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(71) Applicant *(for all designated States except US)*: BPM TECHNOLOGY, INC. [US/US]; Suite A-19, 1200 Woodruff Road, Greenville, SC 29607 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: NOWAK, Michael, T. [US/US]; 70 Regina Drive, Leonminister, MA 01453 (US). FERREIRA, Manual, M. [US/US]; 101 Kingswood Circle, Simpsonville, SC 29681 (US). LEONARD, Nadine, J. [US/US]; 408 Piney Grove Road, Greenville, SC 29607 (US).

(74) Agent: REGAN, Christopher, F.; Allen, Dyer, Doppelt, Franjola and Milbrath, P.A., Suite 1401, 255 South Orange Avenue, Orlando, FL 32802 (US).

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(54) Title: BUILD MATERIAL FOR FORMING A THREE DIMENSIONAL ARTICLE

(57) Abstract

The present invention provides a three-dimensional article formed from a build material comprising a solution of a resin having a hydroxyl number from about 5 to 1000 and a molecular weight greater than about 500, dissolved in at least one primary aromatic sulfonamide. The present invention also provides a method for making a three-dimensional article based upon article defining data. The method comprises the step of dispensing a meltable build material comprising a solution of a resin having a hydroxyl number from about 5 to 1000 and a molecular weight greater than about 500, dissolved in at least one primary aromatic sulfonamide in a plurality of droplets toward a platform and which solidify after dispensing to construct the article in successive layers based upon the three-dimensional coordinate data.

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BUILD MATERIAL FOR FORMING A THREE-DIMENSIONAL ARTICLE

Field of the Invention

The present invention relates to a build material and method for forming a three-dimensional article, and, more particularly to a build material and related method for forming a three-dimensional article, such as a model or prototype based upon article defining data.

Background of the Invention

In the design of a three-dimensional articles, it is common practice to first create a design of the article and then produce a prototype of the article. After reviewing the initial design and prototype, design revisions are often made requiring the production of yet another prototype. This process of review and redesign may be repeated a number of times before finding the desired design thereby requiring that a number of prototypes be produced for a single article.

Accordingly, the process of designing and prototyping an article may involve a considerable expense of time, effort and money.

Computer aided design (CAD) systems for automating the design process are known. With the aid of a computer, an operator is able to design a three-dimensional article and display the design on a two-dimensional medium such as a screen or paper. The computer aids in the design as called for by the operator according to preexisting design parameters and computer software. These systems alone, however, cannot produce a prototype.

Computer aided milling machines for milling articles in response to computer generated signals are also known. In these machines, a computer generated data file representative of the article to be produced may be used to control the operation of the machine. Milling tools within the machine shape a solid block of material. These machines, however, are large, expensive and limited in the geometries that may be produced, and it is often difficult to work with the solid block of material.

Stereolithography has been another approach for producing a prototype of an article. An example of the production of prototypes by stereolithography is disclosed in United States Patent No. 4,575,330 to Hull entitled "Apparatus for Production of Three-Dimensional Objects By Stereolithography." Hull discloses an apparatus whereby articles are produced by forming successive, adjacent, cross-sectional laminae of the article at the surface of a UV-curable fluid medium. The fluid medium is capable of altering its physical state from a fluid to a solid in response to stimulation, such as by UV radiation, particle bombardment such as electron beams, chemical reaction, or impinging radiation other than UV radiation. The apparatus includes a source of stimulation which may be selectively applied to the surface of the fluid medium to produce cross-sectional laminae of the article. The source of selective stimulation is controlled by a computer in response to computer generated graphics. Stereolithography, however, requires the use of more material than is actually incorporated in the article being produced, and also requires the exact placement of the article being constructed relative to the surface of the fluid medium. In addition, the depth of the layer created when the fluid surface is exposed to the stimulation may be difficult to control. As a result, the resolution of surface features may be difficult to control.

An apparatus and method for forming three-dimensional articles from a material which is normally solid but flowable when heated is disclosed in United States Patent No. 5,141,680 to Almquist et al. entitled "Thermal Stereolithography." This apparatus includes a nozzle for dispensing a material which has been heated to the point that it flows. Suitable materials are listed as including thermoplastics, hot melt glue, wax, and cerro alloys. The material is dispensed through the nozzle by applying pressure, and the flow of material can be stopped by means of a slidable valve or by lessening, ceasing, or reversing the pressure. Accordingly, precise control of the flow of material may be difficult to obtain. Moreover, unsupported portions of the article may be problematic and may collapse unless support is provided. Accordingly, a second support material is provided. This support material must be removed from the article after fabrication is complete.

