

Description

This invention relates to production of three-dimensional objects by photohardening contiguous layers of a photosensitive composition in an imagewise manner.

Many systems for production of three-dimensional modelling by photohardening have been proposed. European Patent Application EP-A-0 250 121 filed by Scitex Corporation Ltd., on June 6, 1987, which discloses a three-dimensional modelling apparatus using a solidifiable liquid, and provides a good summary of documents pertinent to this art. U.S. Patent US-A-4 575 330 (C. W. Hull), issued on March 11, 1986, describes a system for generating three-dimensional objects by creating a cross-sectional pattern of the object to be formed at a selected surface of a fluid medium capable of altering its physical state in response to appropriate synergistic stimulation by impinging radiation, particle bombardment or chemical reaction, successive adjacent laminae, representing corresponding successive adjacent cross-sections of the object, being automatically formed and integrated together to provide a step-wise laminar buildup of the desired object, whereby a three-dimensional object is formed and drawn from a substantially planar surface of the fluid medium during the forming process. U.S. Patent US-A-4 752 498 (E. V. Fudim), issued on June 21, 1988, describes an improved method of forming three-dimensional objects, which comprises irradiating an uncured photopolymer by transmitting an effective amount of photopolymer solidifying radiation through a radiation transmitting material which is in contact with the uncured photopolymer. The transmitting material is a material which does not interfere with the solidified photopolymer's ability to subsequently crosslink. Using this method, multilayer objects can be made.

Publication "Automatic Method for fabricating a three-dimensional plastic model with photohardening polymer" by Hideo Kodama, Rev. Sci. Instrum. 52(11), 1770-1773, Nov. 1981, describes a method for automatic fabrication of a three-dimensional plastic model. The solid model is fabricated by exposing liquid photohardenable polymer to ultraviolet rays, and stacking the cross-sectional solidified layers. Publication "Solid Object Generation" by Alan J. Herbert, Journal of Applied Photographic Engineering, 8(4), 185-188, Aug. 1982, describes an apparatus which can produce a replica of a solid or three-dimensional object much as a photocopier is capable of performing the same task for a two-dimensional object. The apparatus is capable of generating, in photopolymer, simple three-dimensional objects from information stored in computer memory.

A good review of the different methods is also given by a more recent publication, titled "A Review of 3D Solid Object Generation" by A.J. Herbert, Journal of Imaging Technology 15: 186-190 (1989).

Most of these approaches relate to the formation of solid sectors of three-dimensional objects in steps by sequential irradiation of areas or volumes sought to be solidified. Various masking techniques are described as well as the use of direct laser writing, i.e., exposing a photohardenable composition with a laser beam according to a desired pattern and building a three-dimensional model layer by layer. In addition to various exposure techniques, several methods of creating thin liquid layers are described which allow both coating a platform initially and coating successive layers previously exposed and solidified.

Current methods of coating suggested thus far, however, have drawbacks in that they are not capable of ensuring flat uniform layer thickness or of producing such layers quickly, or they do not effectively prevent damage or distortion to previously formed layers during the successive coating process. Furthermore, they omit to recognize very important parameters involved in the coating process such as the effects of having both solid and liquid regions present during the formation of the thin liquid layers, the effects of fluid flow and rheological characteristics of the liquid, the tendency for thin photohardened layers to easily become distorted by fluid flow during coating, and the effects of weak forces such as hydrogen bonds and substantially stronger forces such as mechanical bonds and vacuum or pressure differential forces on those thin layers and on the part being formed.

The Hull patent, for example describes a dipping process where a platform is lowered either one layer thickness or is dipped below the distance of one layer in a vat then brought up to within one layer thickness of the surface of the photohardenable liquid. Hull further suggests that low viscosity liquids are preferable, but for other practical reasons, the photohardenable liquids are generally high viscosity liquids. Although theoretically most liquids will flatten out eventually, high viscosity liquids and even low viscosity liquids take an inordinate amount of time to flatten to an acceptable degree especially if large flat areas are being imaged and if the liquid layer thickness is very thin. Regions where previous layers consist of solid walls surrounding liquid pools further compounds the flattening process of the thin liquid layer coating. In addition, motion of the platform and parts, which have cantilevered or beam (regions unsupported in the Z direction by previous layer sections), within the liquid creates deflections in the

layers, contributing to a lack of tolerance in the finished part.

The Munz patent (US-A-2 775 758, issued in 1956) and Scitex application describe methods by which the photohardenable liquid is introduced into the vat by means of a pump or similar apparatus such that the new liquid level surface forms in one layer thickness over the previously exposed layers. Such methods have all the problems of the Hull methods except that the deflections of the layers during coating is reduced.

The Fudim patent describes the use of a transmitting material, usually rigid and coated or inherently unlikely to adhere to the solidified photopolymer, to fix the surface of the photopolymer liquid to a desired shape, assumably flat, through which photopolymers of desired thickness are solidified. The methods described by Fudim do not address the problems inherent in separating such a transmitting material from a photopolymer formed in intimate contact with the surface of the transmitting material. Whereas the effects of chemical bonding may be reduced significantly by suitable coatings or inherently suitable films, the mechanical bonds along with hydrogen bonds and the like are still present and in some cases substantial enough to cause damage or distortion to the photopolymer during removal from the transmitting material surface. Furthermore, it is believed that forces resisting the separation or even sliding off the solidified layer having been exposed in intimate contact with the suitably non-adhesive transmitting material, are capable of damaging the solidified layer, especially when surrounded by photohardenable liquid and even more especially when the solidified layers are thin. No method is described in the Fudim patent to eliminate these problems.

A serious disadvantage of the dipping processes is that the exposure takes place in an area being part of the huge surface of the photohardenable composition limited only by the dimensions of the vessel containing the composition. Thus, the leveling process for a layer to assume uniform thickness takes an unnecessarily long time.

Another serious disadvantage of the aforementioned methods is that every single portion of each photohardened layer has to be at least partially supported by either the substrate on which the object is being formed or by another layer. This is limiting considerably the freedom of selecting the orientation, parallel to which the layers have to be formed, and also, in a number of cases, it limits the design of the object itself.

Patent application EP-A-0 388 129 describes a method in which each layer is formed by irradiating the boundary of the cross-section of the object to be formed and then irradiating the interior of the

cross-section. Patent application EP-A-0 250 121 (already mentioned above) describes a method of the type comprising the steps of:

- (a) forming a layer of the photo-hardenable composition;
- (b) providing imagewise an object-forming exposure to the cross-sectional portion of the object, adequate to imagewise photo-harden said portion;
- (c) introducing a new layer of the photo-hardenable liquid composition onto the layer subjected to step (b); and
- (d) repeating steps (b) and (c) until all layers of the three-dimensional object have photo-hardened.

Patent applications EP-A-0 250 121 and JP-A-62-32009 also provide an apparatus of the type comprising:

a coating station comprising: a substantially flat support surface for supporting the rigid object; and a dispenser above the support surface for dispensing the photo-hardenable composition in the form of contiguous layers; and

imaging means for selectively exposing to radiation each of the contiguous layers of the photo-hardenable composition, the imaging means including an object-forming exposure element for exposing cross-sectional portions of the contiguous layers corresponding to the three-dimensional object.

It is an object of the present invention to produce 3-dimensional objects of highly improved quality and complexity at a faster rate.

This object is attained according to the invention by the methods as laid out in claims 1 and 5 and by the apparatus as laid out in claim 11.

Particular embodiments of the invention are disclosed in the dependent claims.

One aspect of the present invention provides a method of this type, which is characterised in that:

the photo-hardenable composition is also a photo-gellable composition;

for each object-forming exposure step, a gelling exposure of the layer is provided, adequate to produce a soft-gelled area, surrounding the cross-sectional portion of the object to be formed in the subsequent step;

as a result of step (d) all of the soft-gelled areas have formed a soft-gelled mass surrounding the three-dimensional object, the object being separated from the gelled areas by an interface; and

after step (d) the soft-gelled mass is removed in order to recover the three-dimensional object.

Another aspect of the present invention provides a method of the above type, which is characterised in that: for each object-forming exposure step, a wall-forming exposure step is provided to form a layer of a peripheral wall of the photo-hardenable composition around the respective

cross-sectional portion of the three-dimensional object by exposing the peripheral wall to radiation

Preferably, the solidified layers according to this invention have a thickness of less than 0.76mm and are flat to within 0.001mm per mm.

A further aspect of the present invention provides an apparatus of this type, which is characterised in that:

the support surface is in the form of a substantially flat platform;

the coating station further comprises: a vessel in which the platform is disposed for collecting the liquid photo-hardenable composition; and means for recirculating the photo-hardenable composition from the vessel to the dispenser; and

the imaging means further includes a further exposure element for exposing an area around each cross-sectional portion. Specific embodiments of the present invention will now be described by way of example with reference to the accompanying drawings in which:

Figure 1 is a schematic diagram showing the apparatus utilized in the practice of a preferred embodiment of the instant invention.

Figure 2 illustrates an example of the top view of the preferred configuration in fabricating the three dimensional object, including a soft gelled mass around the object and a photohardened wall in the periphery of the soft gelled mass.

