspects have been described with reference to various specific and preferred embodiments and techniques. However, it should be understood that many variations and modifications may be made while remaining within the spirit and scope herein. As such, the embodiments described herein are not intended to be exhaustive or to limit the invention to the precise forms disclosed in the following detailed description. Rather, the embodiments are chosen and described so that others skilled in the art can appreciate and understand the principles and practices.

It should be noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the content clearly dictates otherwise. It should also be noted that the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

5 It should also be noted that, as used in this specification and the appended claims, the phrase "configured" describes a system, apparatus, or other structure that is constructed or configured to perform a particular task or adopt a particular configuration to. The phrase "configured" can be used interchangeably with other similar phrases such as arranged and configured, constructed and arranged, constructed, manufactured and arranged, and the like.

10 All publications and patent applications in this specification are indicative of the level of ordinary skill in the art to which this invention pertains. All publications and patent applications are herein incorporated by reference to the same extent as if each individual publication or patent application was specifically and individually indicated by reference.

WHAT IS CLAIMED IS:

1. An additive printing composition, the additive printing composition comprising:
a nylon toner; and
a magnetic carrier;
wherein the magnetic carrier comprises less than 1.0 percent of a polymeric coating.
2. The additive printing composition of any of claims 1 and 3-21, wherein the magnetic carrier is coated with less than 0.75% of a polymeric coating.
3. The additive printing composition of any of claims 1-2 and 4-21, wherein the magnetic carrier is coated with less than 0.5% of a polymeric coating.
4. The additive printing composition of any of claims 1-3 and 5-21, wherein the magnetic carrier is coated with less than 0.3% of a polymeric coating.
5. The additive printing composition of any of claims 1-4 and 6-21, wherein the magnetic carrier is coated with greater than 0.025% of a polymeric coating.
6. The additive printing composition of any of claims 1-5 and 7-21, wherein the magnetic carrier comprises a hard magnet.
7. The additive printing composition of any of claims 1-6 and 8-21, wherein the hard magnet comprises strontium ferrite.
8. The additive printing composition of any of claims 1-7 and 9-21, wherein the polymeric coating comprises polymethylmethacrylate.
9. The additive printing composition of any of claims 1-8 and 10-21, wherein the nylon is selected from the group polyamide 6, polyamide 11, polyamide 1012, polyamide 613, polyamide 66, polyamide 612 and combinations thereof.
10. The additive printing composition of any of claims 1-9 and 11-21, further comprising a charge control agent.

11. The additive printing composition of any of claims 1-10 and 12-21, wherein the nylon comprises an infrared absorber.

12. The additive printing composition of any of claims 1-11 and 13-21, wherein the infrared adsorber comprises carbon black.

13. The additive printing composition of any of claims 1-12 and 14-21, wherein the nylon toner has a volume D50 of between 12 and 35 μm .

14. The additive printing composition of any of claims 1-13 and 15-21, wherein the nylon toner has a volume D90 of greater than 10 μm .

15. The additive printing composition of any of claims 1-14 and 16-21, wherein the nylon toner has a volume D50 of less than 40 μm .

16. The additive printing composition of any of claims 1-15 and 17-21, wherein the nylon toner has a number D50 greater than 8 μm .

17. The additive printing composition of any of claims 1-16 and 18-21, wherein the nylon toner has a number D50 greater than 10 μm .

18. The additive printing composition of any of claims 1-17 and 19-21, wherein the nylon toner has a number D50 greater than 15 μm .

19. The additive printing composition of any of claims 1-18 and 20-21, wherein the nylon toner comprises between 7% and 16% of the blend.

20. The additive printing composition of any of claims 1-19 and 21, wherein the nylon toner comprises between less than 20 percent of the composition.

21. The additive printing composition of any of claims 1-20, wherein the nylon toner comprises greater than 20 percent of the composition.

