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STEREOLITHOGRAPHY USING COMPOSITION
PROVIDING REDUCED DISTORTION
DESCRIPTION

Technical Field

5 This invention relates to the production of
stereolithographically formed elements which are
complexly-shaped usually thin-walled polymeric
objects and which are incompletely cured as a result
of having been produced by an exposure to actinic
10 light, usually in or near the ultraviolet range,
which is inadequate to completely cure the polymer
constituting the objects.

Background Art

 It is known, as illustrated in U.S. Pat. No.
15 4,575,330 to C. W. Hull, to form three-dimensional
objects of complex shape using ultraviolet light to
solidify superposed layers of liquid
ultraviolet-curable ethylenically unsaturated
material at the surface of a liquid reservoir of such
20 material. Thin-walled objects are usually formed in
this manner, apparently thick walls being hollow and
dimensionally stabilized by thin internal webs,
albeit this is not always the case. The ultraviolet
dosage is limited to speed the action and to insure
25 that only the irradiated areas near the surface of
the unsaturated liquid will be solidified.

 As will be evident, the thin walled object
is incompletely cured and has inadequate strength and
durability. Of particular significance is the fact
30 that these stereolithographic processes are intended
to form three dimensional models which conform as
accurately as possible with what was intended, this
usually being set forth in drawings which are
cross-sectioned by computer to guide a laser beam in
35 the production of the superposed layers. However,

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the incompletely cured products tend to be somewhat distorted, so the accuracy of the model is less than desired.

As a result, it is necessary to provide
5 relatively low viscosity flowable liquid compositions which cure rapidly and which exhibit decreased distortion when only partially cured to possess some limited "green strength".

It is desired to point out that the
10 ultraviolet lasers used have limited capacity, so a larger exposure dosage would slow the stereolithographic process. Moreover, a greater exposure would increase the thickness and depth of the exposed line which solidifies, thus reducing the
15 dimensional accuracy of the stereolithographic process.

More particularly, the objects under consideration are formed by the ultraviolet polymerization of liquid ultraviolet-curable
20 ethylenically unsaturated material at the surface of a liquid reservoir of such material using an ultraviolet dosage in the range of 1-15, preferably 1-5, Joules per square centimeter which is sufficient to convert the unsaturated liquid into a lightly
25 cross-linked solvent-swellable three dimensional complexly-shaped polymeric thin-walled element constituted by incompletely polymerized solid polymer. A support is positioned beneath the surface of the reservoir to hold the polymerized layer which
30 is formed. The liquid level is then raised, or the support lowered, and another layer is formed until the photoformed object is completed within the liquid reservoir.

The photoformed objects are thus only
35 partially cured and are mechanically weak due to the

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low degree of cross-linking and the presence of unconverted monomers and oligomers (which are still unsaturated) within the partially polymerized polymeric structure of the solid object which is formed. The problem here, then, is to provide a flowable liquid composition which cures rapidly on exposure to light of appropriate wavelength to speed the stereolithographic process but which, at the same time, exhibits less distortion in its partially cured condition so that the gelatinous and weak solid products produced by ultraviolet exposure will more accurately reflect the shape of the object which it is desired to reproduce.

It is desired to point out that the distortion which results is a composite of the extent of shrinkage encountered during the cure, the strength of the partially cured polymer structure, and whatever mechanical stresses are imposed on the product before the object removed from the reservoir is further cured to strengthen the same and make it more rigid. The several different ways in which failure can be encountered make a practical solution much more difficult.

One can proceed in various ways to more completely cure (thermoset) the photoformed incompletely cured and mechanically weak objects after they have been removed from the liquid ultraviolet-curable ethylenically unsaturated material in which they were formed. One must be careful that handling problems and the additional cure does not introduce additional distortion. Nonetheless, if the incompletely cured object is itself distorted, that distortion is retained when the cure is completed. It is the minimization of the distortion in the incompletely cured object which is

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withdrawn from the reservoir which is dealt with herein. The distortion which is encountered is primarily a change in shape, and this is easily measured in various ways, albeit no special measurement technique is advocated herein.

