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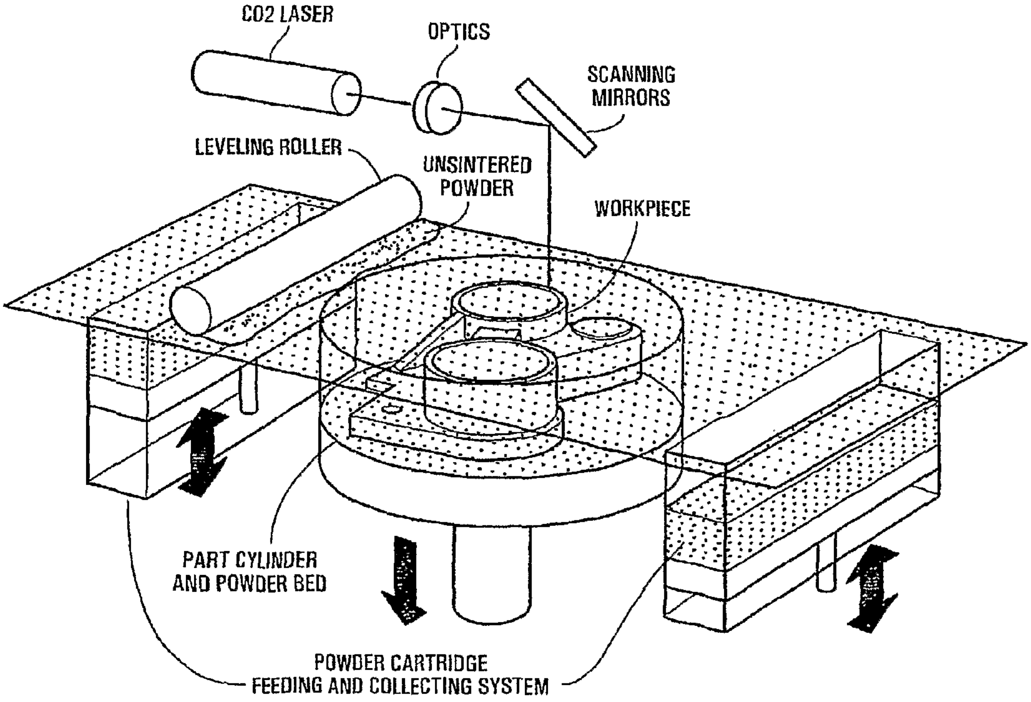
(54) Title: SELECTIVE LASER SINTERING PROCESS AND POLYMERS USED THEREIN



(57) Abstract: A selective laser sintering process to provide an article of manufacture having a plurality of sintered layers is disclosed. The process utilizes an endcapped polymeric particulate material of high stability, and the articles of manufacture prepared therefrom having excellent interlayer adhesion, breakout, surface properties, and strength.

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SELECTIVE LASER SINTERING PROCESS AND POLYMERS USED THEREIN

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit under 35 U.S.C. § 119(e) of U.S. provisional patent application Serial No. 60/557,791 filed March 30, 2004, the disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

The present invention relates to a selective laser sintering (SLS) process to form articles of manufacture, and to polymeric particulate materials used in the SLS process.

BACKGROUND OF THE INVENTION

Selective laser sintering (SLS) is a process wherein an article of manufacture is built layer by layer. The SLS process is based on using a laser beam to selectively fuse a predetermined portion of a layer of particulate material. The particulate material exposed to the laser beam is heated to a temperature above its melting point, after which adjacent molten particles are fused together, as are adjacent layers of fused material.

The SLS process alternatively has been termed a selective laser melting (SLM) process. As used herein, the term "SLS" is defined as encompassing a selective laser sintering process and a selective laser melting process.

Selective laser sintering generally is performed according to the following steps:

1. A piston of a process chamber is lowered by one layer thickness, and simultaneously, a piston of a reservoir containing a particulate material is raised;

2. The particulate material is introduced into the process chamber, and a leveling roller spreads the particulate material evenly over a build surface of the process chamber;

3. The particulate material is heated to a temperature near, but below, its softening point;

4. A laser beam then traces a predetermined cross section of the article on the layer of heated particulate material in the build surface, thus forming a solid layer; and

5. Steps 2 through 4 are repeated until manufacture of the article is completed.

The particulate material in areas that have not been sintered by the laser remains unfused and in place, and acts as a natural support for the article being manufactured. Accordingly, no need exists for support structures during manufacture of the article. After cooling, the article of manufacture and the unfused particulate material are removed from the process chamber, and the article of manufacture is separated from the unfused particulate material, i.e., "breakout."

Figures 1 and 2 are schematics illustrating the laser-sintering process for the manufacture of an article having a complex shape. Clausen et al. U.S. Patent No. 6,110,411, incorporated herein by reference, provides a detailed description of the selective layer sintering process.

The unfused particulate material typically is recycled to the reservoir containing the particulate material, and reused in subsequent selective laser sintering cycles to manufacture additional articles of manufacture. However, it is known that the performance of the particulate material can change as the material is subjected to a plurality of SLS cycles. These changes in physical properties can adversely affect the article of manufacture, e.g., cause "orange peel" effects and diminished mechanical properties. To avoid such adverse effects, the particulate material is discarded after a number of SLS recycles, which increases raw material costs.