United States Patent No. 5,121,329 to Crump discloses another apparatus wherein a flow of material through a nozzle is used to create a three-dimensional object. Suitable materials include a variety of thermoplastic resins, waxes, metals and metal alloys. In this disclosure, the flow of material is determined by the size of the outlet orifice, a constant pressure, and the vertical height of the tip of the nozzle. In addition, a spring-loaded ball check valve may assist in metering the flow of material. Again, precise control of this flow may be difficult to obtain.

A major advance in the art of three-dimensional modeling is disclosed in United States Patent No. 4,665,492 to Masters entitled

"Computer Automated Manufacturing Process and System." This patent discloses an apparatus including: an ejection head for emitting small mass particles or droplets of particulate matter; a servo-mechanism for manipulating the ejection head; and a machine controller for controlling the servo-mechanism in response to a data file containing coordinate information representing the design of the article being produced. The mass particles are directed to the coordinates of a three-dimensional article as defined by the computer data file. The mass particles may comprise a ceramic or plastic material, a slurry material having water content, or charged particles which are electrically deflected.

A method and apparatus for forming three-dimensional solid form objects is disclosed in United States Patent No. 5,257,657 to Gore entitled "Method for Producing A Solid-Phase Object From A Material in the Liquid Phase." According to this patent, droplets of a liquid-phase metal material are ejected to form a spheroid. This method, however, may not work well for glasses and plastics which do not have a set transition temperature at which they become rigid.

Another method and apparatus for forming three-dimensional objects is disclosed in United States Patent No. 5,136,515 to Helinski entitled "Method and Means for Constructing Three-Dimensional Articles by Particle Deposition." This patent discloses a device including two jetting heads, or alternately a single jetting head with two feeder lines. In either embodiment, the controller causes fabrication particle material to be ejected as droplets forming the three-dimensional object, while a complementary support structure is created by the ejection of support particles. While this scheme allows the fabrication of layers having various angles, the three-dimensional object must later be separated from the support structure. Accordingly, this device requires the use of more material than is ultimately incorporated in the three-dimensional object. United States Patent No. 5,260,009 to Penn entitled "System, Method, and Process for Making Three-Dimensional Objects" discloses another apparatus for forming three-dimensional objects wherein a second material is dispensed with each layer of the three-dimensional article as it is formed.

The formation of three-dimensional articles by jetting a photosetting or thermosetting material is disclosed in United States Patent No. 5,059,266 to Yamane et al. entitled "Apparatus and Method for Forming Three-Dimensional Article." Jet head sequentially or intermittently jets the photosetting or thermosetting material in a droplet form along a flight path to an overhead stage. An exposure unit is then used to cure the material. If a photosetting material is used, the exposure unit is a source of light radiation. A mesh sheet may be required in order to form an article having a complicated shape. United States Patent No. 5,140,937 also to Yamane et al. discloses an apparatus for forming a three-dimensional article having plural jet heads for jetting a thermosetting material and a heat supplying unit for curing the thermosetting material. Suitable thermosetting resins are listed as including: (1) materials cured through oxidation polymerization reaction by heat (e.g., epoxy resin); (2) materials cured through condensation polymerization reaction by heat (e.g., amino melamine or urea resins); and (3) materials cured through additional reaction by heat (e.g., bisphenol A type epoxy resin). United States Patent No. 5,149,548, also to Yamane et al., discloses an apparatus for forming a three-dimensional article having jet head for jetting a two part curable material including microcapsules. This apparatus also includes a microcapsule rupturing unit such as a source of heat, pressure or light radiation. Each of these patents disclose an apparatus requiring a curing unit.

Other United States patents related to three-dimensional modeling are listed as follows: 5,207,371 to Prinz et al.; 5,301,415 to Prinz et al.; 5,301,863 to Prinz et al.; 5,204,124 to Secretan et al.; 4,749,347 to Valavaara; 5,303,141 to Batchelder et al.; 5,031,120 to Pomerantz et al.; and 5,287,435 to Cohen et al.