Disclosure of Invention

In accordance with this invention, the ultraviolet-curable liquid ethylenically unsaturated composition which is used in the stereolithographic process is formulated to include from about 20% to about 80%, preferably from 35% to 70%, of a resinous polyacrylate or polymethacrylate. This resinous polyacrylate or polymethacrylate is dissolved in from about 80% to about 20%, preferably from 65% to 30%, of a liquid polyacrylate or polymethacrylate. The terms "polyacrylate" and "polymethacrylate" identify a plurality of acrylic acid or methacrylic acid ester groups. The proportions are by weight based on the weight of the unsaturated material present.

In the preferred practice of this invention, the ultraviolet-curable liquid composition which is used is formulated to include from 20% to 80%, preferably from 35% to 70%, of a resinous polyacrylate or polymethacrylate. This resinous polyacrylate or polymethacrylate is dissolved in a combination of 10% to 40%, preferably from 15% to 30%, of a liquid polyacrylate or polymethacrylate, and 10% to 40%, preferably from 15% to 30%, of a liquid N-vinyl monomer.

It is important that one of the foregoing liquid and resinous polyacrylates or polymethacrylates be a polyacrylate and that the other be a polymethacrylate. If both were polymethacrylates, the composition would cure too slowly. If both were polyacrylates, then severe

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distortion is seen. It is only when the resinous material is selected to contain one of the two specified types of ethylenic unsaturation and the liquid material is selected to provide the other type of ethylenic unsaturation that it is found that good cure speed is accompanied by good distortion resistance.

Other liquid or non-liquid unsaturated materials can be present in the liquid composition so long as they do not change the essential character of the combination of resinous and liquid poly(meth)acrylate.

More particularly, the above-described unsaturated liquid compositions are employed as a liquid reservoir which forms a thin liquid layer above a supporting platform, and the surface of this liquid reservoir is usually exposed to an ultraviolet dosage in the range of 1-15, preferably 1-5, Joules per square centimeter to partially cure the liquid at the surface. This process is repeated many times to superimpose one layer upon another and ultimately produce a three-dimensional object of partially cross-linked polymer within the liquid reservoir.

The specified exposure to light, e.g., the ultraviolet exposure, is sufficient to convert the unsaturated liquid into a lightly cross-linked solvent-swellable three dimensional complexly-shaped polymeric usually thin-walled element constituted by heat-softenable solid polymer. As a result, the photoformed objects are incompletely cured and mechanically weak due to the low degree of cross-linking and the presence of unconverted monomers and oligomers (which are still unsaturated) within the partially polymerized polymeric structure of the solid object which is formed. In this

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invention, the liquid compositions specified are found to cure rapidly to a dimensionally stable solid (rigid) condition which exhibits reduced distortion.

The resinous polyacrylate or
5 polymethacrylate provides a polymeric matrix which allows the ultimately fully cured rigid object to have the structural strength which is desired, and liquid polyacrylate or polymethacrylate provides the liquidity needed to have the easily flowable liquid
10 which is required by the process. The specified liquid polyacrylates or polymethacrylates, which are preferably illustrated by trimethylol propane trimethacrylate and pentaerythritol trimethacrylate, or the corresponding triacrylates, serve to reduce
15 the distortion encountered in going from the drawings which activate the computer-directed laser beam and the three dimensional model which is formed in the liquid reservoir.

In preferred practice, the resinous
20 component is combined with two other components which provide the liquidity needed to have the easily flowable liquid which is desired by the process. One of these two components, the N-vinyl monomer, is rapid curing to enable the rapid achievement of
25 "green strength", and the specified liquid polyacrylates or polymethacrylates, which are preferably illustrated by trimethylol propane trimethacrylate and pentaerythritol trimethacrylate, or the corresponding triacrylates, serve to reduce
30 the distortion encountered in going from the drawings which activate the computer-directed laser beam and the three dimensional model which is formed in the liquid reservoir.