SUMMARY OF THE INVENTION

The present invention is directed to an improved SLS process, and to polymeric particulate materials used in the SLS process. The polymeric particulate material is laser sinterable and overcomes several disadvantages associated with present-day polymeric particulate materials used in SLS processes. The polymeric particulate materials used in the present method have improved stability for recycling in an SLS process, and therefore provide articles of manufacture of high and uniform quality.

It is theorized, but not relied upon herein, that a change in physical properties of a particulate material can be attributed, at least in part, to chemical reactions induced by repeated heating of the particulate material over a number of SLS processes using particulate material recycled from one SLS cycle to the next.

One polymeric particulate material commonly used in SLS processes is nylon-12, as disclosed in U.S. Patent No. 6,245,281, for example. Nylon-12 is polylaurolactam, and also is known as PA-12. Additional polymers used as a polymeric particulate material in an SLS process include, but are not limited to, other nylons, such as nylon-11 (PA-11), polyacetals, polyethylenes, polypropylenes, ionomers, polycarbonates, elastomeric block copolymers, and polystyrenes.

The most widely used polymeric particulate materials in SLS processes, e.g., PA-12, exhibit a disadvantage during recycling. While not intending to be bound by any theory, it is proposed that the performance of PA-12 decreases after recycling through a number of SLS cycles because the molecular weight and solution viscosity of PA-12 increase during thermal exposures encountered during recycling through a plurality of SLS processes. This molecular weight increase can lead to gelling of particulate material particles, especially at particle surfaces, which prevents proper processing of the particulate material after several SLS cycles. Therefore, such polymeric particulate materials are not ideally suited for SLS processes because fresh and recycled particulate materials can produce articles of manufacture of different quality, and possibly regions of differing quality within a single article.

More particularly, the present invention is directed to an SLS process utilizing a polymeric particulate material having improved stability, and that substantially retains the physical properties of virgin particulate material, i.e., particulate material unprocessed through an SLS process, after undergoing one or more SLS cycle. A polymeric particulate material utilized in the present SLS process essentially retains its physical properties over a plurality of SLS cycles, and, therefore, provides articles of manufacture having properties essentially equal to an SLS manufactured article solely from virgin polymeric particulate material. As a result, articles made from virgin and recycled particulate material have essentially uniform and consistent properties.

Accordingly, one aspect of the present invention is to provide an SLS process wherein the particulate material can be recycled through a plurality of SLS cycles, and the resulting articles of manufacture from each cycle have excellent breakout, layer-to-layer adhesion, surface finish, and strength. The articles, prepared at least in part from recycled particulate material, also exhibit consistent properties because each successively prepared article has properties essentially equal to a previously prepared article.

Another aspect of the present invention is to provide a particulate material that maintains its physical properties and chemical identity, e.g., melting point, solution viscosity, and molecular weight, over a plurality of SLS cycles. The retention of physical properties of the particulate material allows SLS production of articles using recycled particulate materials, wherein the article has essentially the same properties as an article manufactured solely from a virgin particulate material.

We have discovered that polymeric particulate materials widely used in SLS processes can be modified to maintain their physical and chemical properties in a number of different ways. For example, we have discovered that the polymeric particulate material can be stabilized by positioning nonreactive endcaps on a polymeric particulate material. The nonreactive endcaps prevent, or at least retard, chemical reactions induced by SLS heating steps, and maintain a more constant molecular weight of the particulate material over a plurality of SLS cycles. The endcapped polymeric particulate material therefore maintains an essentially constant molecular weight and an essentially constant solution viscosity over a plurality of SLS cycles to facilitate the SLS process and improve the quality and uniformity of the manufactured articles.

Yet another aspect of the present invention is to further stabilize an endcapped polymeric particulate material, and further improve the SLS process and articles prepared thereby, by subjecting the polymeric particulate material to an extraction step to remove low molecular weight components from the endcapped particulate material.

Still another aspect of the present invention is to provide a method of manufacturing an article of manufacture using selective laser sintering comprising the steps of

(a) depositing a quantity of a particulate material from a reservoir into a process chamber;

(b) leveling the particulate material to form a build surface of the material;

(c) then directing an energy beam over a predetermined target area on the build surface of the material causing a portion of the particulate material to fuse and form an integral layer;

(d) repeating steps (a) to (c) to form additional integral layers that are integrally bonded to adjacent layers to form a three-dimensional article;

(e) separating unfused particulate material from the article; and

(f) recycling the particulate material of steps (e) to the reservoir to manufacture a second article of manufacture;

wherein a solution viscosity and/or molecular weight of the unfused particulate material remains essentially constant over ten repeating cycles.

Yet another aspect of the present invention is to provide an article manufacture by an SLS process using recycled particulate material, at least in part, said article having properties essentially equivalent to an article prepared in an SLS process solely from an identical virgin particulate material.

These and other novel aspects and advantages of the present invention will become apparent from the following detailed description of the preferred embodiments taken in conjunction with the figures.