Summary of the Invention

Although there have been advancements in the apparatus for forming three-dimensional models or prototypes, there is a need for improved build materials used in the formation of such models or prototypes, and particularly models formed by ballistically jetting successive droplets of build material (i.e., ballistic particle manufacturing) or other dispensing techniques wherein the build material is resin based. To this end, it would be desirable to provide a meltable build material that melts at a temperature of between about 250°C, which cools quickly and adheres to itself, and has a low rate of shrinkage. Such a build material comprises a solution of a resin having a hydroxyl number of from about 5 to 1000, and molecular weight greater than about 500, dissolved in at least one primary aromatic sulfonamide. Preferably, the primary aromatic sulfonamide has a melting point greater than about 25°C.

The present invention also provides a method for making a three-dimensional article based upon article defining data. The method comprises the step of dispensing a meltable build material comprising a solution of a resin having a hydroxyl number of from about 5 to 1000, and molecular weight greater than about 500, dissolved in at least one primary aromatic sulfonamide in a plurality of droplets toward a platform and which solidify after dispensing to construct the article in successive layers based upon the article defining data.

Detailed Description of the Invention

Processes for forming or building three-dimensional models or prototypes (i.e., articles) which use a dispenser, such as a ballistic jet require a build material with specific properties. In the operation of building a three-dimensional model or prototype, the meltable build material is dispensed onto a platform and solidifies. Successive layers are then dispensed based upon article defining data to construct the model or prototype. The build material typically must melt at a temperature of from about 50°C to 250°C, should cool quickly and adhere to itself, and have a low rate of shrinkage. Such a build material comprises a solution of a resin having a hydroxyl number of from about 5 to 1000, and a molecular weight greater than about 500, dissolved in at least one primary aromatic sulfonamide preferably having a melting point greater than about 25°C.

Various three-dimensional modeling apparatus and methods are described, for example, in commonly assigned copending U.S. Patent Application Serial Nos. ________, _______, ________, and ______, filed concurrently herewith, and having Attorney Docket Nos. 4855-20, 4855-21, 4855-22, and 4855-27, the disclosures of which are incorporated herein by reference in their entirety.

In one embodiment, the modeling apparatus includes a platform on which the three-dimensional model or prototype is built, and a ballistic droplet jetting head. Ballistic droplets of liquid build material are jetted from the piezoelectric jet on the jetting head to the platform in order to form a model or prototype. The build material is normally solid when at the temperature of the interior of the apparatus. The build material is heated to a temperature of from about 50°C to 250°C and maintained at this temperature within the jetting head in order to maintain the build material in a liquid state. Accordingly, heated liquid droplets of build material are jetted from the jetting head to either the platform or previously jetted build material. On contact with the platform or previously jetted build material, the heated liquid droplets cool quickly, and harden at a low rate of shrinkage. The rheology of the build material is preferably such that a droplet remelts portions of deposited material so as to form a flowable bead. Typically, the jet is capable of dispensing at least about 10,000 droplets per second.

With respect to the resin portion of the build material, Applicants do not wish to be bound by any one theory, but believe that a resin having hydroxyl functionality, as defined by hydroxyl number, through hydrogen bonding, holds together the droplet after jetting through the jetting head. The upper limit of hydroxyl number (i.e., 1000) is important in that the higher the hydroxyl number, the higher the heat capacity of the resin, and the resin cools slower. Slower cooling is undesirable in that the build material tends to sag if it cools slowly as the article is being built. Exemplary resins include polyester resins, phenolic resins, polyamides, vinyl ester resins, polyurethanes, amino resins, melamine resins, urea resins, epoxy resins, and naturally-derived polymers such as polystyrene, acrylic polymers, and styrene-acrylic copolymers, coumarin-indene, shellac, protein and celluosics (e.g. ethyl cellulose, ethyl hydroxy ethyl cellulose, nitro cellulose, etc.), and mixtures thereof.