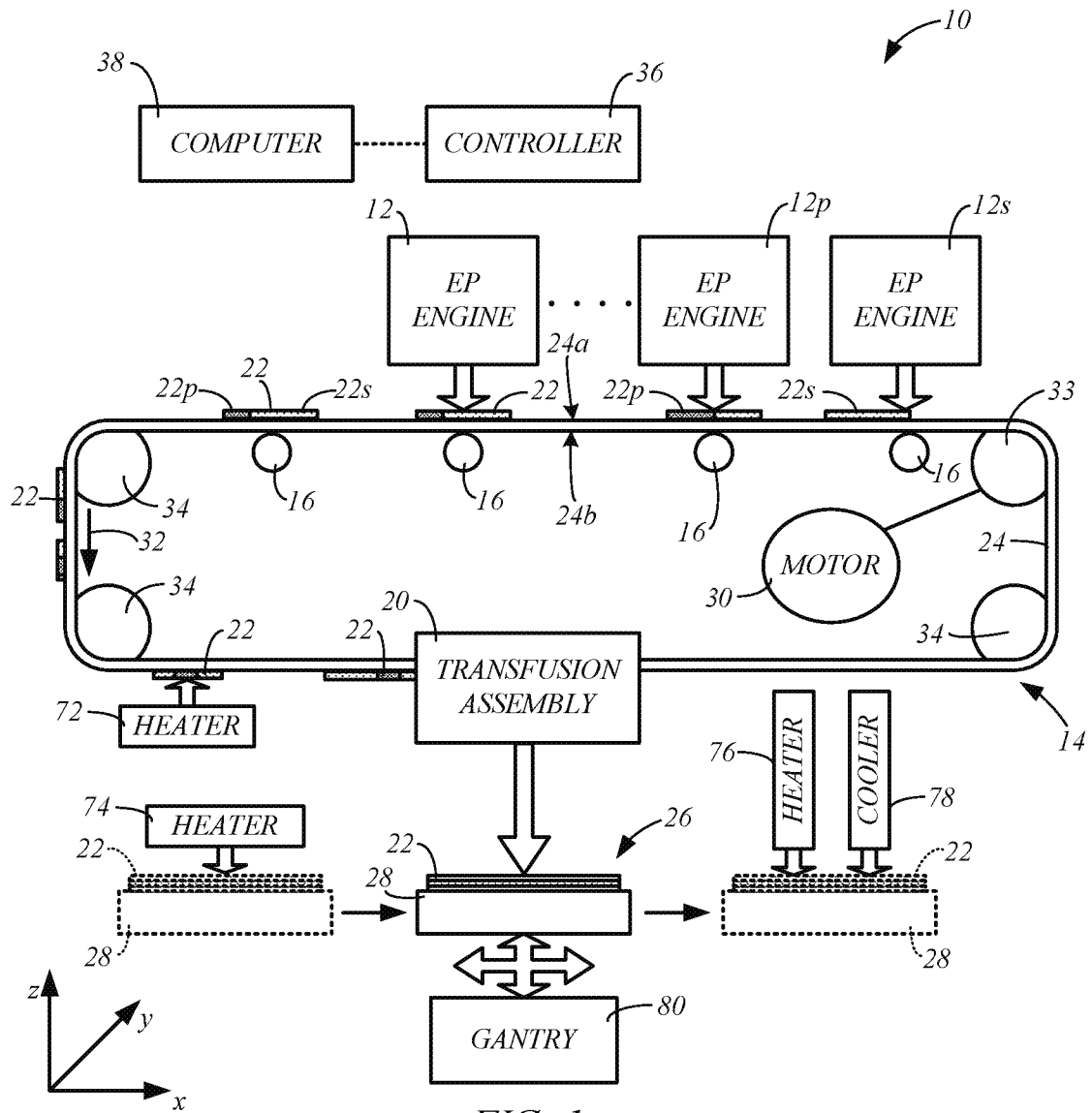