BRIEF DESCRIPTION OF THE FIGURES

Figs. 1 and 2 are schematics illustrating the laser sintering process; and

Fig. 3 contains plots of solution viscosity for an endcapped and an uncapped polymeric particulate material over ten SLS cycles.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Present-day polymeric particulate materials utilized in SLS processes typically contain chemically reactive groups. Examples of such particulate materials include DURAFORM PA, DURAFORM GF, EOSINT PA, and RILSAN PA-11. In particular, the most commonly used polymeric particulate materials are PA-12, i.e., polylaurolactam, and PA-11, which contain reactive amino ($-NH_2$) and carboxyl ($-COOH$) end groups. It is theorized that these reactive end groups can undergo a condensation reaction at elevated temperatures encountered in the SLS process to increase the molecular weight of the polymeric particulate material, including chain extension and/or branching.

An increase in molecular weight of a polymeric particulate material impacts the SLS process and articles of manufacture resulting therefrom. In particular, an increase in molecular weight of the particulate material that occurs over repeated SLS cycles affects the solution viscosity of the polymeric material. The solution viscosity is an important property of the particular material in an SLS process because too high of a solution viscosity leads to insufficient flow out and article density and, therefore, insufficient mechanical properties. This negates an important benefit of the SLS process, i.e., that only the natural flow of a molten particulate material is required to produce a dense article. No additional compaction forces, such as injection molding, need to be applied. In addition, highly viscous particulate materials associated with a high molecular weight provide articles having a rough surface and orange peel effects, which adversely affect the surface of the article.

Therefore, an important feature of the present SLS method is to utilize a polymeric particulate material having an essentially constant solution viscosity over a plurality of, e.g., ten, SLS cycles. As used herein, the term an "essentially constant solution viscosity" is defined as a solution viscosity of a particulate material after a plurality of, e.g., ten, SLS recycles that has increased no more than 20% over the solution viscosity of the identical virgin particulate material as described below. In preferred embodiments, the solution viscosity increases no more than 10% over a plurality of SLS cycles.

In other preferred embodiments, the solution viscosity of the recycled particulate material (after 10 cycles) is no more than 0.15, and more preferably 0.10, greater than the solution viscosity of virgin particulate material.

It should be understood that the solution viscosity typically remains essentially constant over more than ten SLS cycles, for example, twenty to thirty SLS cycles. Accordingly, the particulate material has optimal stability for recycling through an SLS apparatus in cases wherein virgin particulate material is not added to recycled particulate method, and in cases when virgin particulate material is added to recycled particulate material.

As used herein, the term "essentially constant molecular weight" is defined as a molecular weight of a recycled polymeric particulate material after ten SLS cycles that is no more than 50%, preferably no more than 25%, greater than an identical virgin polymeric particulate material. More preferably, the molecular weight of the recycled polymeric particulate material (after 10 cycles) is no more than 20% greater than an identical virgin polymeric material.

The solution viscosity and the molecular weight of the recycled particulate material after ten SLS cycles is determined as follows. An article of manufacture is prepared using a 3D Systems Vanguard HS apparatus. The Vanguard HS apparatus contains two reservoirs for a particulate material, and about 15 kilograms of particulate material is introduced into each reservoir.

A quantity of the particulate material is introduced into the process chamber of the apparatus. A sufficient quantity of the particulate material is introduced into the process chamber to provide a layer of particulate material about 2.5 cm deep. The particulate layer then is leveled to form a build surface. The surface area of the process chamber is about 38 cm by 32 cm.

The particulate material in the process chamber is heated to about 10C° below its melting point, then a laser beam is directed over a predetermined area on the build surface to form a first fused layer of particulate material. Next, the process chamber, which is positioned on a piston, is lowered about 0.1 mm, and a new layer of particulate material of 0.1 mm height is introduced into the process chamber and leveled. The newly added particulate also is heated and subjected to a laser beam to form a second fused layer, that also is fused to the first fused layer. This process is repeated until articles of manufacture weighing about 500 g have been prepared. At this time, the process chamber contains about 15 kg of heated, but unfused, particulate material. The reservoirs contain about 14.5 kg of particulate material that is remixed with the previously heated, unfused particulate material.

The new blend of particulate material from the unfused particulate material of the first SLS cycle and the reservoirs is sieved, then recycled in the above-described SLS process to form a second article of manufacture. This second article is prepared from particulate material that a portion of which undergone one SLS cycle. The particulate material in the reservoirs again is set aside and remixed with the unfused material that has been subjected to two SLS cycles and used to manufacture a third article of manufacture. The SLS cycling is continued until the unfused particulate material has undergone ten cycles without adding virgin particulate material.

After each SLS cycle, a portion of the unfused particulate material is tested for solution viscosity using the DIN-EN-ISO Norm 307 method for polyamides, and for molecular weight using GPC (gas-phase chromatography) method.