Figure 3 is a schematic diagram of an enlarged view of the coating station shown in Figure 1, including the first exposure element, second exposure element, and third exposure element.

Figure 4 is a schematic diagram showing the first exposure element exposing an area of a layer in the configuration of the preferred embodiment shown in Figure 3.

Figure 5 is a schematic diagram showing the second exposure element exposing an area of a soft gelled portion in the configuration of the preferred embodiment shown in Figure 4.

Figure 6 is a schematic diagram showing the third exposure element exposing an area in the periphery of the soft gelled portion in the configuration of the preferred embodiment shown in Figure 5.

Figure 7 is a schematic diagram of an enlarged view of the coating station shown in Figure 1, including the second exposure element, and the third exposure element, but lacking the first exposure element, in a different embodiment of the instant invention. It also illustrates the second exposure element exposing a portion of a layer of the photohardenable composition.

Figure 8 is a schematic diagram showing the third exposure element exposing an area of a layer surrounding the area which was previously exposed by the second exposure element in the

configuration of the embodiment shown in Figure 7.

The instant invention is directed to a method of fabricating an integral three-dimensional object from a multiplicity of cross sectional portions of the object, the cross sectional portions corresponding to photohardened portions of contiguous layers of a photohardenable and preferably also photogellable liquid composition.

In the context of this discussion, photogellable composition is defined as one for which there is an exposure level and exposure wavelength of actinic radiation capable of transforming the liquid composition to a loosely polymerized and/or cross linked soft gel, also herein referred to as simply "gel" for purposes of brevity. On the other hand, photohardenable composition is defined as one for which there is an exposure level and an exposure wavelength of actinic radiation capable of transforming the liquid or the soft gelled composition to a solid well polymerized and/or cross linked structure. It is important to note that the same effect may be produced by different mechanisms. For example, a soft gel may be produced either by the low availability of polymerizable or cross linkable bonds at a certain wavelength range, regardless of the exposure level above a certain limit at the wavelengths under consideration, or it may be produced by a low level of exposure in an abundance of polymerizable and/or cross linkable bonds at a certain wavelength range. In the former case, if it is desirable to render the composition also photohardenable, the composition may be formulated to contain an adequate amount of polymerizable or cross linkable bonds at a different range of wavelengths. Examples of ways to achieve this would be selection of the type of the bonds, selection of different initiators in type and amount, or even selection of completely different mechanisms of polymerization or cross linking. In the latter case, the composition may be considered both photogellable and photohardenable and may be used as such, depending on the amount of exposure at a predetermined range of wavelengths. Exposure to different wavelengths for which the composition has different sensitivities may also be used for this purpose. It is worth noting that low exposure may be attained not only by decreasing the time and/or intensity of the radiation, but also by distributing the radiation over the area to be exposed in the form of dots or lines or other patterns of varying size and distance between each other. For example, in the case of laser scanning, where good solidification of the composition may occur by overlapping the scanned lines, the overall exposure may be decreased and become suitable for gelation by increasing the distance between the lines adequately. The mass of the gel is not expected to

be uniform, but it will be easily removable from the rest of the solidified three dimensional object, and it will serve the purposes of this invention. The same is valid for breaking the lines into dots of suitable size and distance between each other in order to form a gelled mass of desirable consistency. A pattern of odd-sized spatter-like spots could also serve the same purpose, as long as the exposed areas form a gel-like, easily removable mass from the solidified three-dimensional object. It is not necessary to create the lines or dots or other patterns by scanning. Any mask having the desired line, dot, or other pattern configuration in conjunction with any projection system would serve the objectives of the instant invention very well. It is only important in this case, that the overall exposure is lowered in a way to produce a gel or easily removable mass from the rest of the three-dimensional object. In other words the gelled area may be produced by widely spaced scan lines or dots, in which exposure is adequate to solidify the lines or dots, but due to the small cross section of the lines or dots, there is only very weak cohesive strength between them, and thus the area is "gelled" simply by the fact that the lines act as loosely connected threads or islands, respectively, in a viscous liquid.

It is preferred that when the mechanism of the gel formation is carried out by lowering the exposure level, this lowering of exposure level is performed by using a line pattern. It is also preferable that within the gelled mass, the center axes of the lines corresponding to consecutive layers are immediately above each other so that vertical ribbon-like structures may be formed, wherein the bonds between lines in the vertical direction are stronger than the bonds between lines in the horizontal direction. This can be arranged easily by programming the scanning, and the projection. Since accurate registration of the gelled area is not necessary, the aforementioned arrangement is straightforward.

It is also preferable that a thin portion or barrier being subjected to very low or no exposure is allowed at the interface between the gel and the three-dimensional object, to facilitate clean removal of the gel from the photohardened three dimensional object, and to promote better resolution.

The apparatus of the preferred embodiment of this invention is illustrated in Figure 1. Its elements and operation are described below.

There is provided an imaging station or means 70 including a radiation source 10, a modulator 14, a computer 34, a first exposure element 15, a second exposure element 16 and a third exposure element 17. There is also provided a coating station 80. Radiation means 10 is preferably a laser, producing a radiation beam 12. Being desirable to

produce solid objects at high speed, the apparatus of the instant invention preferably utilizes relatively high power radiation means 10, such as a high power laser, which may have major bands in the visible, infrared, or ultraviolet regions. High power is considered to be a power greater than 20mW, and preferably over 100 mW as measured from the intensity of radiation beam 12. This is so with the present photospeeds of photohardenable compositions. However, as faster compositions become available, the values of 20 mW and 100 mW for the beam intensity will become lower accordingly, since photospeed of the composition and intensity of the radiation beam have an inverse relation to each other in order to achieve the same results. The selection of a certain type of laser should be coordinated with the selection of the photohardenable composition in a way that the sensitivity of the photohardenable composition agrees reasonably well with the wavelength of the laser's emission. Other types of radiation means may also be utilized such as electron beams, x-rays, and the like, as long as their energy type is matched with the sensitivity of the photohardenable composition, a beam is provided, and the appropriate conditions for their handling are observed according to established ways, well known in the art. Although means may be provided to modify the shape of the beam cross-section to any desirable shape, the ordinary shape is circular, and the profile of the intensity of the beam is gaussian with a maximum at the center of the circular shape.

The radiation beam 12 passes through modulator 14, the modulator being preferably an acousto-optical modulator. The modulated radiation beam 12' passes in turn through the second exposure element 16, which comprises two mirrors 20 and 22, each mirror having an axis (not shown), allowing reflection of the beam towards the coating station 80 in the X and Y directions, the X and Y directions being perpendicular to each other. The mirrors 20 and 22 may rotatably move around their corresponding axes by means of motors 24 and 26, respectively for controllably deflecting the beam in a vector scanning mode, in the X and Y directions towards predetermined positions of the coating station 80, in which the photogellable and photohardenable composition is processed. Examples of suitable photohardenable compositions are given at a later section of this description.

As the beam is guided by the second exposure element 16, it assumes an acceleration from zero level to a maximum acceleration and a velocity from zero level to a maximum constant velocity. The velocity and the intensity of the beam remain proportional to each other, so that the exposure remains substantially constant. The beam exposes imagewise preselected portions of the composition

to a substantially constant depth as described below.

For the purposes of this invention in general, the radiation beam 12" may be not only a focused beam from a laser, but also other light source or light, modified in a number of different ways. For example, it may be transmitted through any type of variable optical density photomask such as a liquid crystal display, silver halide film, electro-deposited mask etc., or reflected off of any variable optical density device, such as a reflective liquid crystal cell. In that respect, exposure elements 15 and 17 may also comprise or constitute such devices, or even be in the form of beams of actinic radiation.

As aforementioned, in the preferred embodiment, there is also provided a first exposure element 15 and a third exposure element 17. The function of the first exposure element 15 is to provide radiation in an imagewise form to the photohardenable composition, in a way that there is a soft gel formed around the article or object which is fabricated by photohardening the contiguous layers of the photohardenable composition by means of laser beam 12". The third exposure element 17 functions in a way to provide radiation imagewise to the periphery of the soft gelled area so that a wall is built around the soft gelled area. This wall, among other functions, prevents small fragments of the fragile gel to fall into the recirculated composition. The second exposure element 16 can be used by itself to perform all functions. However, by using only the second exposure element 16 which is preferably a scanner, the speed of forming the three dimensional object may be reduced considerably. It is, therefore, advantageous in many occasions to use a combination of exposure elements 15, 16, and 17, especially because elements 15 and 17 can provide a repeatable image layer after layer. In some occasions, elements 15 and 16 or elements 16 and 17, or even element 16 alone will be adequate for the purposes of this invention. The combined function of these elements will become much clearer as the description of the operation of this apparatus continues.

Figure 3, depicts in more detail the coating station 80 of the preferred embodiment of this invention.