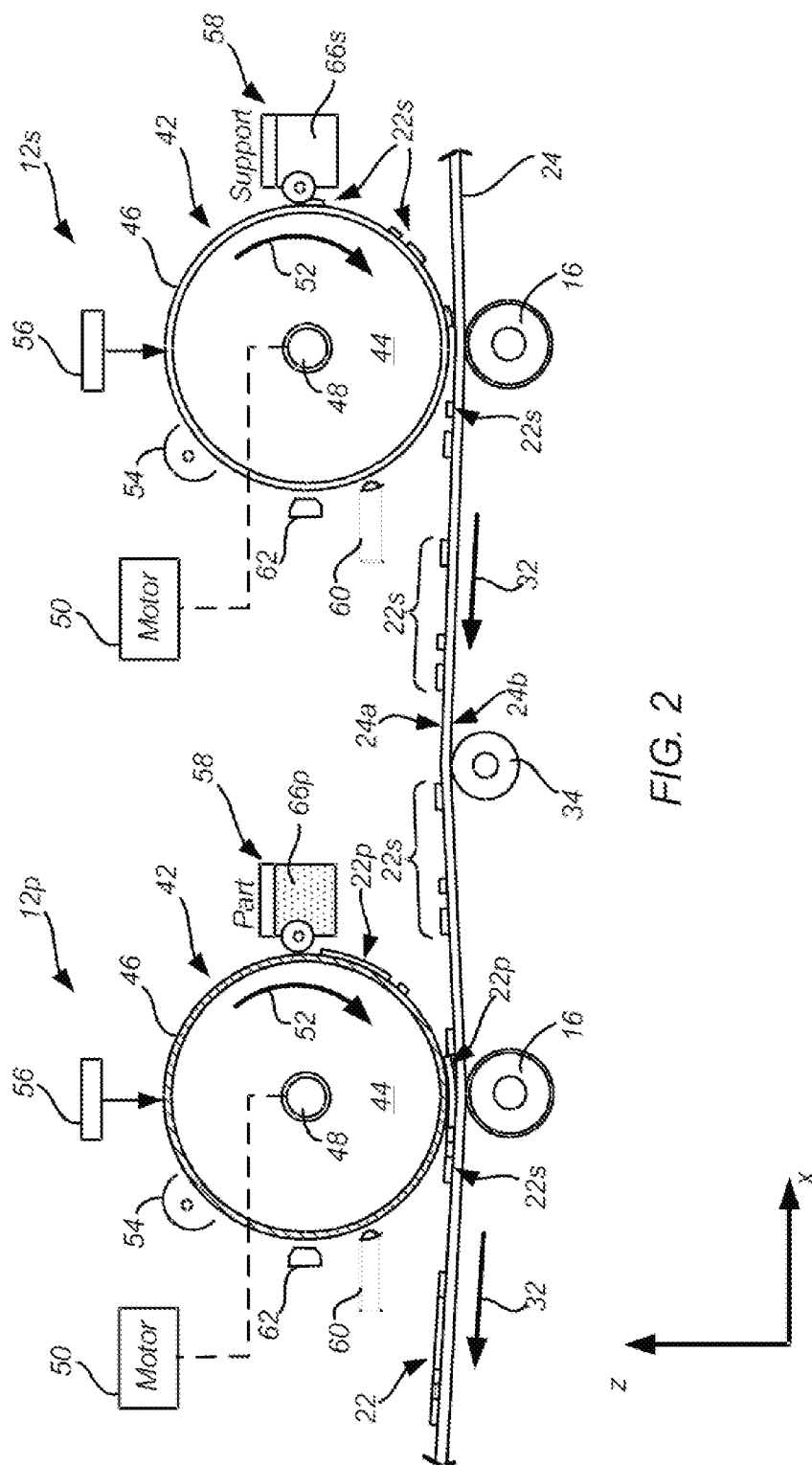