An essentially constant solution viscosity can be achieved by improving the stability of the virgin particulate material, e.g., by reducing or eliminating chemical reactions that can occur during an SLS cycle. We have discovered that the stability of the polymeric particulate material is adversely affected by the presence of reactive end groups during the SLS process. We have also discovered that inactivating these reactive end groups alleviates this instability problem. For example, we have discovered that thermal stability can be imparted to a polymeric particulate material by endcapping the polymeric particulate material used in the preparation of an article of manufacture. The endcapped polymers have a substantially increased stability for use in an SLS process, and eliminate heat-induced reactions during the SLS process that increase polymer molecular weight and ultimately reduce article quality.

It is theorized, but not relied upon herein, that the polymer at the surface of the particles can undergo chemical reactions to increase the molecular weight of the polymer at the particle surface. Particle softening, and increases in molecular weight at particle surfaces, lead to particle agglomeration that adversely affect the SLS process. By providing a more stable polymeric particulate material, these surface changes are substantially reduced or eliminated, and the SLS process using recycled particulate material is facilitated. In particular, articles made from recycled particulate material over a plurality of SLS cycles have consistent and uniform properties.

We have discovered that polymeric particulate materials widely used in SLS processes can be modified to maintain their physical and chemical properties in a number of different ways. For example, we have discovered that a polymeric particulate material useful in the present SLS process can be endcapped to prevent reactive groups from further chain propagation and branching. The particulate material can be endcapped using monofunctional organic compounds or multifunctional organic compounds. Preferably, endcapping is achieved using a monofunctional organic compound.

An endcapping compound typically is a low molecular weight compound, e.g., a compound containing one to about eight carbon atoms. For example, an amino end group on a polymeric particulate material can be endcapped using a monocarboxylic acid, an acid anhydride, an ester, an acid halide, an aldehyde, a ketone, an epoxy-containing compound, or other compound having a functional group capable of reacting with an $-NH_2$ group. For particulate materials having a carboxyl end group, the polymer can be endcapped using an amine, alcohol, ester, epoxy-containing compound, or other compound having a functional group capable of reacting with a $-CO_2H$ group. The amine typically is a secondary amine. A hydroxyl end group on a polymeric particulate material can be endcapped using an alkyl halide, for example.

The endcapped, polymeric particulate material can be prepared in a number of different ways. For example, the endcapped polymer can be prepared using the same polymerization method used to prepare the uncapped polymer, except an endcapping compound is present in the monomer mixture. In a more preferred method, the polymerization process is allowed to proceed until a predetermined molecular weight is achieved. Then the endcapping compound is added to the polymerization reaction. This method is preferred because the molecular weight and physical properties of the polymer can be more precisely controlled for effective use in an SLS process. A more precise molecular weight range of the polymeric particulate material is preferred in SLS processes because a polymer having a more narrow molecular weight range exhibits a more definite melting point.

The endcapped polymeric particulate material can be either a granular form of the polymer or a precipitated form of the polymer. In SLS processes, a large difference between the melting point and the solidification point of the polymeric particulate material is preferred. The precipitated form of the polymeric particulate material is preferred because the precipitated form has a higher melting point and higher melting enthalpy than the granular form. In addition, the endcapped polymeric particulate material can be used as is, or can be glass filled, as is known in the art.

The chemical identity of the endcapped polymeric particulate material is not limited, except the material must be capable for use in an SLS process. Therefore, the endcapped polymeric particulate material can be an endcapped version of any polymer having functional groups and useful in an SLS process. The endcapped polymeric particulate material therefore can be, for example, a polylactam or other nylon, an ionomer, or a polyacetal.

A preferred endcapped particulate material is an endcapped PA-11 or PA-12, i.e., a polylaurolactam, having endcapped amino and carboxyl groups. Such polymers are prepared by Degussa AG, Marl, Germany, as VESTOSINT X1546 LV (low viscosity), VESTOSINT X1546 HV (high viscosity), and VESTOSINT X4175. The properties of these endcapped polymeric particle materials are summarized in the following Table 1, and compared to a conventional uncapped PA-12, i.e., DURAFORM PA, manufactured by The Valspar Corporation AG, CH-8627 Grüningen, Switzerland and distributed by 3D Systems, Valencia, CA.

TABLE 1

Product Code (standard)	**Vestosint X4175**	**Vestosint X1546 LV**	**Vestosint X1546 HV**	**Vestosint 1115**
Type	Precipitated PA-12	Precipitated PA-12	Precipitated PA-12	Precipitated PA-12
Color	Transparent	Transparent	Transparent	Transparent
Bulk density (g/cm^3)	0.47	--	0.44	0.33
Solution viscosity [1)]	1.60	1.48	1.56	1.70
Melting point (°C)	186	186	185	185
Recrystallization point (°C) (cooling rate of 10°C/ min)	147	155	150	152
Melting enthalpy (J/g)	102	111	99	106
Recrystallization enthalph (J/g)	51	65	60	58
Particle size (d50) (µm)	53	67	57	53

[1)] Solution viscosity determined by PIN-EN-ISO Norm 307, incorporated herein by reference.

Regardless of the chemical identity of the endcapped particulate material, the material preferably has a melting point of about 170°C to about 210°C, and more preferably about 180°C to about 200°C. To achieve the full advantage of the present invention, the particulate material has a melting point of about 180°C to about 195°C.