The coating station 80 comprises a vessel 44 which preferably has an inclined bottom portion for collecting the excess of composition 40, and a recirculation pump 47. Recirculation pump 47 can be replaced by any other means capable of recirculating the composition 40. Recirculation pump 47 causes the photohardenable and photogellable composition 40 to be carried into dispenser 43. Dispenser 43 reciprocates back and forth and in some occasions also sideways in order to deliver the liquid on a platform 41, which is substantially

flat. The function of dispenser 43 is to provide layers of the composition. The dispenser may comprise such conventional mechanisms as curtain coaters, extruders, or sprayers. Other mechanisms of layer formation, of course, may be used. Due to the fact that only an area commensurate to the size of the three-dimensional object has to be coated according to the present invention, leveling and uniformity of each layer is accomplished in a fast rate as compared to other techniques, and there is no strict requirement for the dispenser to provide itself high uniformity to the layer in most instances, depending on the viscosity of the composition. Optionally, platform 41 may be supported by placement means 42 so that it can move up and down or in a translational manner sideways. This is not, however, necessary for the operation of the invention. Dispenser 43 provides a layer 48 of composition 40 on platform 41. A doctor blade (not shown for purposes of simplicity) may be used optionally to control better the thickness and uniformity of the layers. The first exposure element 15 provides a flood exposure in an image wise pattern to a portion 45 of layer 48, as shown in Figure 4. This imagewise pattern may include a perspective portion of a cross sectional portion of the three dimensional object or it may be limited around it. In either case, it may be considered as surrounding the cross sectional portion. Thus an interface 99 is formed, shown better in Figures 5 and 6. The exposure given by element 15 is of such energy which is capable to produce soft gel 45. The beam 12" photohardens an area 11 surrounded by the soft gelled area 45.

The gelled mass surrounding the object need not actually be formed up to the edges of the object. It is preferable to form a thin region or barrier at the interface 99 of the gelled area and the three dimensional object by subjecting said thin region to only a fourth exposure equivalent to no or lower exposure than the first exposure. This thin region should be such in thickness and consistency as to provide adequate support to the object within the soft gelled area, depending on the properties of the composition, such as viscosity, viscoelasticity, tackiness, surface energy, photospeed, and the like. This configuration of a loose barrier ensures better object edge resolution and provides easier gel removal from the object during post processing.

Although any sequence, including simultaneous action, of exposure by elements 15, 16, and 17 may be used, it is preferable that the photohardening of the area corresponding to a respective cross sectional portion 11 of the three dimensional object takes place following the formation of the soft gelled area 45. This is because in consecutive layers, photohardening by beam 12" may also start

in an isolated manner on the soft gelled mass alone, and not even be in contact with any other photohardened areas of any layers. This is important since it gives wider freedom in the design of a three dimensional object corresponding to more complicated structural designs. In addition, the soft gel provides a better substrate to accept a new layer of liquid composition, as compared to plain liquid under the new liquid layer. The third exposure element 17 provides an adequate radiation to photoharden areas 46, as shown in figures 6 and 2, so that areas 46 are located in the periphery of the soft gelled area 45. The wall that is produced by the photohardened areas 46 is intended to include within it the soft gel areas 45, so that fragments of the soft gel will not fall in and impair the function of the recirculation of composition 40. After the two photohardening steps and the soft gel step have been carried out, dispenser 43 applies a new layer on top of the previously formed configuration. The same steps of soft gel formation, photohardening, and layer deposition are repeated until the object becomes complete. The wall is subsequently separated, for example by pulling it away from the object and breaking the weakly structured soft gel between the wall and the object. The rest of the soft gel is then removed preferably by mechanical means including spraying with a solvent which does not swell the photohardened portions, or by vibrations, or the like. Since in the preferred embodiment, photohardenable composition 40 comprises a thermally coalescible material, and more particularly a plastisol, a subsequent step of thermal treatment is desirable for the object to assume its ultimate strength.

It is worth mentioning that every time a layer is completed, placement means 42 moves the platform 41 down by the thickness of a layer. The platform may also be moved down more than the thickness of one layer to expedite liquid flow over previously exposed areas or the platform, and then moved back up to the one layer thickness position. However, instead of moving the platform 41, one can move accordingly the whole coating station 80 lower, or the assembly of the second exposure element 16 and the first and third exposure elements 15 and 17, respectively, or readjust the focus of these exposure elements. The height of dispenser 43 may also be readjusted to provide better layer uniformity.

Just one projection or other type of mask may be used by the first exposure element 15. Also, a single mask may be used by the third exposure element 17. Thus, the gel portion as well as the wall portion may very well be repeatable for each and every layer, during the fabrication of the three-dimensional object. Although this is desirable for simplicity purposes, it is not necessary, and some-

times it is desirable to change the shape of the soft gel and of the wall. For example, it may be desirable to minimize the area of the soft gel and the area within the wall in order to minimize the leveling time of each layer.

As shown in Figure 1, communication lines 52, 50, 54, 60, 55, and 56 are also provided for computer 34 to control the radiation source 10, the modulator 14, the second exposure element 16, the placement means 42, the first exposure element 15, and the third exposure element 17, respectively, by methods well known to the art. The aforementioned doctor blade (not shown) may also be controlled by the computer 34. The graphic data corresponding to the shape of the solid object under production, are also stored in computer 34. The graphic data stored in computer 34, after being processed cause motors 24 and 26 to turn and move mirrors 20 and 22 accordingly in order to guide the radiation beam towards predetermined positions on the thin layer 48.

Although this method is not limited relative to layer thickness, it is preferable that layers of 30 mils or less be produced.

In another embodiment of this invention, illustrated in Figures 8 and 9, dispenser 143 provides a layer 148 of composition 140 on platform 141. No first exposure element is used. The second exposure element 116 photohardens an area of the layer corresponding to a cross sectional portion 111 of the three dimensional object. The third exposure element 117 provides an adequate radiation to photoharden area 146, as shown in figures 8, so that area 146 surrounds the respective cross sectional portion 111 of the three dimensional object. After the two photohardening steps have been carried out, dispenser 143 applies a new layer on top of the previously formed configuration, and optionally the aforementioned doctor blade (not shown) smoothes further the liquid layer. The same steps of photohardening, and layer deposition are repeated until the object becomes complete. The wall than is produced by the photohardened areas 146 is intended to form an automatically fabricated container of considerably smaller size than the side of vessel 144, so that the leveling process for each individually applied layer is considerably reduced. Every time a layer is completed, placement means 142 may move the platform 141 down by the thickness of a layer, or similar mechanisms as described in the preferred embodiment may be used.

In a different embodiment of the instant invention, no third exposure element is used, while the first exposure element and the second exposure element proceed with their functions as described above to produce a photohardened three dimensional object within a soft gel mass.

In still another embodiment of this invention, the first exposure element 15 may provide radiation of different and less effective wavelength regarding polymerization and/or cross linking of composition 40 than either element 16 or element 17.

In yet another embodiment, only exposure element 16 is used to produce the gel, the wall, the cross sectional area of the part, and if desired, the thin portion or barrier at the interface of the gelled mass and the three-dimensional object. The differences in exposure by element 16 for the various regions may be accomplished by modulation means 14 of beam 12" and/or the scanning distance between scan lines controlled by the second exposure element 16 itself, which is preferably a scanner. Both the scanner 16 and the modulation means are controlled in turn by computer 34. Referring to Figure 1, the region 45 to be gelled receives a first exposure adequate to form a soft gel. Each cross sectional portion 11 of the three dimensional object and the wall 46, receive preferably about equal exposures to be photohardened. The barrier at the interface 99 receives a fourth exposure, the fourth exposure being the lowest of all including the case of no exposure at all. The first exposure may be achieved by increasing the distance between scan lines such that the photohardened lines are essentially individual lines that have no substantial stiffness in themselves but are somewhat constrained by relative motion by their proximity and the viscous nature of the surrounding liquid, or by creating dots loosely connected to each other, or by changing the wavelength of radiation beam 12, 12', and 12" through a filter, prism or reflective mirror coating means, such that the absorption of said wavelength creating polymerization inducing radicals is lower, and therefore less polymerization takes place per given volume. This embodiment is preferred when a fourth exposure is used at the interface of the three dimensional object and the soft gelled areas.

As already explained, the exposure elements 15, 16 and 17 may take the form of projectors, scanners, or combinations thereof, or they may be combined even in a single element. Of course the different versions will have advantages and disadvantages when compared to each other. Nevertheless, it is preferable that the first exposure element 15 and the third exposure element 17 constitute a first projector and a third projector, respectively, providing repeatable flood exposure in an imagewise manner, while in contrast, the second exposure element 16 is a scanner providing point by point exposure. As aforementioned, a line pattern in the form of ribbons would be the preferable way of reducing the exposure level at the areas to be soft gelled, according to the above description.

Although Figures 1 and 3 to 8 show a recirculation pattern for the photohardenable composition, the level of the composition 40 in vessel 44 might also be such as to cover the most recent photohardened cross sectional portion of the three dimensional object, as well as the respective gel and wall portions by the thickness of a layer. Then, it would be desirable for platform 41 to be adaptable to vertical movement for positioning the object suitably for the imagewise exposures.