The resinous polyacrylate or
35 polymethacrylate which provides a polymeric matrix

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enabling the ultimately fully cured rigid object to have its structural strength is subject to considerable variation so long as it is of resinous nature and contains an average of at least 2.0
5 acrylate or methacrylate groups per molecule. Resinous character generally denotes relatively viscous and sticky materials, and these generally have a molecular weight of at least about 500. These can be illustrated by epoxy diacrylates, such as Epon
10 1001 diacrylate or Epon 828 diacrylate, or one can use polyester diacrylates or polyurethane diacrylates. The Epon epoxy resins are diglycidyl ethers of bisphenol A, Epon 828 having a number average molecular weight of about 390 and Epon 1001
15 having a number average molecular weight of about 1,000. The corresponding methacrylate resins are also useful, but less preferred. Further useful materials are disclosed in the Examples.

As will be evident from the preference for
20 resinous polyacrylates, blends of polyacrylate resins and polymethacrylate liquids are the preferred blends.

The polyacrylate resins which are now preferred are polyurethane diacrylates, and especially those which employ a polyester base. More
25 particularly, one can take an hydroxy-functional polyester, preferably one having an average of from 2.1-5.0 hydroxy groups per molecule, and react it with monoacrylate monoisocyanate to form an acrylate-capped polyurethane polyacrylate. One such
30 product which is available in commerce is identified as Uvithane 893 from Morton Thiokol, Inc., Chicago, IL, and the use of this commercial polyacrylate polyurethane polyester will be illustrated later.

The preferred N-vinyl liquid monomer is
35 N-vinyl pyrrolidone, and N-vinyl caprolactam is also

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useful.

As previously indicated, it is preferred to combine a resinous polyacrylate with a liquid polymethacrylate. While liquid trimethacrylates are preferred, such as trimethylol propane trimethacrylate, dimethacrylates are also useful, such as 1,6-hexane diol dimethacrylate. Liquid polymethacrylates of higher functionality are also useful, such as pentaerythritol tetramethacrylate.

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10 When the resinous material is a polymethacrylate, the liquid material must be a polyacrylate, and 1,6-hexane diacrylate and polyacrylates of high functionality, like trimethylol propane triacrylate and pentaerythritol tetraacrylate, can be used in

15 such instance. The liquid materials which are intended are free flowing and generally have a molecular weight of less than about 350.

As will be evident from the examples presented later, the compositions of this invention

20 may include materials other than those which have been identified as essential herein, such as liquid monoacrylates and monomethacrylates, or other liquid or resinous materials of diverse nature. So long as the specified proportions of the two essential

25 components are selected as taught herein, these other materials do not change the reduction in distortion achieved herein.

From about 1% to about 10%, based on the weight of unsaturated material present, of a

30 photoinitiator effective on ultraviolet exposure to initiate the polymerization of acrylate unsaturation is included in the reservoir, albeit a liquid composition of this invention can be supplied without the photoinitiator which is added by the user prior

35 to use. These photoinitiators are themselves well

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known and in common use. They are usually ketonic, and frequently aromatic, such as benzophenone. It is presently preferred to use the phenyl ketone photoinitiators shown in the examples. It will be appreciated that photoinitiators for the ultraviolet polymerization of (meth)acrylate functional compounds are well known and in common use.

As will be understood, after the 3-dimensional model (object) has been formed within the liquid reservoir, it is withdrawn and excess unsaturated liquid is allowed to drain therefrom, usually back into the reservoir from which it was withdrawn where it can be reused. If desired, one can wash the incompletely cured solid model with an alcoholic liquid before proceeding to complete the cure, but this is usually dispensed with and is not necessary.