The particulate material can comprise one or more endcapped polymers. Each particulate material preferably has a melting point of about 170°C to about 210°C. In a mixture of polymeric particulate materials, it is preferred that the melting points of the polymers are within 10C°, and more preferably 5C° or less, of one another.

To further improve the properties of an article of manufacture prepared in an SLS process using an endcapped particulate material, the polymeric particle material optionally is extracted to remove low molecular weight monomers, oligomers, and impurities from the endcapped polymer.

In particular, as previously discussed, polymeric particulate materials used in an SLS process have the disadvantage of increasing molecular weight under thermal exposure. This molecular weight increase is theorized to lead to gelling, which prevents proper melting after several cycles in use. Therefore, such particulate materials are not ideally suited for SLS processes because the virgin and recycled particulate material produce different quality parts.

Extraction of low molecular weight components from the endcapped polymeric particulate material is believed to provide improvements because these components potentially are reactive, and have a lower melting point and higher vapor pressure than the particulate material. These low molecular weight compounds, therefore, can cause problems in an SLS process, such as fuming below and at the melting temperature of the particulate material. The low molecular weight compounds also can migrate to areas where they form agglomerates with particulate material that is not exposed to the laser beam, and can produce undesirable deposits on the laser sintering equipment.

Extraction of the endcapped polymer particulate material can be achieved using any method known in the art, for example, Soxhlet extraction or counter-current extraction. U.S. Patent Nos. 3,423,183; 6,326,457; 6,320,021; 6,326,460; 6,160,086; 4,978,743; and 3,639,659, each incorporated by reference, disclose extraction techniques for polyamides and other polymers.

In one method, a polymer was extracted with ethanol for about four hours using a Soxhlet extraction apparatus. It was found that ethanol extraction removed about 2 to about 3 wt% of low molecular weight components from the polymer. Using an extracted and endcapped polymeric particulate material in an SLS process reduced fuming during the SLS cycles, and the manufactured articles had improved color, i.e., yellowing of the articles after sun exposure was substantially reduced.

Optional ingredients also can be added to the endcapped particulate material, for example, to facilitate the SLS process or to improve the esthetics of the manufactured article. These optional ingredients are particulate materials and include organic and inorganic materials, such as fillers, optical brighteners, UV stabilizers, and coloring agents. Inorganic optional materials are preferred.

An optional ingredient is added to the endcapped polymer particular material in a sufficient amount to perform its intended function, without adversely affecting the endcapped material or an article prepared therefrom. Optional ingredients have a particle size in the range of the particle size of the endcapped material. Each optional ingredient is milled, if necessary, to the desired median particle size and particle size distribution.

Each individual optional ingredient, if present at all, typically is added to the endcapped polymer particular material in an amount of about 0.1% to about 150%, by weight, of the endcapped material. The total amount of optional ingredients added to the endcapped material ranges from 0% up to about 150%, by weight.

Each optional ingredient must be compatible with the particulate material in order to provide a strong and durable article of manufacture. The optional ingredient, therefore, can be inorganic filler that imparts additional strength to the article of manufacture.

One optional ingredient is a coloring agent, for example a pigment or a dye, like carbon black, to impart a desired color to the article of manufacture. The coloring agent is not limited, as long as the coloring agent does not adversely affect the particulate material or an article prepared therefrom, and is sufficiently stable to retain its color under conditions of the laser sintering process and during exposure to the laser.

The optional ingredient also can be a second polymer that modifies the properties of the particulate material. One useful second polymer is a nylon, such as nylon 6, nylon 66, nylon 11, nylon 610, nylon 12, nylon 612, copolymerized nylons, and mixtures thereof. One nonlimiting example of a nylon that can be included in the present invention is the RILSAN line of PA-11 resins, available from Elf Atochim.

To illustrate the new and unexpected results achieved by utilizing an endcapped polymeric particulate material in an SLS process, an endcapped polymer, i.e., VESTOSINT X1546, was used to manufacture three-dimensional articles of manufacture. The article was manufactured using a 3D Systems Vanguard HS apparatus. The endcapped polymer was heated to about 10C° below the melting point of the polymer prior to fusing a portion of the polymer with a laser.

Articles made using an endcapped polymer in the Vanguard HS apparatus included T-bars for tensile strength and flexibility tests, quadratic short pipes, gear box casings, pyramid platforms. The quadratic pipes were positioned in the corners of the process chamber, and show orange peel effects when the particulate material becomes defective after a plurality of SLS cycles.

It is believed that present-day polymeric particulate materials, e.g., DURAFORM PA-12, have recyclability problems. Our studies have shown that these problems are attributable, at least in part, to an increase of the molecular weight of the PA-12 nylon. In turn, the increase in molecular weight causes an increase of the melt viscosity, which then in turn causes a surface distortion problem termed "orange peel." It has been found that when the molecular weight of a polymeric particulate material increases by about 75%, orange peel effects can be expected. An SLS process utilizing an endcapped polymer substantially overcame the orange peel problem because molecular weight increases were controlled.