The photohardenable compositions which can be used in the practice of the instant invention are compositions which undergo solidification under exposure to an adequate dose of radiation. At low radiation levels, due to incomplete polymerization and/or cross linking, a soft gel is formed, which may be easily broken down by mechanical means. Thus, by providing different areas with different amounts of radiation, one may produce hard areas corresponding to layers which constitute part of the three dimensional object surrounded by a soft gelled mass. Such compositions comprise usually but not necessarily a photosensitive material and a photoinitiator. A similar effect may be produced by using combinations of monomers or oligomers, which undergo different degrees of polymerization and/or cross linking due to the relative amounts used, or to the different sensitivities at different wavelengths, or to the different types (for example cationic/free-radical), or the like, and combinations thereof. The word "photo" is used here to denote not only light, but also any other type of actinic radiation which may transform a liquid composition to a photohardened and solidified one by exposure to radiation. Cationic or anionic polymerizations, as well as condensation and free radical polymerizations and combinations thereof are examples of such behavior. It is only important that the types and amounts of oligomers or monomers, photoinitiators and other components in the composition are coordinated with the characteristics of the exposure elements 15, 16, and 17 in order to produce the desired results according to the teachings of the present invention. Any photopolymer formulator of ordinary skill in the art can tailor formulate such compositions without undue experimentation.

Photohardenable compositions containing thermally coalescible materials are of preference. A liquid thermally coalescible photohardenable composition is a composition which photohardens and solidifies upon exposure to actinic radiation without attaining necessarily its ultimate physical properties, particularly with respect to their adhesive and cohesive characteristics. However, it develops adequate integrity to be handled until such time when further treatment is provided. The composition is considered as coalescible when it comprises par-

ticulate matter in dispersed form, which particulate matter undergoes coalescence under a certain set of conditions, such as increased temperature for example. Coalescence is the transformation of a dispersed phase to a cohesive continuous solid phase.

Preferably the photohardenable composition comprises a thermally coalescible polymeric cohesive material, a photohardenable monomer, and a photoinitiator. Preferably the photohardenable material comprises an ethylenically unsaturated monomer. Upon exposure to the actinic radiation, even the exposed areas of the photohardenable composition must remain thermally coalescible after removing the unexposed areas. This is important to improve both adhesion in the joining surfaces between the layers and cohesion within the layers for a multilayer integral three dimensional object. Actually, cohesive bonds are formed at the joining surfaces by the thermally coalescible material providing superior properties to the structure of the final three dimensional object.

Although in the case of photohardenable compositions which are not based on coalescible materials, post treatment after the exposure is not always required, in the case where a coalescible material is an essential component of the formulation, further heat treatment is needed for the object to attain its ultimate strength. Thus in such cases, when all the layers of the three dimensional object have been formed by the method described above, the unexposed and the soft gelled portions of the composition may be removed by any conventional means, such as shaking the object, blowing gas towards the object, and the like. Further removal may be achieved by rinsing or spraying the object with poor, noncoalescing solvents. Water, alcohols, and in general polar solvents are poor solvents for non-polar compositions and vice versa. As long as the solvent under consideration does not extract excessive amounts of materials from the photohardened area or it does not swell excessively the object to be rinsed within the rinsing time, it is considered to be a poor, non-coalescing solvent. The object then is thermally coalesced in order to develop high cohesive and adhesive strength. This step may be performed in an oven, such as convection, IR, microwave, and the like. Optimum temperature and time are dependent on the individual composition. Typically the temperature range is 100° - 250°C and the time range is 5 - 30 minutes. However, temperature and times outside these regions may be used.

A very important group of thermally coalescible materials are plastisols. Plastisols are fluid mixtures, ranging in viscosity from pourable liquids to heavy pastes, obtained by dispersing fine particle size polymeric resins in nonvolatile liquid thermal

plasticizers, i.e., materials which are compatible with the polymer or resin and increase its workability and flexibility but have no substantial solvent activity for the resin or polymer under ordinary conditions of storage (e.g., room conditions). When the plastisol has been formed into a desired shape, e.g., by molding or coating, it can be heated to coalesce the polymeric resin particles and the non-volatile liquid constituent, thereby forming a homogeneous solid mass. Volatile diluents can be added to plastisol dispersions to modify their viscosity and to achieve desirable handling characteristics in coating or other forming operations. A dispersion that contains no more than 10% volatile diluent is regarded as a plastisol. Since the plasticizer used in the case of plastisols acts as a plasticizer to solvate the polymer only at higher temperatures than storage temperatures, it may also be called thermal plasticizer.

The most widely used plastisols are based on polyvinyl chloride homopolymer in a plasticizer. Dispersion resins (particle size 0.1 to 2 micrometer range) are generally used. They are characterized by the polymer type (homopolymer or copolymer with vinyl acetate or polyvinyl chloride containing carboxyl functional groups) molecular weight and size, shape and distribution of particles. Resins of a given molecular weight are usually chosen according to the physical requirements of the finished product. High molecular weight resins yield higher physical strength. Copolymers are used when lower fusion temperature is required. Particle size, shape, and distribution have significant effect on plastisol rheology. Blending resin (particle size range 10-150 microns) may be incorporated with the dispersion resin. They usually have low oil absorption which reduces the viscosity of the plastisol at a given plasticizer level.

Polyvinyl chloride has been described in the literature as the primary polymer used in forming plastisols. Polyvinyl chloride plastisols have been described in U.S. Patent US-A-3 795 649 wherein the polyvinyl chloride is copolymerized with other monomers, including acrylic monomers, that constitute a minority (35%) of the polymer composition. In U.S. Patent US-A-2 618 621 there are disclosed polyvinyl chloride plastisols wherein part of the plasticizer content is replaced with an acrylic monomer, which is then conventionally thermally polymerized at the temperature encountered in the step of coalescing the polyvinyl chloride resin.

Polyvinyl chloride plastisol dispersions can be made photoactive by incorporating therein a photosensitive monomer and photoinitiator, such as described in U.S. Patent US-A-4 634 562, or by having attached to the backbone of the polyvinyl chloride polymer photopolymerizable or photocrosslinkable groups, such that upon exposure to ac-

tinic radiation, the modified polyvinyl chloride polymer becomes polymerized or crosslinked. Such compositions may be used, preferably as part of total coalescible material, or as part or total of the unsaturated monomer. The photoinitiator may also constitute part of the polymer, as described for example in U.S. Patents US-A-4 251 618 and US-A-4 276 366, and be employed by the present invention, preferably as part of the total coalescible material.

In general, polyvinyl halides, polyvinylidene halides, polyvinyl halide acetates, polyvinylidene halide acetates, polyphenylene oxide, polyvinyl acetal, and mixtures thereof may be used effectively as thermally coalescible polymers. It is preferable that the halide is chloride and or fluoride. Polyvinyl halide compositions usually include thermal stabilizers, well known in the art. Stabilizers have the ability to accept the hydrogen halide which is released from the polymer as a result of thermal degradation. They also prevent discoloration. Materials commonly used as stabilizers are the barium-cadmium-zinc types. They are frequently improved through addition of epoxidized oils and phosphates (chelates).

Polyelectrolyte compositions, such as described in U.S. Patent US-A-4 176 028, as well as acrylic and methacrylic plastisols, such as described in U.S. Patents US-A-4 421 619, US-A-4 309 331, US-A-4 465 572, US-A-4 125 700 and Belgian Patent BE-A-865,180 may also be used. Other thermally coalescible compositions, such as those described in U.S. Patents US-A-4 523 983, US-A-4 568 405, and US-A-4 623 558 are also examples of compositions which may be employed in the practice of the present invention.

Plasticizers used in plastisols are generally categorized either by function or structure. Structurally, they may be classified as monomeric or polymeric, and functionally as primary or secondary. Plasticizers which have good permanence, compatibility, and plasticizing efficiency are considered primary; less compatible ones are secondary. Typical non-polymerizable plasticizers for polyvinyl chloride resins include but are not limited to: diisodecyl phthalate, diisononyl phthalate, diisooctyl phthalate, di-2-ethylhexyl phthalate, di-2-ethylhexyl azelate, diisodecyl adipate, n-octyl-n-decyl adipate, diisononyl adipate, di-2-ethylhexyl adipate, C7 and C9 adipate, n-C6-C8-C10 phthalates, n-octyl-n-decyl phthalates, ditiidecyl phthalate, tri-2-ethylhexyl trimellitate, triisononyl trimellitate, n-octyl-n-decyl trimellitate, Polyester (Paraplex G-54, of Rohm & Haas Co., Plastolein 9750 of Emery Industries, Inc.), butyl benzyl phthalate, dihexyl phthalate, Butyl Octyl phthalate, Tricresyl phosphate, cresyl diphenyl phosphates, 2-ethylhexyl diphenyl phosphate, decyl diphenyl phosphate,

dicapryl phthalate, di-2-ethylhexyl isophthalate, epoxide containing plasticizers such as epoxidized soybean oil, octyl epoxy tallate, and isooctyl epoxy tallate, hydrocarbons, chlorinated hydrocarbons and others.

Polymerizable plasticizers may be used together with nonpolymerizable plasticizers. They include but are not limited to 1,3-butylene glycol dimethacrylate, trimethylol propane bis-(methacrylate), trimethylol propane trimethacrylate.