FIG. 1



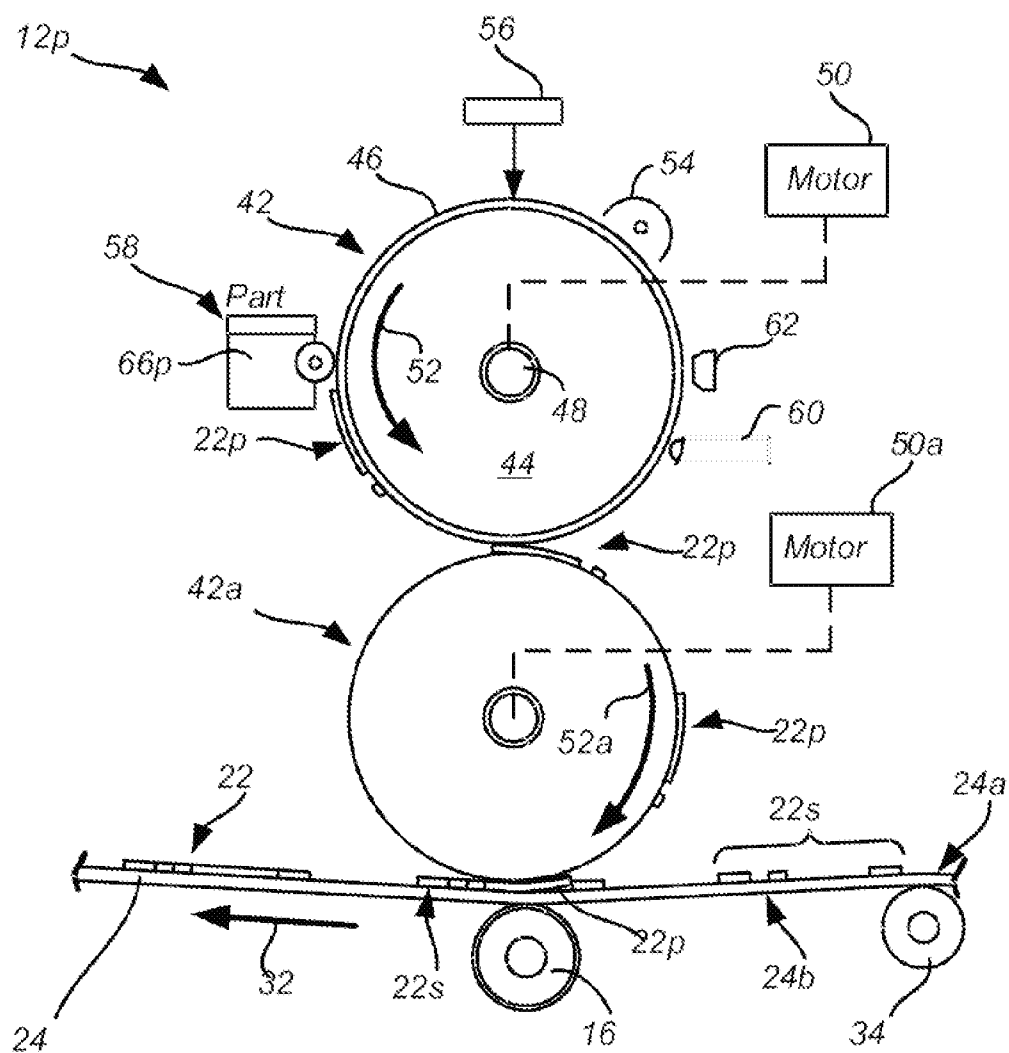
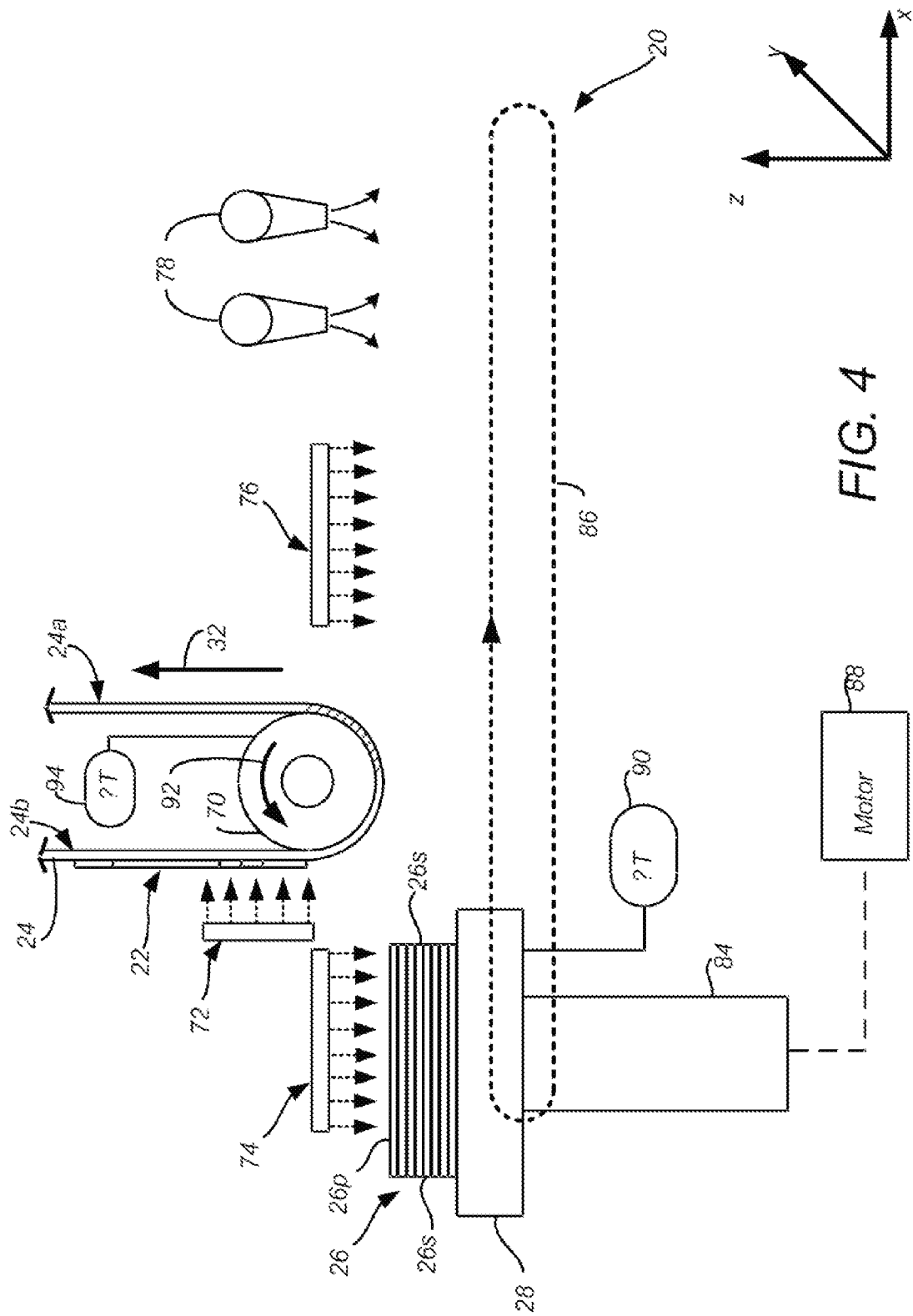