In one test, an endcapped PA-12 (i.e., VESTOSINT X1546) and an uncapped PA-12 (i.e., EOS 2200 PA) were subjected to repeated SLS cycles. The solution viscosity was determined using a standard method in the art, i.e., DIN-EN-ISO Norm 307. The plots in Fig. 3 show that the solution viscosity of the endcapped polymer remains essentially constant over twelve SLS cycles (i.e., about 1.55). In contrast, the uncapped polymer demonstrated a solution viscosity increase from 1.55 to 1.9 over the twelve SLS cycles. Fig. 3 shows that the uncapped material substantially increased in molecular weight over the 12 cycles, whereas the endcapped material maintained an essentially constant molecular weight. The stable solution viscosity of the endcapped polymer provided articles produced after several SLS cycles having good surface quality and homogeneous article density, for both unfilled and glass-filled endcapped PA-12.

It further was found that after thirteen SLS cycles using an endcapped polymeric particulate material, orange peel was reduced. In addition, the density of the articles made using an endcapped material was more constant, and does not decrease with recycling of the particulate material.

In total, the tests show that using an endcapped polymeric particulate material in a plurality of SLS cycles, SLS provides substantial benefits, including improved breakout of unfused particulate material from the article of manufacture, homogenous article density , improved layer-to-layer adhesion, reduced orange peel, and articles prepared from virgin and recycled particulate materials having properties and qualities essentially equal to an article prepared solely from a virgin particulate material.

Obviously, many modifications and variations of the invention as hereinbefore set forth can be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated by the appended claims.

WHAT IS CLAIMED IS:

1. A method of manufacturing an article comprising

(a) depositing a quantity of a particulate material from a reservoir into a process chamber;

(b) leveling the particulate material to form a build surface of the material;

(c) then directing an energy beam over a predetermined target area on the build surface of the material causing a portion of the particulate material to fuse and form an integral layer;

(d) repeating steps (a) to (c) to form additional integral layers that are integrally bonded to adjacent layers to form a three-dimensional article;

(e) separating unfused particulate material from the article; and

(f) recycling the unfused particulate material of step (e) to the reservoir to manufacture a second article of manufacture;

wherein the unfused particulate material maintains at least one of an essentially constant solution viscosity and an essentially constant molecular weight over ten repeating cycles.

2. The method of claim 1 wherein the recycled particulate material of step (f) has a solution viscosity that is no more than 20% greater than the solution viscosity of an identical, virgin particulate material over twenty repeating cycles.

3. The method of claim 1 wherein the recycled particulate material of step (f) has a solution viscosity that is no more than 10% greater than the solution viscosity of an identical, virgin particulate material.

4. The method of claim 1 wherein the recycled particulate material of step (f) has a solution viscosity that is no more than 0.15 greater than an identical, virgin particulate material.

5. The method of claim 1 wherein the recycled particulate material of step (f) has a solution viscosity that is no more than 0.10 greater than an identical, virgin particulate material.

6. The method of claim 1 wherein the particulate material comprises an endcapped polymeric particulate material.

7. The method of claim 6 wherein the endcapped polymeric particulate further comprises glass.

8. The method of claim 6 wherein the endcapped polymeric particulate material is in a precipitated form.

9. The method of claim 6 wherein the endcapped polymeric particulate material is in a granular form.

10. The method of claim 6 wherein the endcapped polymeric particulate material has been subjected to an extraction procedure.

11. The method of claim 1 wherein the particulate material has been subjected to an extraction procedure.

12. The method of claim 6 wherein the endcapped polymeric particulate material comprises a polyamide, a polyacetal, an ionomer, a polycarbonate, a polyethylene, a polypropylene, an elastomeric block copolymer, a polystyrene, or a mixture thereof.

13. The method of claim 12 wherein the endcapped polymeric particulate material comprises a polyamide.

14. The method of claim 13 wherein the polyamide comprises a polylaurolactam.

15. The method of claim 6 wherein the endcapped polymeric particulate material contains one or more endcapped amino groups, endcapped carboxyl groups, or endcapped hydroxyl groups.

16. The method of claim 6 wherein the endcapped polymeric particulate material is endcapped with an endcapping compound selected from the group consisting of an amine, a monocarboxylic acid, an ester, an acid chloride, an acid anhydride, an alcohol, an aldehyde, a ketone, an epoxy-containing compound, and an alkyl halide.

17. The method of claim 1 wherein the particulate material further comprises an optional ingredient selected from the group consisting of a coloring agent, a filler, a second modifying polymer, and mixtures thereof.

18. An article of manufacture prepared by the method of claim 1.

19. The method of claim 1 wherein the molecular weight of the recycled particulate material is no more than 50% greater than an identical, virgin particulate material over twenty repeating cycles.

20. The method of claim 1 wherein the molecular weight of the recycled particulate material is no more than 25% greater than an identical, virgin particulate material.

21. The method of claim 1 wherein the molecular weight of the recycled particulate material is no more than 10% greater than an identical, virgin particulate material.

22. A method of manufacturing an article comprising laser sintering a particulate composition comprising an endcapped polymer, wherein the endcapped polymer maintains an essentially constant solution viscosity over at least ten laser sintering recycles.