The draining operation is a simple one which can be carried out at room or slightly elevated temperature to reduce the viscosity of the unconverted liquid adhering to the photoformed object. It is convenient to allow the object to drain for periods of from 5 to 10 minutes, albeit this is not critical.

The removal of polymerizable liquid clinging to the photoformed object can be aided by rinsing with an alcoholic solvent having the capacity to dissolve the polymerizable liquid, but which does not dissolve the partially polymerized solid formed from that liquid, albeit present practice does not usually employ such a wash.

A typical alcoholic solvent is represented by an alcohol, such as isopropanol. If desired, one can add a minor proportion of an ester solvent, such as butyl acetate. Other useful alcohols are

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illustrated by ethyl alcohol and butanol. When water-miscible solvents are used, water can be present in the solvent mixture.

The time of immersion in the alcoholic wash composition is of secondary significance, albeit it is convenient to immerse the object in the solvent at room temperature for from 5 to 30 seconds to dissolve the adhering polymerizable liquid. The partially cured object is then removed and adhering solvent is allowed to drain therefrom.

Completion of the cure can be carried out in various ways. Most simply, the drained (and possibly washed) solid object is placed in an ultraviolet chamber and exposed uniformly to ultraviolet radiation to complete the cure. Other techniques can be used for completing the cure, such as employing other more penetrating radiation or heat, and any of these can be used. It will be understood, however, that the specific technique employed to increase the strength of the incompletely polymerized object withdrawn from the polymerizable liquid reservoir is not itself of importance in this invention.

On the other hand, the compositions of this invention cure well when exposed to a temperature of about 250°F, and this is unusual. A thermal cure at a temperature up to about 325°F is thus surprisingly effective and is a feature of this invention.

Preferably the baking temperature will not exceed about 300°F to insure avoidance of distortion during the cure. The thermal cure is advantageous since heat permeates all portions of the three dimensional object whereas exposure of that object to ultraviolet light might not reach all portions of the object.

On the other hand, the compositions of this invention cure well when exposed to elevated

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temperature, temperatures in the range of 325°F to 350°F being appropriate, albeit catalysts can be added to modify the baking temperature. The thermal cure is advantageous since heat permeates all
5 portions of the three dimensional object whereas exposure of that object to ultraviolet light might not reach all portions of the object.

As previously indicated, the removal of polymerizable liquid clinging to the photoformed
10 object can be aided by rinsing with an alcoholic solvent having the capacity to dissolve the polymerizable liquid, but which does not dissolve the partially polymerized solid formed from that liquid, albeit present practice does not usually employ such
15 a wash.

A typical alcoholic solvent is represented by an alcohol, such as isopropanol. If desired, one may add a minor proportion of an ester solvent, such as butyl acetate. Other useful alcohols are
20 illustrated by ethyl alcohol and butanol. When water-miscible solvents are used, water may be present in the solvent mixture.

The time of immersion in the alcoholic wash composition is of secondary significance, albeit it
25 is convenient to immerse the object in the solvent at room temperature for from 5 to 30 seconds to dissolve the adhering polymerizable liquid. The partially cured object is then removed and adhering solvent is allowed to drain therefrom.

30 An illustration of a (meth)acrylate-functional photocurable liquid which is useful to provide the bath of liquid ultraviolet-curable ethylenically unsaturated material the surface of which is exposed to
35 ultraviolet radiation in accordance with this

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invention was provided by mixing 60 grams of a polyacrylate-functional polyurethane polyester resin (hydroxy-terminated polyester of ethylene glycol and adipic acid (number average molecular weight of 1500) reacted with isophorone diisocyanate and then capped with 2-hydroxyethyl acrylate (Uvithane 893 from Morton Thiokol can be used]), 40 grams of trimethylol propane trimethacrylate, and 4 grams of a benzyl ketal-based photoinitiator (2-hydroxypropyl phenone [Darocur 1173 from EM Chemicals can be used]).