Plasticizers have a profound effect in all aspects of plastisols including viscosity, rheological properties, storage ability, fusion temperature, application method, and ultimate physical properties (for example, tensile strength, % elongation, flame retardation and permanence after the thermal coalescing step). The importance of plasticizers in the case of plastisols is very high since they solvate the thermally coalescible material at an elevated temperature, and they become integral part of the final structure. Poor plasticizers may exude from the structure at a later time. Thus, they must be carefully considered in plasticizer selection for the particular polymer dispersion resin in question. Two or more plasticizers are commonly used in addition to the epoxide plasticizer since the epoxides give additional improvement in heat stability along with barium-cadmium-zinc stabilizers for polyvinyl chloride dispersion resins. Through proper combination of polymer dispersion resins and plasticizers, stabilizers, fillers, viscosity modifiers, etc., a wide range of properties may be attained upon thermal coalescence. For example, ultimate tensile and tear strength is obtained when using high molecular weight polymer resin, low amount of plasticizer, and sufficient processing time and temperature for complete fusion. To obtain increased elongation, increased amount of plasticizer and copolymer resin (i.e., vinyl chloride with 7% vinyl acetate copolymer) may be used. A desirable and important property plastisols impart to photohardenable formulations is lack of substantial shrinkage during the photohardening and fusion (thermal coalescing) step.

One or more monomers may be used in the composition. Monomers may be mono-, difunctional, trifunctional or multifunctional acrylates, methacrylates, vinyl, allyl, and the like. They may comprise other functional and/or photosensitive groups, such as epoxy, vinyl, isocyanate, urethane, and like, either by themselves if they are capable of rendering the monomer photohardenable, or in addition to acrylates or methacrylates.

Examples of suitable ethylenically unsaturated monomers which can be used alone or in combination with other monomers include but are not limited to t-butyl acrylate and methacrylate, 1,5-pentanediol diacrylate and dimethacrylate, N,N-

diethylaminoethyl acrylate and methacrylate, ethylene glycol diacrylate and dimethacrylate, 1,4-butanediol diacrylate and dimethacrylate, diethylene glycol diacrylate and dimethacrylate, hexamethylene glycol diacrylate and dimethacrylate, 1,3-propanediol diacrylate and dimethacrylate, decamethylene glycol diacrylate and dimethacrylate, 1,4-cyclohexanediol diacrylate and dimethacrylate, 2,2-dimethylolpropane diacrylate and dimethacrylate, glycerol diacrylate and dimethacrylate, tripropylene glycol diacrylate and dimethacrylate, glycerol triacrylate and trimethacrylate, trimethylolpropane triacrylate and trimethacrylate, pentaerythritol triacrylate and trimethacrylate, polyoxyethylated trimethylolpropane triacrylate and trimethacrylate and similar compounds as disclosed in U.S. Patent US-A-3 380 831, 2,2-di(p-hydroxyphenyl)-propane diacrylate, pentaerythritol tetraacrylate and tetramethacrylate, 2,2-di(p-hydroxyphenyl)-propane dimethacrylate, triethylene glycol diacrylate, polyoxyethyl-2,2-di(p-hydroxyphenyl)propane dimethacrylate, di-(3-methacryloxy-2-hydroxypropyl) ether of bisphenol-A, di-(2-methacryloxyethyl) ether of bisphenol-A, di-(3-acryloxy-2-hydroxypropyl) ether of bisphenol-A, di-(2-acryloxyethyl) ether of bisphenol-A, di-(3-methacryloxy-2-hydroxypropyl) ether of 1,4-butanediol, triethylene glycol dimethacrylate, polyoxypropyltrimethylol propane triacrylate, butylene glycol diacrylate and dimethacrylate, 1,2,4-butanetriol triacrylate and trimethacrylate, 2,2,4-trimethyl-1,3-pentanediol diacrylate and dimethacrylate, 1-phenyl ethylene-1,2-dimethacrylate, diallyl fumarate, styrene, 1,4-benzenediol dimethacrylate, 1,4-diisopropenyl benzene, and 1,3,5-trisopropenyl benzene. Also useful are ethylenically unsaturated compounds having a molecular weight of at least 300, e.g., alkylene or a polyalkylene glycol diacrylate prepared from an alkylene glycol of 2 to 15 carbons or a polyalkylene ether glycol of 1 to 10 ether linkages, and those disclosed in U.S. Patent US-A-2 927 022, e.g., those having a plurality of addition polymerizable ethylenic linkages particularly when present as terminal linkages. Also included are all methacrylates, tetrahydrofurfuryl methacrylate, cyclohexyl methacrylate, diallylfumarate, n-benzylacrylate, Carbowax® 550 acrylate, methyl Cellosolve® acrylate, dicyclopentenyl acrylate, isodecyl acrylate, 2(2-ethoxyethoxy) ethylacrylate, polybutadiene diacrylate, tris (2-hydroxyethyl) isocyanurate triacrylate, epoxy diacrylate tetrabromo bisphenol A diacrylate. Monomers with vinyl group like vinyl pyrrol, N-vinyl pyrrolidone and vinyl ethers are usable. Also, oligomers with mono or multifunctional groups such as the ones with carbon group for alkali removability, and the ones with both acrylate and isocyanate end groups are useful. Particularly

preferred monomers are polyoxyethylated trimethylolpropane triacrylate, ethylated pentaerythritol triacrylate, dipentaerythritol monohydroxypentaacrylate and 1,10-decanediol dimethylacrylate. Others are caprolactone acrylates and methacrylates, propoxylated neopentyl glycol diacrylates and methacrylates.

Di-(3-acryloxy-2-hydroxypropyl) ether of bisphenol A and Di-(3-methacryloxy-2-hydroxypropyl) ether of bisphenol A oligomers, generally referred to as unsaturated bisphenol A oligomers are of particular interest because they provide higher photospeed; also urethane diacrylates and methacrylates with aliphatic or aromatic backbones, referred to as unsaturated urethane oligomers are of particular interest, because they provide both higher photospeed and higher flexibility.

Monomers which expand on polymerization can be used in part with the standard monomers to achieve compositions giving no shrinkage or warpage upon exposure. These monomers are based on polycyclic ring opening mechanisms. Spiro-ortho-carbonates, spiro-ortho-esters and bicyclic ortho-esters are known to belong to this class. Typical monomers are norborene spiro-ortho-carbonate, and bismethylene-spiro-ortho-carbonate. Monomers which undergo cationic polymerization are also useful in this invention. Representative classes of monomers are cyclic ethers cyclic formals and acetals, lactones, vinyl monomers, sulfur containing monomers, organosilicone monomers, monofunctional epoxies, difunctional epoxies, epoxy prepolymers and higher oligomers and epoxy end-capped silicone resins. They can be found in the open literature. One such reference is "Photoinitiated cationic polymerization" by James V. Crivello in "UV Curing: Science and Technology" edited by S. P. Pappas, published by Technology Marketing Corporation, 1978. Other ring opening monomers can be found in "Ring Opening Polymerization" Edited by K. J. Ivin and T. Saegusa, Elsevier Applied Science Publishers, London and New York, 1984.

Examples of photoinitiators which are useful in the present invention alone or in combination are described in U.S. Patent US-A-2 760 863 and include vicinal ketaldehydyl alcohols such as benzoin, pivaloin, acyloin ethers, e.g., benzoin methyl and ethyl ethers, benzil dimethyl ketal; α -hydrocarbon-substituted aromatic acyloins, including α -methylbenzoin α -allylbenzoin and α -phenylbenzoin, others are 1-hydroxycyclobenzyl phenol ketone, diethoxyphenol acetophenone, 2-methyl-1-[4-(methyl thio)phenyl], 2-morpholino-propane-1, benzophenone, Michler's ketone, substituted triphenyl imidazolyl dimers with chain transfer agent camphoquinone etc. Photoreducible dyes and reducing agents disclosed in U.S. Patents US-A-2 850 445, US-A-2

875 047; US-A-3 097 096, US-A-3 074 974, US-A-3 097 097 and US-A-3 145 104, as well as dyes of the phenazine, oxazine, and quinone classes, Mich-
 z's ketone, benzophenone, acryloxy ben-
 zophenone, 2,4,5-triphenylimidazolyl dimers with
 hydrogen donors including leuco dyes and mix-
 tures thereof as described in U.S. Patents US-A-3
 427 161, US-A-3 479 185 and US-A-3 549 367 can
 be used as initiators. Also useful with photoiniti-
 ators and photoinhibitors are sensitizers disclosed in
 U.S. Patent US-A-4 162 162. The photoinitiator or
 photoinitiator system is present in 0.05 to 10% by
 weight based on the total weight of the photohar-
 denable composition. Other suitable photoinitiation
 systems which are thermally inactive but which
 generate free radicals upon exposure to actinic
 light at or below 185 °C include the substituted or
 unsubstituted polynuclear quinones which are com-
 pounds having two intracyclic carbon atoms in a
 conjugated carbocyclic ring system, e.g., 9,10-an-
 traquinone, 2-methylantraquinone, 2-ethylantra-
 quinone, 2-tert-butylantraquinone, octamethylan-
 traquinone, 1,4-naphthoquinone, 9,10-phenanth-
 raquinone, benz(a)anthracene-7,12-dione, 2,3-naph-
 thacene-5,12-dione, 2-methyl-1,4-naphthoquinone,
 1,4-dimethyl-antraquinone, 2,3-dimethylantra-
 quinone, 2-phenylantraquinone, 2,3-diphenylan-
 traquinone, retenequinone, 7,8,9,10-
 tetrahydronaphthacene-5,12-dione, and 1,2,3,4-
 tetrahydrobenz(a)anthracene-7,12-dione. Also, al-
 pha amino aromatic ketones, halogenated com-
 pounds like trichloromethyl substituted cyclohex-
 adienones and triazines or chlorinated acetophe-
 none derivatives, thioxanthenes in presences or
 tertiary amines, and titanocenes.