23. The method of claim 22 wherein the endcapped polymer has been subjected to an extraction process.

24. The method of claim 22 wherein the endcapped polymer maintains an essentially constant molecular weight over at least ten laser sintering recycles.

25. A method comprising laser sintering a particulate composition, the composition comprising a polymer having one or more reactive end groups and a compound reactive with the end groups.

26. A particulate material comprising a polymer capable of maintaining at least one of essentially constant solution viscosity, essentially constant molecular weight, and essentially constant melting point, when repeatedly exposed to an energy source.

27. The particulate material of claim 26, wherein the polymer is endcapped.

28. The particulate material of claim 27, wherein the endcapped polymer contains one or more members selected from the group consisting of endcapped amino groups, endcapped carboxyl groups, and endcapped hydroxyl groups.

29. The particulate material of claim 27, wherein the endcapped polymer is endcapped with one or more endcapping compounds selected from the group consisting of an amine, a monocarboxylic acid, an ester, an acid chloride, an acid anhydride, an alcohol, an aldehyde, a ketone, an epoxy-containing compound, and an alkyl halide.

30. The particulate material of claim 27, wherein the endcapped polymer is one or more compounds selected from the group consisting of a polyamide, a polyacetal, an ionomer, a polycarbonate, a polyethylene, a polypropylene, an elastomeric block copolymer, and a polystyrene.

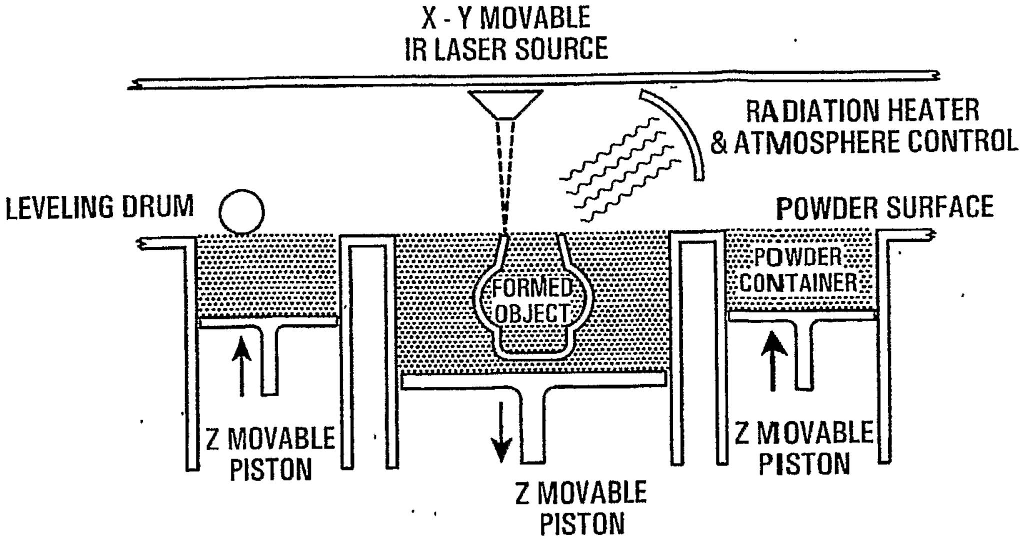
X - Y MOVABLE
IR LASER SOURCE
RADIATION HEATER
& ATMOSPHERE CONTROL
LEVELING DRUM
POWDER SURFACE
POWDER
CONTAINER
FORMED
OBJECT
Z MOVABLE
PISTON
Z MOVABLE
PISTON
Z MOVABLE
PISTON