Another photoinitiator which is fully useful in this example in the same proportion is 1-hydroxycyclohexyl phenyl ketone available from Ciba-Geigy Corporation, Ardsley, NY, under the trade designation Irgacure 184.

The liquid bath of the above photopolymerizable liquid was exposed to ultraviolet light using a Liconix model 4240 N, helium-cadmium light having an output of 15 milliwatts at 325 nanometers focused to 350 micron diameter. The usually used dosage is about 3.0 Joules per square centimeter of surface which results in test specimens of about 20 mil thickness.

After draining for 10 minutes, the drained piece can be washed briefly in an alcoholic solvent mixture of isopropanol and butyl acetate in a weight ratio of 64/33 to facilitate complete removal of polymerizable liquid, but in this example washing was not employed.

The drained parts were then exposed to ultraviolet light in a sealed chamber to provide a post-cure, and the exposure was continued until the parts are as fully cured as desired. As will be apparent, the drained parts must be rigid enough to avoid distortion when handled and subjected to additional cure. After such additional cure, the

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cured parts are expected to sustain some significant load without distortion.

Repeating the foregoing, but using an oven at 330°F to provide the post-cure, a good cure is
5 obtained in about 10 minutes.

The above example is also repeated by mixing 60 grams of a polymethacrylate-functional resin (the dimethacrylate of Shell Chemical Company product Epon 1001 which is a diglycidyl ether of bisphenol A
10 having a number average molecular weight of about 1000) 40 grams of trimethylol propane triacrylate, and 4 grams of a benzyl ketal-based photoinitiator (2-hydroxypropyl phenone [Darocur 1173 from EM Chemicals can be used]). Corresponding results are
15 obtained.

A further illustration of a (meth)acrylate-functional photocurable liquid which is useful to provide the bath of liquid ultraviolet-curable ethylenically unsaturated
20 material is provided by mixing 50 grams of a resinous diacrylate of a bisphenol A-based diepoxide (a diglycidyl ether of bisphenol A having a molecular weight of about 390 reacted with 2 molar proportions of acrylic acid [the Celanese Corporation,
25 Louisville, KY, product Celrad 3700 can be used]), 15 grams of a dimethacrylate of a bisphenol A-based diepoxide (the dimethacrylate of the same diglycidyl ether used in Celrad 3700) [the Celanese product RDX 26936 can be used]), 25 grams of liquid tetraethylene
30 glycol dimethacrylate (the Sartomer Company, Westchester PA, product SR 209 can be used), 10 grams of liquid hexane diol dimethacrylate (Sartomer product SR 239), 4 grams of a benzyl ketal-based photoinitiator (2-hydroxypropyl phenone [Darocur 1173
35 from EM Chemicals can be used]), 2 grams of ethyl

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diethanol amine (from Aldrich Chemical Company, Incorporated, Milwaukee, WI), and 0.1 grams of methoxy phenol (from Eastman Kodak Company, Rochester, NY). This composition is fully useful in
5 this invention and its use in the method provides reduced distortion in comparison with the use of a similar all acrylate-functional composition. An all methacrylate-functional composition cures too slowly to be practical.

10 Another illustration of a (meth)acrylate-functional photocurable liquid which is useful to provide the bath of liquid ultraviolet-curable ethylenically unsaturated material useful in this invention is provided by
15 mixing 50 grams of a resinous diacrylate of a bisphenol A-based diepoxide (the Celanese product Celrad 3700 can be used), 21 grams of liquid tetraethylene glycol dimethacrylate (Sartomer 209), 17 grams of methoxy hexane diol monoacrylate, 8 grams
20 of liquid hexane diol dimethacrylate (Sartomer SR 239), 4 grams of an oligomer amine monoacrylate (Celrad 7100 from Celanese), 4 grams of a benzyl ketal-based photoinitiator (2-hydroxypropyl phenone [Darocur 1173 from EM Chemicals can be used]), and
25 0.1 grams of methoxy phenol (from Eastman Kodak Company). This composition is fully useful in this invention and exhibits reduced distortion in comparison with the use of a similar all acrylate-functional composition.