Typical classes of initiators for cationic poly-
 merization are aryldiazonium salts, diaryliodonium
 salts comprising nonnucleophilic counterions such
 as SbF_6^- , BF_4^- , PF_6^- , ClO_4^- , CF_3SO_3^- , AsF_6^- ,
 triacylsulfonium salts, triarylselenium salts or iron
 arene complex. Examples of these include but are
 not limited to 2,5-diethoxy-4-(p-tolylmercapto) ben-
 zene diazonium PF_6^- , 4-dimethylamine-naphthalene
 diazonium PF_6^- , diphenyliodonium hexafluoroar-
 senate, di-*t*-butyldiphenyliodonium hex-
 afluorophosphate FX-512 sulfonium salt (by 3M
 Company), triethylsulfonium iodide, CG24-61 (by
 Ciba Geigy). One good reference book is
 Photoinitiation of Cationic Polymerization men-
 tioned earlier.

Sensitizers useful with these photoinitiators for
 radical polymerization include but are not limited to
 methylene blue and those disclosed in U.S. Patents
 US-A-3 554 753, US-A-3 563 750, US-A-3 563 751,
 US-A-3 647 487, US-A-3 652 275, US-A-4 162 162,
 US-A-4 268 667, US-A-4 351 893, US-A-4 454 218,
 US-A-4 535 052 and US-A-4 565 769. A preferred
 group of sensitizers include the bis(p-dial-

kylaminobenzylidene) ketones disclosed in Baum et
 al., U.S. Patent US-A-3 652 275 and the arylidene
 aryl ketones disclosed in Dueber, U.S. Patent US-
 A-4 162 162, as well as in U.S. Patents US-A-4 268
 667 and US-A-4 351 893. Useful sensitizers are
 also listed in Dueber, U.S. Patent US-A-4 162 162
 column 6, line 1 to line 65. Particularly preferred
 sensitizers include the following: DBC, i.e.,
 cyclopentanone; 2,5-bis-[4-(diethylamino)-2-methyl-
 phenyl]methylene]; DEAW, i.e., cyclopentanone,
 2,5-bis[4-(diethylamino)phenyl]methylene];
 dimethoxy-JDI, i.e., 1H-inden-1-one, 2,3-dihydro-
 5,6-dimethoxy-2-[(2,3,6,7-tetrahydro-1H,5H-benzo-
 [i,j]quinolizin-9-yl)methylene]-, and JAW, i.e.,
 cyclopentanone, 2,5-bis[(2,3,6,7-tetrahydro-1H,5H-
 b-enzo[i,j]quinolizin-1-yl)methylene]-. Also useful
 are cyclopentanone 2,5-bis[2-(1,3-dihydro-1,3,3-
 trimethyl-2H-indol-2-ylidene)ethylidene], CAS
 27713-85-5; and cyclopentanone, 2,5-bis-[2-
 ethylnaphtho[1,2-d]thiazol-2(1H)-ylidene)-
 ethylidene], CAS 27714-25-6.

Sensitizers for cationic polymerization include
 but are not limited to perylene, acridine orange,
 acridine yellow, phosphene R, benzoflavin &
 Setoflavin T. Hydrogen donor compounds useful as
 chain transfer agents in the photopolymer composi-
 tions include: 2-mercaptobenzoxazole, 2-mercapto-
 benzothiazole, 4-methyl-4H-1,2,4, triazole-3-thiol,
 and the like; as well as various types of com-
 pounds, e.g., (a) ethers, (b) esters, (c) alcohols, (d)
 compounds containing allylic or benzylic hydrogen
 cumene, (e) acetals, (f) aldehydes, and (g) amides
 as disclosed in column 12, lines 18 to 58 of
 MacLachlan, U.S. Patent US-A-3,390,996

Other components may also be present in the
 photohardenable compositions, e.g., dyes, pig-
 ments, extenders, organic or inorganic fillers, or-
 ganic or inorganic reinforcement fibers, polymeriza-
 tion inhibitors, thermal stabilizers, viscosity modifi-
 ers, interlayer and generally interfacial adhesion
 promoters, such as organosilane coupling agents,
 coating aids, etc., so long as the photohardenable
 compositions retain their essential properties as set
 forth above.

Claims

1. A method of fabricating an integral three-di-
 mensional object from a multiplicity of cross-
 sectional portions of the object, the cross-sec-
 tional portions corresponding to photo-harden-
 ed portions of contiguous layers of a photo-
 hardenable liquid composition, comprising the
 steps of:

- (a) forming a layer (48) of the photo-har-
 denable composition (Figure 3);
- (b) providing imagewise an object-forming
 exposure to the cross-sectional portion (11)



875 047, US-A-3 097 096, US-A-3 074 974, US-A-3 097 097 and US-A-3 145 104, as well as dyes of the phenazine, oxazine, and quinone classes, Michler's ketone, benzophenone, acryloxy benzophenone, 2,4,5-triphenylimidazolyl dimers with hydrogen donors including leuco dyes and mixtures thereof as described in U.S. Patents US-A-3 427 161, US-A-3 479 185 and US-A-3 549 367 can be used as initiators. Also useful with photoinitiators and photoinhibitors are sensitizers disclosed in U.S. Patent US-A-4 162 162. The photoinitiator or photoinitiator system is present in 0.05 to 10% by weight based on the total weight of the photohardenable composition. Other suitable photoinitiation systems which are thermally inactive but which generate free radicals upon exposure to actinic light at or below 185 °C include the substituted or unsubstituted polynuclear quinones which are compounds having two intracyclic carbon atoms in a conjugated carbocyclic ring system, e.g., 9,10-anthraquinone, 2-methylanthraquinone, 2-ethylanthraquinone, 2-tert-butylanthraquinone, octamethylanthraquinone, 1,4-naphthoquinone, 9,10-phenanthraquinone, benz(a)anthracene-7,12-dione, 2,3-naphthacene-5,12-dione, 2-methyl-1,4-naphthoquinone, 1,4-dimethyl-anthraquinone, 2,3-dimethylanthraquinone, 2-phenylanthraquinone, 2,3-diphenylanthraquinone, retenequinone, 7,8,9,10-tetrahydronaphthacene-5,12-dione, and 1,2,3,4-tetrahydrobenz(a)anthracene-7,12-dione. Also, alpha amino aromatic ketones, halogenated compounds like trichloromethyl substituted cyclohexadienones and triazines or chlorinated acetophenone derivatives, thioxanthenes in presences or tertiary amines, and titanocenes.

Typical classes of initiators for cationic polymerization are aryldiazonium salts, diaryliodonium salts comprising nonnucleophilic counterions such as SbF_6^- , BF_4^- , PF_6^- , ClO_4^- , CF_3SO_3^- , AsF_6^- , triacylsulfonium salts, triarylselenium salts or iron arene complex. Examples of these include but are not limited to 2,5-diethoxy-4-(p-tolylmercapto) benzene diazonium PF_6^- , 4-dimethylamine-naphthalene diazonium PF_6^- , diphenyliodonium hexafluoroarsenate, di-*t*-butyldiphenyliodonium hexafluorophosphate FX-512 sulfonium salt (by 3M Company), triethylsulfonium iodide, CG24-61 (by Ciba Geigy). One good reference book is Photoinitiation of Cationic Polymerization mentioned earlier.

Sensitizers useful with these photoinitiators for radical polymerization include but are not limited to methylene blue and those disclosed in U.S. Patents US-A-3 554 753, US-A-3 563 750, US-A-3 563 751, US-A-3 647 467, US-A-3 652 275, US-A-4 162 162, US-A-4 268 667, US-A-4 351 893, US-A-4 454 218, US-A-4 535 052 and US-A-4 565 769. A preferred group of sensitizers include the bis(p-dial-

kylaminobenzylidene) ketones disclosed in Baum et al., U.S. Patent US-A-3 652 275 and the arylidene aryl ketones disclosed in Dueber, U.S. Patent US-A-4 162 162, as well as in U.S. Patents US-A-4 268 667 and US-A-4 351 893. Useful sensitizers are also listed in Dueber, U.S. Patent US-A-4 162 162 column 6, line 1 to line 65. Particularly preferred sensitizers include the following: DBC, i.e., cyclopentanone; 2,5-bis-[4-(diethylamino)-2-methylphenyl]methylene-; DEAW, i.e., cyclopentanone, 2,5-bis[4-(diethylamino)phenyl]methylene-; dimethoxy-JDI, i.e., 1H-inden-1-one, 2,3-dihydro-5,6-dimethoxy-2-[(2,3,6,7-tetrahydro-1H,5H-benzo-[i,j]quinolizin-9-yl)methylene]-, and JAW, i.e., cyclopentanone, 2,5-bis[(2,3,6,7-tetrahydro-1H,5H-benzo-[i,j]quinolizin-1-yl)methylene]-. Also useful are cyclopentanone 2,5-bis[2-(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)ethylidene], CAS 27713-85-5; and cyclopentanone, 2,5-bis-[2-ethylnaphtho[1,2-d]thiazol-2(1H)-ylidene)ethylidene], CAS 27714-25-6.