FIG. 1

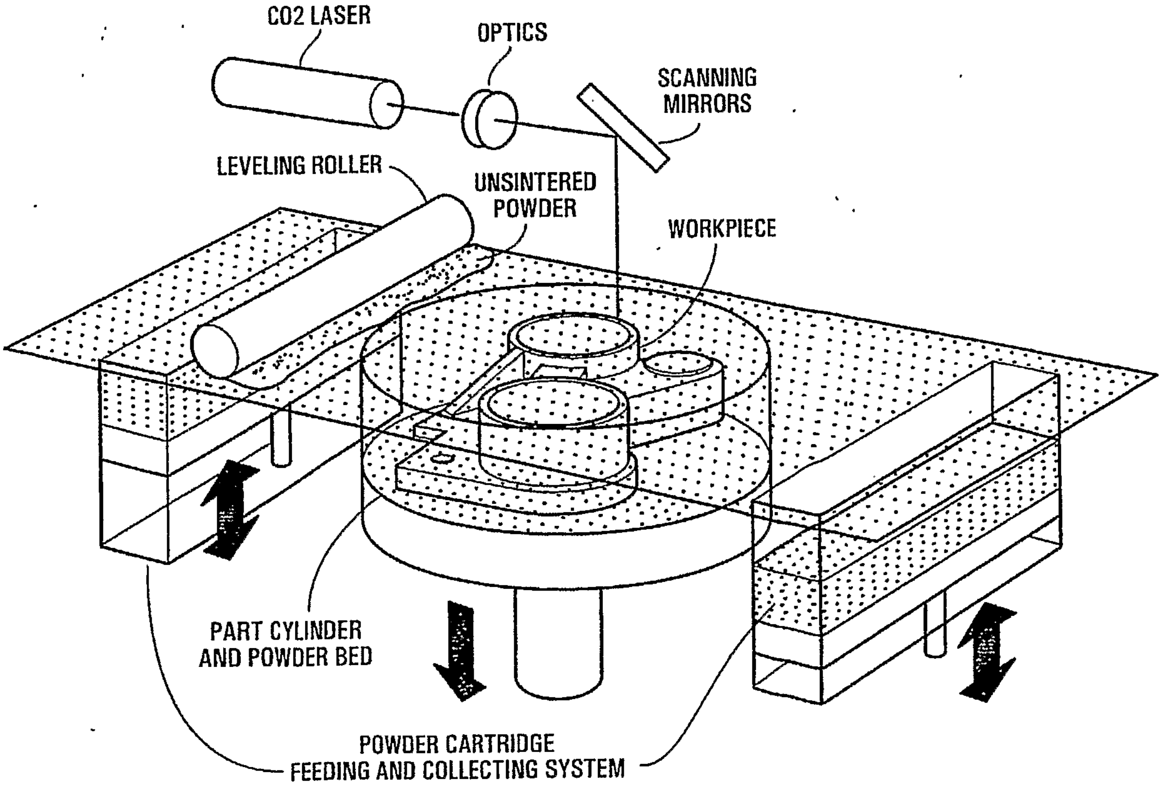
CO2 LASER
OPTICS
SCANNING
MIRRORS
LEVELING ROLLER
UNSINTERED
POWDER
WORKPIECE
PART CYLINDER
AND POWDER BED
POWDER CARTRIDGE
FEEDING AND COLLECTING SYSTEM

FIG. 2

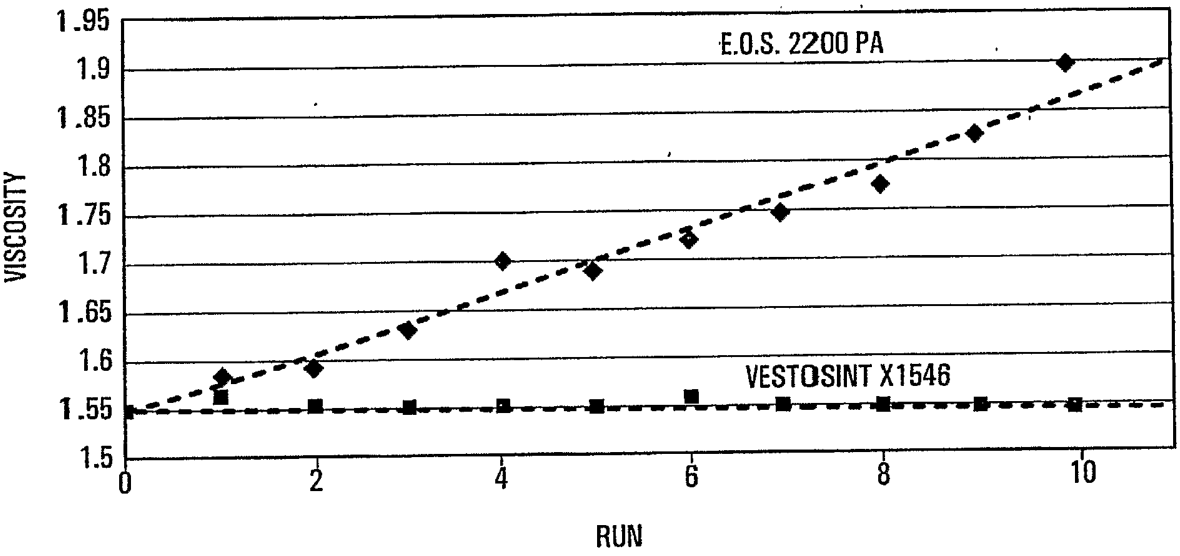
E.O.S. 2200 PA
VESTOSINT X1546
VISCOSITY
1.95
1.9
1.85
1.8
1.75
1.7
1.65
1.6
1.55
1.5
0
2
4
6
8
10
RUN

FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/010210

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B29C67/00

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)
IPC 7 B29C

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 384 759 A (DEGUSSA AG) 28 January 2004 (2004-01-28) paragraph ‘0028! -----	26-30
A	US 6 245 281 B1 (SCHOLTEN HEINZ ET AL) 12 June 2001 (2001-06-12) cited in the application column 1, line 28 - line 57 -----	1-25

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document 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 11 July 2005	Date of mailing of the international search report 22/07/2005
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Van Wallene, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US2005/010210

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
EP 1384759	A	28-01-2004	DE	10233334	B3	26-02-2004
			EP	1385180	A1	28-01-2004
			EP	1384759	A1	28-01-2004
US 6245281	B1	12-06-2001	DE	19747309	A1	29-04-1999
			CA	2251405	A1	27-04-1999
			EP	0911142	A1	28-04-1999
			JP	3634969	B2	30-03-2005
			JP	11216779	A	10-08-1999