30 Another illustration of a (meth)acrylate-functional photocurable liquid which is useful to provide the bath of liquid ultraviolet-curable ethylenically unsaturated material useful in this invention is provided by
35 mixing 34 grams of a resinous diacrylate of a

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diglycidyl ether of bisphenol A having a number average molecular weight of about 390 (the Cargill Incorporated, Carpenterville, IL, product PN 1570 can be used), 33 grams of a liquid dimethacrylate of a bisphenol A-based ethoxylate (Sartomer SR 348 can be used), 33 grams of the reaction product of isocyanatoethyl methacrylate from Dow Chemical Company, Midland MI, and 2-ethyl hexanol from Aldrich, 4 grams of a benzyl ketal-based photoinitiator (2-hydroxypropyl phenone [Darocur 1173 from EM Chemicals can be used]), 2 grams of ethyl diethanol amine (from Aldrich), and 0.1 grams of methoxy phenol (from Eastman Kodak Company). This composition is fully useful in this invention and exhibits reduced distortion in comparison with the use of a similar all acrylate-functional composition.

Still another illustration of a (meth)acrylate-functional photocurable liquid which is useful to provide the bath of liquid ultraviolet-curable ethylenically unsaturated material is provided by mixing 34 grams of a resinous diacrylate of a diglycidyl ether of bisphenol A having a number average molecular weight of about 390 (the Cargill Incorporated, Carpenterville, IL, product PN 1570 can be used), 33 grams of a liquid dimethacrylate of a bisphenol A-based ethoxylate (Sartomer SR 348 can be used), 33 grams of liquid tetraethylene glycol dimethacrylate (Sartomer SR 209), 4 grams of a benzyl ketal-based photoinitiator (2-hydroxypropyl phenone [Darocur 1173 from EM Chemicals can be used]), 2 grams of ethyl diethanol amine (from Aldrich), and 0.1 grams of methoxy phenol (from Eastman Kodak Company). This composition is fully useful in this invention and exhibits reduced distortion in comparison with the use of a similar

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all acrylate-functional composition.

A further illustration of a (meth)acrylate-functional photocurable liquid which is useful to provide the bath of liquid

5 ultraviolet-curable ethylenically unsaturated material is provided by mixing 30 grams of a diacrylate-functional urethane polyester resin (Uvithane 783 from Morton Thiokol can be used), 30

10 grams of liquid trimethylol propane ethoxylate triacrylate (SR 454 from Sartomer), 40 grams of liquid tetraethylene glycol dimethacrylate, (Photomer 2050 from Henkel Corporation, Morristown, NJ can be used), 4 grams of a benzyl ketal-based photoinitiator (2-hydroxypropyl phenone [Darocur 1173 from EM

15 Chemicals can be used]), and 0.1 grams of methoxy phenol (from Eastman Kodak Company). This composition is fully useful in this invention and exhibits reduced distortion in comparison with the use of a similar all acrylate-functional composition.

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WHAT IS CLAIMED IS:

1. A method of forming a three-dimensional object comprising, providing a reservoir of liquid ultraviolet-curable ethylenically unsaturated material comprising a photoinitiator and from about 20% to about 80%, of a resinous polyacrylate or polymethacrylate dissolved in from about 80% to about 20% of a liquid polyacrylate or polymethacrylate, one of the foregoing being a polyacrylate and the other being a polymethacrylate, said photoinitiator being effective to initiate the ultraviolet cure of (meth)acrylate functionality and being present in an amount of from 1% to 10%, said proportions being based on the weight of ethylenically unsaturated material present, repeatedly exposing the surface of said reservoir to a beam of actinic light in or near the ultraviolet range to said surface to solidify the liquid near said surface to form a plurality of superposed layers of lightly cross-linked solvent-swellable three dimensional complexly-shaped polymeric element constituted by incompletely polymerized solid polymer in said reservoir, removing said element from said reservoir, draining excess polymerizable liquid from said element, and then completing the cure of said element to rigidify and strengthen the same.