Sensitizers for cationic polymerization include but are not limited to perylene, acridine orange, acridine yellow, phosphene R, benzoflavin & Setoflavin T. Hydrogen donor compounds useful as chain transfer agents in the photopolymer compositions include: 2-mercaptobenzoxazole, 2-mercaptobenzothiazole, 4-methyl-4H-1,2,4-triazole-3-thiol, and the like; as well as various types of compounds, e.g., (a) ethers, (b) esters, (c) alcohols, (d) compounds containing allylic or benzylic hydrogen cumene, (e) acetals, (f) aldehydes, and (g) amides as disclosed in column 12, lines 18 to 58 of MacLachlan, U.S. Patent US-A-3,390,996

Other components may also be present in the photohardenable compositions, e.g., dyes, pigments, extenders, organic or inorganic fillers, organic or inorganic reinforcement fibers, polymerization inhibitors, thermal stabilizers, viscosity modifiers, interlayer and generally interfacial adhesion promoters, such as organosilane coupling agents, coating aids, etc., so long as the photohardenable compositions retain their essential properties as set forth above.

Claims

1. A method of fabricating an integral three-dimensional object from a multiplicity of cross-sectional portions of the object, the cross-sectional portions corresponding to photo-hardened portions of contiguous layers of a photohardenable liquid composition, comprising the steps of:

- (a) forming a layer (48) of the photohardenable composition (Figure 3);
- (b) providing imagewise an object-forming exposure to the cross-sectional portion (11)



of the object, adequate to imagewise photo-harden said portion (Figure 5);

(c) introducing a new layer of the photo-hardenable liquid composition onto the layer subjected to step (b); and

(d) repeating steps (b) and (c) until all layers of the three-dimensional object have photo-hardened;

characterised in that:

the photo-hardenable composition is also a photo-gellable composition;

for each object-forming exposure step, a gelling exposure of the layer is provided, adequate to produce a soft-gelled area (45), surrounding the cross-sectional portion of the object to be formed in the subsequent step (b) (Figure 4);

as a result of step (d) all of the soft-gelled areas have formed a soft-gelled mass surrounding the three-dimensional object, the object being separated from the gelled areas by an interface; and

after step (d) the soft-gelled mass is removed in order to recover the three-dimensional object.

2. A method as defined in claim 1, wherein each gelling exposure is a flood exposure.

3. A method as defined in claim 1 or 2, further comprising the step of providing an interface-forming exposure at the interface (99) of the object and the gelled area, said interface-forming exposure being lower than the gelling exposure.

4. A method as defined in any preceding claim, further comprising the step of providing a wall-forming exposure to the periphery of the gelled area, after step (a) and before step (c), the wall-forming exposure being adequate to photo-harden a layer (46) of a circumferential wall, the wall being built to contain the gelled area.

5. A method of fabricating an integral three-dimensional object from a multiplicity of cross-sectional portions of the object, the cross-sectional portions corresponding to photo-hardened portions of contiguous layers of a photo-hardenable liquid composition, comprising the steps of:

(a) forming a layer (48) of the photo-hardenable composition (Figure 3);

(b) providing imagewise an object-forming exposure to the cross-sectional portion (11) of the object, adequate to imagewise photo-harden said portion (Figure 5);

(c) introducing a new layer of the photo-hardenable liquid composition onto the layer subjected to step (b); and

(d) repeating steps (b) and (c) until all layers of the three-dimensional object have photo-hardened;

characterised in that:

for each object-forming exposure step, a wall-forming exposure step is provided to form a layer (46) of a peripheral wall of the photo-hardenable composition around the respective cross-sectional portion of the three-dimensional object by exposing the peripheral wall to radiation.

6. A method as defined in any preceding claim, wherein each wallforming exposure is a flood exposure.

7. A method as defined in any preceding claim, wherein the layers are formed by one of curtain coating, extrusion and spraying.

8. A method as defined in any preceding claim, wherein the layers are levelled by doctoring.

9. A method as defined in any preceding claim, wherein the photo-hardenable composition comprises a plastisol.

10. A method as defined in any preceding claim, further comprising the step of heat treating the three-dimensional object.

11. An apparatus for fabricating an integral three-dimensional rigid object from contiguous layers of a liquid photo-hardenable composition, comprising:

a coating station (80) comprising: a substantially flat support surface (41) for supporting the rigid object; and a dispenser (43) above the support surface for dispensing the photo-hardenable composition in the form of contiguous layers; and

imaging means (70) for selectively exposing to radiation each of the contiguous layers of the photo-hardenable composition, the imaging means (70) including an object-forming exposure element (16) for exposing cross-sectional portions of the contiguous layers corresponding to the three-dimensional object;

characterised in that:

the support surface is in the form of a substantially flat platform (41);

the coating station (80) further comprises: a vessel (44) in which the platform is disposed for collecting the liquid photo-hardenable composition; and means (47) for recirculating the



photo-hardenable composition from the vessels (44) to the dispenser (43); and

the imaging means (70) further includes a further exposure element (15) for exposing an area around each cross-sectional portion.

12. An apparatus as defined in claim 11, wherein the object-forming exposure element provides a laser beam (12").

13. An apparatus as defined in claim 11 or 12, wherein the further exposure element comprises an image projector (15).

14. An apparatus as defined in any of claims 11 to 13, further comprising a third exposure element in the form of another image projector (17).

5. An apparatus as defined in any of claims 11 to 14, further comprising a computer (34) for controlling the functions of the exposure elements with regard to the functions of the coating station (80).

Patentansprüche

1. Verfahren zur Herstellung eines einstückigen dreidimensionalen Objekts aus einer Vielzahl von Querschnittsteilen des Objekts, wobei die Querschnittsteile lichtgehärteten Bereichen aneinander angrenzender Schichten einer lichthärtbaren Flüssigkeitszusammensetzung entsprechen, wobei das Verfahren die folgenden Schritte aufweist:

(a) Bilden einer Schicht (48) aus der lichthärtbaren Zusammensetzung (Figur 3);

(b) bildweises objektformendes Belichten des Querschnittsbereichs (11) des Objekts in einer zum bildweisen Lichthärten des Bereichs geeigneten Weise (Figur 5);

(c) Einleiten einer neuen Schicht der lichthärtbaren Flüssigkeitszusammensetzung auf die dem Schritt (b) ausgesetzte Schicht; und

(d) Wiederholen der Schritte (b) und (c), bis sämtliche Schichten des dreidimensionalen Objekts lichtgehärtet sind;

dadurch gekennzeichnet, daß

- die lichthärtbare Zusammensetzung auch eine durch Licht gelierbare Zusammensetzung ist;

- in jedem objekt-formenden Belichtungsschritt eine gelbildende Belichtung durchgeführt wird, die zur Bildung einer weich-gelierten Fläche (45) geeignet ist, welche den Querschnittsbereich des im nachfolgenden Schritt

(b) zu formenden Objekts umgibt (Figur 4);

- als Ergebnis des Schritts (d) sämtliche weich-gelierten Flächen eine weich-gelierte Masse bilden, die das dreidimensionale Objekt umschließt, wobei das Objekt durch eine Zwischenschicht von den gelierten Flächen getrennt ist; und

- die weich-gelierte Masse nach dem Schritt (d) zur Gewinnung des dreidimensionalen Objekts entfernt wird.

2. Verfahren nach Anspruch 1, bei dem jede gelbildende Belichtung eine Flut-Belichtung ist.

3. Verfahren nach Anspruch 1 oder 2, ferner mit dem Schritt des Vorsehens einer Belichtung zur Bildung einer Zwischenschicht an der Berührungsfläche (99) des Objekts und der gelierten Fläche, wobei die Belichtung zur Bildung der Zwischenschicht schwächer als die gelbildende Belichtung ist.

4. Verfahren nach einem der vorhergehenden Ansprüche, ferner mit dem Schritt des Aufbringens einer wandbildenden Belichtung auf den Umfang der gelierten Fläche nach dem Schritt (a) und vor dem Schritt (c), wobei die wandbildende Belichtung zum Lichthärten einer Schicht (46) einer Umfangswand geeignet ist, und wobei die Wand zum Einschließen der gelierten Fläche erstellt wird.