FIG. 3



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2023/017092

A. CLASSIFICATION OF SUBJECT MATTER

B29C 64/106(2017.01)i; **B29C 64/314**(2017.01)i; **B29C 64/218**(2017.01)i; **B33Y 10/00**(2015.01)i; **B33Y 30/00**(2015.01)i; **B33Y 70/10**(2020.01)i; B29K 77/00(2006.01)n; B29K 33/00(2006.01)n; B29K 105/00(2006.01)n

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B29C 64/106(2017.01); B29C 64/165(2017.01); C08K 3/00(2006.01); C08L 23/08(2006.01); C08L 3/04(2006.01); G03G 9/083(2006.01); G03G 9/113(2006.01)

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

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: additive printing, composition, nylon, toner, magnetic carrier, polymeric coating

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 11029618 B2 (POWDERTECH CO., LTD.) 08 June 2021 (2021-06-08) claims 1, 5, 11	1
A	CN 105419075 A (JIANGSU DAOQIN NEW MATERIAL TECHNOLOGY CO., LTD.) 23 March 2016 (2016-03-23) the whole document	1
A	KR 10-2017-0093696 A (LG CHEM. LTD.) 16 August 2017 (2017-08-16) the whole document	1
A	US 2022-0088859 A1 (HEWLETT-PACKARD DEVELOPMENT COMPANY, L.P.) 24 March 2022 (2022-03-24) the whole document	1
A	US 5180650 A (SACRIPANTE; GUERINO G. et al.) 19 January 1993 (1993-01-19) the whole document	1



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance
“D” document cited by the applicant in the international application
“E” earlier application or patent but published on or after the international filing date
“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
“O” document referring to an oral disclosure, use, exhibition or other means
“P” document published prior to the international filing date but later than the priority date claimed

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

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

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

“&” document member of the same patent family

Date of the actual completion of the international search

17 July 2023

Date of mailing of the international search report

17 July 2023

Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2023/017092

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: **2-21**
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

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