Suitable polyester resins include practically any esterification product of a polybasic organic acid and a polyhydric alcohol. Polyester resins can also be derived from the esterification of a polycarboxylic acid or anhydride with a polyhydric alcohol. Suitable phenolic resins include practically any reaction product of an aromatic alcohol with an aldehyde. Particularly preferred, are the phenolic resins prepared by the reaction of phenol with formaldehyde. Suitable vinylester resins include practically any reaction product of an unsaturated polycarboxylic acid or anhydride with anepoxy resin. Exemplary epoxies include virtually any reaction product of a polyfunctional halohydrin, such as epichlorohydrin, with a phenol or polyhydric phenol. Specific resins include acrylics, styrene-acrylic copolymers and styrene-allyl alcohol copolymers. Typically, the build material includes about 1 to 50 percent of the resin, preferably about 5 to 30 percent, and more preferably about 5 to 15 percent, by weight of the resin.

With respect to the primary aromatic sulfonamide, it is believed that the primary aromatic sulfonamides provide the necessary self adhesion properties to the build material. Suitable aromatic sulfonamides are preferably primary C_1 to C_{15} benzenesulfonamides, and most preferably the substitution is alkyl and is at the *para* position. Exemplary primary aromatic sulfonamides include p-toluenesulfonamide, p-n-ethylbenzenesulfonamide, p-methoxy-benzenesulfonamide, p-n-nonylbenzene-sulfonamide, p-n-butylbenzenesulfonamide, and mixtures thereof. Typically the build material includes about 1 to 50 percent, preferably about 70 to 90 percent, and more preferably about 75 to 90 percent by weight of one or more of the aromatic sulfonamides. Particularly preferred is a 50/50 mixture of p-toluenesulfonamide and p-n-ethylbenzenesulfonamide.

The build material can include antioxidants (e.g., Ultranox 626 available from Borg Warner Chemicals, Inc.), flexibilizers, magnetic particles, pigments, and fluorescent agents, and other additives, the addition of which is within the skill of one in the art. Dyes can be added to the build material. Suitable dyes include FD &C Blue #1, Neozapon Red 492, Savinyl Black RLS and the like. Another additive could be a secondarily reactive organic compound such as one activated by exposure to UV light. These compounds can be used to provide an article which can be hardened so as to be unmeltable or machinable. Typically, the build material includes from about 1 to 10 percent by weight of the various additives.

EXAMPLE

Build Material Composition

Compound	% By Weight
Styrene/allyl alcohol copolymer	10
p-toluenesulfonamide	42
p-n-ethylbenzenesulfonamide	42
p-n-butylbenzenesulfonamide	4
Ultranox 626	1
FD&C Blue #1	1

Such a build material has a minimum surface tension minimum of 25 dyne cm (measured at 125°C using a DuNoy platinum ring surface tensionmeter) and a Brookfield viscosity at 115°C to 135°C of between about 1 and 20 cps at the jetting temperature of about 120°C. The build material is stable having no significant changes in surface tension, color, or viscosity on aging over 4 weeks.

Article Manufacturing

The build material having the above composition is heated to a temperature of 120°C within a reservoir and build material jet, such as described in copending U.S. patent application Serial No. ________, assigned attorney work docket no. 4855-20. The build material is in its liquid state. Heated liquid droplets are jetted from the jetting head at a rate of 0 to 12,000 droplets/sec initially to a platform, and then onto previously solidified build material to form a two inch model rocket. The flat velocity over the frequency is essentially about 3 m/sec. The droplets are jetted for 120 minutes. The droplets quickly cool at room temperature in 125 microseconds.

The jet, such as a piezoelectric jet, may be positioned in spaced relation from a target point. Also, the jet may be positioned relatively close to the target position so that the build material may, in a sense, not be considered as traveling ballistically. Accordingly, the terms ejected and jetted may also e used to describe a relatively small gap or no gap between the jet and the target position. The piezoelectric jet is but one embodiment of a dispenser for dispensing build material in metered quantities and to precise target landing positions. It being readily understood by those of skill in the art, that other types of build material dispensers are also contemplated that can meter build material and accurately deliver it to a target position. Moreover, the term droplet as used herein is intended to cover individual or discrete volumes of build material that may be ejected, for example, by the piezoelectric jet. In addition, the term droplet is also intended to cover a volumetrically modulated stream of build material, wherein small quantities or volumes of build material may be connected to adjacent volumes without becoming discrete entities, such as because of a relatively small gap or because of the speed of dispensed build material, for example.