2. A method as recited in claim 1 in which said object is thin-walled and a dosage in the range of 1-15 Joules per square centimeter is applied to the surface of said reservoir.

3. A method as recited in claim 1 in which said liquid polyacrylate or polymethacrylate is at least trifunctional.

4. A method as recited in claim 1 in which said resinous polyacrylate or polymethacrylate is a

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polyacrylate used in an amount of from 35% to 70%.

5. A method as recited in claim 4 in which said liquid is trimethylol propane trimethacrylate.

6. A method as recited in claim 1 in which
5 said photoinitiator is a ketonic photoinitiator and said reservoir contains from 10% to 40% of liquid N-vinyl monomer in place of a portion of said liquid polyacrylate or polymethacrylate.

7. A method as recited in claim 1 in which
10 said resinous polyacrylate or polymethacrylate has a molecular weight of at least about 500 and said liquid polyacrylate or polymethacrylate is a free flowing liquid having a molecular weight below about 350.

15 8. An ultraviolet-curable liquid composition adapted to cure rapidly to a lightly cross-linked solvent-swella-
ble three dimensional complexly-shaped polymeric element constituted by heat-softenable solid polymer and which possesses
20 reduced distortion comprising, from 20% to 80%, of a resinous polyacrylate or polymethacrylate dissolved in a combination of 10% to 40% of a liquid polyacrylate or polymethacrylate, one of the foregoing being a polyacrylate and the other being a
25 polymethacrylate, and 10% to 30% of N-vinyl monomer.

9. An ultraviolet-curable liquid composition as recited in claim 8 in which said resinous polyacrylate is used in an amount of from 45% to 70% and said liquid polymethacrylate is at
30 least trifunctional and is used in an amount of from 15% to 30%.

10. An ultraviolet-curable liquid composition as recited in claim 8 in which said N-vinyl monomer is N-vinyl pyrrolidone or N-vinyl
35 caprolactam and said composition includes from 1% to

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10% of a ketonic photoinitiator effective to initiate the ultraviolet cure of (meth)acrylate functionality.

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INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US89/00774**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC(4): B29D 11/00; G03C 1/70, 9/08		
U.S. CL: 430/282; 264/22; 425/174.4		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
U.S.	264/22, 236, 344, 347; 425/174.4; 430/286, 916, 282, 269; 525/203, 205, 228, 418, 419, 451, 471; 526/227, 232, 264, 328, 329.7; 522/92, 96, 44, 46, 116, 120, 187	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US, A, 4,575,330 (HULL) 11 MARCH 1986, SEE	1-7
Y	THE ENTIRE DOCUMENT COLUMN 6.	1-10
X	US, A, 4,195,103 (CHANG) 25 MARCH 1980, SEE	8-10
	EXAMPLE 3, COLUMN 3, LINES 19-47.	
X	US, A, 4,477,327 (CASSATTA ET AL) 16 OCTOBER	8-10
	1984, SEE COLUMN 1, LINES 5-57, COLUMNS 4-5,	
	COLUMN 8, LINES 26-36, COLUMN 11, LINES	
	28-46.	
Y	US, A, 4,011,084 (HARTMANN ET AL) 08 MARCH	8-10
	1977, SEE COLUMN 2.	
Y	US, A, 4,690,502 (ZIMMERMAN ET AL)	8-10
	01 SEPTEMBER 1987, SEE COLUMN 5, LINES 4-10.	
<p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
06 APRIL 1989		07 JUL 1989
International Searching Authority		Signature of Authorized Officer
ISA/US		<i>Paul Michl</i> PAUL MICHL