5. Verfahren zur Bildung eines einstückigen dreidimensionalen Objekts aus einer Vielzahl von Querschnittsbereichen des Objekts, wobei die Querschnittsbereiche lichtgehärteten Bereichen aneinander angrenzender Schichten einer lichthärtbaren Flüssigkeitszusammensetzung entsprechen, mit den folgenden Schritten:

(a) Bilden einer Schicht (48) aus der lichthärtbaren Zusammensetzung (Figur 3);

(b) bildweises objekt-formendes Belichten des Querschnittsbereichs (11) des Objekts in einer zum bildweisen Lichthärten des Bereichs geeigneten Weise (Figur 5);

(c) Einleiten einer neuen Schicht der lichthärtbaren Flüssigkeitszusammensetzung auf die dem Schritt (b) ausgesetzte Schicht; und

(d) Wiederholen der Schritte (b) und (c), bis sämtliche Schichten des dreidimensionalen Objekts lichtgehärtet sind;

dadurch gekennzeichnet, daß

- in jedem objekt-formenden Belichtungsschritt ein wandbildender Belichtungsschritt durchgeführt wird, um



- eine Schicht (46) einer Umfangswand aus der lichthärtbaren Zusammensetzung um den jeweilige Querschnittsbereich des dreidimensionalen Objekts zu bilden, indem die Umfangswand einer Strahlung ausgesetzt wird.
6. Verfahren nach einem der vorhergehenden Ansprüche, bei dem jede Belichtung zur Bildung einer Wand eine Flut-Belichtung ist.
7. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Schichten entweder durch Gießen, Extrudieren oder Sprühen gebildet werden.
8. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Schichten durch Rakeln vergleichmäßig werden.
9. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die lichthärtbare Zusammensetzung ein Plastisol aufweist.
10. Verfahren nach einem der vorhergehenden Ansprüche, ferner mit dem Schritt des Wärmebehandelns des dreidimensionalen Objekts.
11. Vorrichtung zum Bilden eines einstückigen dreidimensionalen starren Objekts aus aneinander angrenzenden Schichten einer flüssigen lichthärtbaren Zusammensetzung, mit:
- einer Beschichtungsstation (80) mit: einer im wesentlichen ebenen Stützfläche (41) zum Stützen des starren Objekts; und einer über der Stützfläche befindlichen Ausgabeeinrichtung (43) zum Ausgeben lichthärtbaren Zusammensetzung in Form von durchgehenden Schichten; und
 - einer Abbildungseinrichtung (70), um wahlweise jede der zusammenhängenden Schichten der lichthärtbaren Zusammensetzung Strahlung auszusetzen, wobei die Abbildungseinrichtung (70) ein objektformendes Belichtungselement (16) zum Belichten von Querschnittsbereichen der durchgehenden Schichten entsprechend dem dreidimensionalen Objekt aufweist;
- dadurch gekennzeichnet, daß
- die Stützfläche die Form einer im wesentlichen ebenen Plattform (41) aufweist;
 - die Beschichtungsstation (80) ferner aufweist: ein Gefäß (44), in dem die Plattform angeordnet ist, zum Sammeln der flüssigen lichthärtbaren Zusammensetzung; und eine Einrichtung (47) Rückfüh-
- ren der lichthärtbaren Zusammensetzung von dem Gefäß (44) zur Ausgabeeinrichtung (43); und
- die Abbildungseinrichtung (70) ferner ein weiteres Belichtungselement (15) zum Belichten einer Fläche um jeden Querschnittsbereich aufweist.
12. Vorrichtung nach Anspruch 11, bei der das Objektformungsbelichtungselement einen Laserstrahl (12'') abgibt.
13. Vorrichtung nach Anspruch 11 oder 12, bei der das weitere Belichtungselement einen Bildprojektor (15) aufweist.
14. Vorrichtung nach einem der Ansprüche 11 bis 13, ferner mit einem dritten Belichtungselement in Form eines weiteren Bildprojektors (17).
15. Vorrichtung nach einem der Ansprüche 11 bis 14, ferner mit einem Computer (34) zum Steuern der Funktionen der Belichtungselemente in bezug auf die Funktionen der Beschichtungsstation (80).

Revendications

1. Un procédé de fabrication d'un objet tridimensionnel monobloc à partir d'une multiplicité de parties de sections transversales de l'objet, les parties de sections transversales correspondant à des parties photo-durcies de couches contiguës d'une composition liquide photo-durcissable comprenant les étapes consistant :
- a) à former une couche (48) de la composition photodurcissable (figure 3);
 - b) à appliquer une exposition de formation d'objets conformes à une image à la portion de section transversale (11) de l'objet, adéquate pour photo-durcir ladite portion conformément à une image (figure 5);
 - c) à introduire une nouvelle couche de la composition de liquide photo-durcissable sur la couche soumise à l'étape (b);
 - d) à répéter les étapes (b) (c) jusqu' à ce que toutes les couches de l'objet tridimensionnel aient été photodurcies; caractérisé en ce que :
- la composition photo-durcissable est également une composition photo-gélifiable;
 - pour chaque étape d'exposition de formation d'objets, on applique une exposition de gélification de la couche, adéquate pour former une zone (45) mollement gélifiée entourant la



- partie de section transversale de l'objet à former dans l'étape ultérieure (b) (figure 4);
- en résultat de l'étape (d) toutes les zones mollement gélifiées ont formé une masse mollement gélifiée entourant l'objet tridimensionnel, l'objet étant séparé des zones gélifiées par une interface; et
- après l'étape (d), la masse mollement gélifiée est retirée afin de récupérer l'objet tridimensionnel.
2. Un procédé selon la revendication 1, dans lequel chaque exposition de gélification est une exposition à la lumière flood (par projecteurs).
 3. Un procédé selon la revendication 1 ou 2, comprenant en outre l'étape consistant à appliquer une exposition de formation d'interface à l'interface (99) de l'objet et de la zone gélifiée, cette exposition de formation d'interface étant inférieure à l'exposition de gélification.
 4. Un procédé selon une quelconque revendication précédente, comprenant en outre l'étape qui consiste à appliquer une exposition de formation d'une paroi à la périphérie de la zone gélifiée, après l'étape (a) et avant l'étape (c), l'exposition de formation de paroi étant adéquate pour photodurcir une couche (46) d'une paroi circonférentielle, cette paroi étant prévue pour contenir la zone gélifiée.
 5. Un procédé de fabrication d'un objet tridimensionnel monobloc à partir d'une multiplicité de parties de sections transversales de l'objet, les parties de sections transversales correspondant à des parties photo-durcies de couches contiguës d'une composition liquide photo-durcissable, comprenant les étapes consistant :
 - (a) à former une couche (48) de la composition photo-durcissable (figure 3);
 - (b) à appliquer une exposition de formation d'objets conformes à une image à la portion de section transversale (11) de l'objet, adéquate pour photo-durcir cette portion conformément à une image (figure 5);
 - (c) à introduire une nouvelle couche de la composition de liquide photo-durcissable sur la couche soumise à l'étape (b);
 - (d) à répéter les étapes (b) (c) jusqu'à ce que toutes les couches de l'objet tridimensionnel aient été photodurcies; caractérisé en ce que :
 - pour chaque étape d'exposition de formation d'objets, on prévoit une étape d'exposition de formation de paroi pour former une couche (46) d'une paroi périphérique de la composition photo-durcissable autour de la partie de section transversale correspondante de l'objet tridimensionnel en exposant la paroi périphérique au rayonnement.
 6. Un procédé selon une quelconque revendication précédente, dans lequel chaque exposition de formation de paroi est une exposition à la lumière flood (par projecteurs).
 7. Un procédé selon l'une quelconque revendication précédente, dans lequel les couches sont formées par une étape de revêtement, d'extrusion et de pulvérisation de rideau.
 8. Un procédé selon une quelconque revendication précédente, dans lequel les couches sont nivelées par râclage.
 9. Un procédé selon une quelconque revendication précédente, dans lequel la composition photo-durcissable comprend un plastisol.
 10. Un procédé selon une quelconque revendication précédente, comprenant en outre l'étape de traitement thermique de l'objet tridimensionnel.
 11. Un dispositif de fabrication d'un objet rigide tridimensionnel monobloc à partir de couches contiguës d'une composition liquide photo-durcissable, comprenant :
 - un poste de revêtement (80) comprenant : une surface de support sensiblement plane (41) pour supporter l'objet rigide; et un distributeur (43) au-dessus de la surface de support pour distribuer la composition photo-durcissable sous la forme de couches contiguës; et
 - des moyens d'imagerie (70) pour exposer sélectivement au rayonnement chacune des couches contiguës de la composition photo-durcissable, les moyens d'imagerie (70) comprenant un élément (16) d'exposition de formation d'objets pour exposer des portions en coupe transversale des couches contiguës correspondant à l'objet tridimensionnel;
 caractérisé en ce que :
 - la surface de support se présente sous la forme d'une plate-forme sensiblement plane (41)
 - le poste de revêtement (80) comprend en outre : un récipient (44) dans lequel la



- plate-forme est disposée pour recueillir la composition photo-durcissable liquide; et des moyens (47) pour remettre la composition photo-durcissable en circulation depuis le récipient (44) jusqu'au distributeur (43); et
- les moyens d'imagerie (70) comprennent en outre un autre élément d'exposition (15) pour exposer une zone autour de chaque partie de section transversale.
12. Un dispositif selon la revendication 11, dans lequel l'élément d'exposition de formation d'objets émet un faisceau laser (12").
13. Un dispositif selon la revendication 11 ou 12, dans lequel l'autre élément d'exposition comprend un projecteur d'image (15).
14. Un dispositif selon l'une quelconque des revendications 11 à 13, comprenant en outre un troisième élément d'exposition sous la forme d'un autre projecteur d'image (17).
15. Un dispositif selon l'une quelconque des revendications 11 à 14, comprenant en outre un ordinateur (34) pour contrôler les fonctions des éléments d'exposition en corrélation avec les fonctions du poste de revêtement (80).

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