The foregoing example is illustrative of the present invention, and is not to be construed as limiting thereof. The invention is defined by the following claims, with equivalents of the claims to be included therein.

THAT WHICH IS CLAIMED IS:

1. A three-dimensional article formed from a build material using a dispenser, the build material comprising a solution of a resin having a hydroxyl number from about 5 to 1000 and a molecular weight greater than about 500, dissolved in at least one primary aromatic sulfonamide.

2. The three-dimensional article according to Claim 1, wherein the resin is selected from the group consisting of polystyrene, acrylic polymers, and styrene-acrylic copolymers, polyester resins, phenolic resins, polyamides, vinyl ester resins, polyurethanes, amino resins, melamine resins, urea resins, and epoxy resins, and mixtures thereof.

3. The three dimensional article according to Claim 1, wherein the resin is a naturally-derived polymer.

4. The three-dimensional article according to Claim 1, wherein the resin is a copolymer of styrene and an allyl alcohol.

5. The three-dimensional article according to Claim 1, wherein the aromatic sulfonamide is selected from the group consisting of p-n-ethylbenzene-sulfonamide, p-toluenesulfonamide, p-methoxybenzene-sulfonamide, p-n-nonylbenzenesulfonamide, p-n-butylbenzenesulfonamide, and mixtures thereof.

6. The three-dimensional article according to Claim 1, including an antioxidant.

7. The three-dimensional article according to Claim 1, including a flexibilizer.

8. The three-dimensional article according to Claim 1, including a colorant.

9. In a manufacturing process for forming a three- dimensional article based upon article defining data and dispensing a build material to form the three-dimensional article, the improvement comprising the use of a build material comprising a solution of a

resin having a hydroxyl number from about 5 to 1000 and a molecular weight greater than about 500, dissolved in at least one primary aromatic sulfonamide.

10. In a manufacturing process according to Claim 9, wherein the resin is selected from the group consisting of polystyrene, acrylic polymers, and styrene-acrylic copolymers, polyester resins, phenolic resins, polyamides, vinyl ester resins, polyurethanes, amino resins, melamine resins, urea resins, and epoxy resins, and mixtures thereof.

11. In a manufacturing process according to Claim 9, wherein the resin is a naturally-derived polymer.

12. In a manufacturing process according to Claim 9, wherein the resin is a copolymer of styrene and an allyl alcohol.

13. In a manufacturing process according to Claim 9, wherein the aromatic sulfonamide is selected from the group consisting of p-n-ethylbenzene-sulfonamide, p-toluenesulfonamide, p-methoxybenzene-sulfonamide, p-n-nonylbenzenesulfonamide, p-n-butylbenzenesulfonamide, and mixtures thereof.

14. In a manufacturing process according to Claim 9, including an antioxidant.

15. In a manufacturing process according to Claim 9, including a flexibilizer.

16. In a manufacturing process according to Claim 9, including a colorant.

17. A method for making a three-dimensional article based upon article defining data, said method comprising the step of:

dispensing a meltable build material comprising a solution of a resin having a hydroxyl number of about 5 to 1000 and a molecular weight greater than about 500, dissolved in at least one primary aromatic sulfonamide in a plurality of droplets toward a platform and which solidify after dispensing to construct the article in successive layers based upon the three-dimensional coordinate data.

18. The method according to Claim 17, wherein the build material is heated to a temperature of from about 50°C to 250°C prior to dispensing.

19. The method according to Claim 17, wherein the resin is selected from the group consisting of polystyrene, acrylic polymers, and styrene-acrylic copolymers, polyester resins, phenolic resins, polyamides, vinyl ester resins, polyurethanes, amino resins, melamine resins, urea resins, and epoxy resins, and mixtures thereof.

20. The method according to Claim 17, wherein the resin is a naturally-derived polymer.

21. The method according to Claim 17, wherein the resin is a copolymer of styrene and an allyl alcohol.

22. The method according to Claim 17, wherein the aromatic sulfonamide is selected from the group consisting of p-n-ethylbenzenesulfonamide, p-toluenesulfonamide, p-methoxybenzenesulfonamide, p-n-nonylbenzenesulfonamide, p-n-butylbenzene-sulfonamide, and mixtures thereof.