FORM 1

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

I\We,

E. I. DU PONT DE NEMOURS
AND COMPANY

608403

of   1007 MARKET STREET
        WILMINGTON
        DELAWARE, 19898
        U.S.A.

hereby apply for the grant of a standard patent for an
invention entitled:

PROCESS OF FORMING REFLECTION HOLOGRAMS IN
PHOTOPOLYMERIZABLE LAYERS

which is described in the accompanying complete specification

Details of basic application(s):

Number of basic application	Name of Convention country in which basic application was filed	Date of basic application
144840	US	15 JAN 88

My/our address for service is care of GRIFFITH HACK & CO., Paten
Attorneys, 601 St. Kilda Road, Melbourne 3004, Victoria,
Australia.

DATED this 13th day of January 1989

E. I. DU PONT DE NEMOURS
AND COMPANY

GRIFFITH HACK & CO.

TO: The Commissioner of Patents.

APPLICATION ACCEPTED AND AMENDMENTS
7 - 1. 91

Forms 7 and 8

IM-0066

AUSTRALIA

Patents Act 1952

DECLARATION IN SUPPORT OF A CONVENTION ~~OR×NON×CONVENTION~~ APPLICATION FOR A PATENT ~~OR×PATENT×OF×ADDITION~~

Name(s) of Applicant(s)

In support of the application made by_____
_E. I. DU PONT DE NEMOURS AND COMPANY_____

Title

for a patent for an invention entitled_PROCESS FOR FORMING_
REFLECTION HOLOGRAMS IN PHOTOPOLYMERIZABLE LAYERS

Name(s) and address(es) of person(s) making declaration

I/We, James J. Flynn, Asst. Secretary-Patent Board of E. I.
DU PONT DE NEMOURS AND COMPANY, 2604 Montchanin Bldg.,
Wilmington, Delaware 19898, United States of America

do solemnly and sincerely declare as follows:-

1. I am/~~we×are×the×applicant(s)×for×the×patent,×or~~
    am/are authorised by the abovementioned applicant
    to make this declaration on its behalf.

2. The basic application~~(s)~~ as defined by Section 141
    of the Act was/~~were~~ made in the following country
    ~~or×countries~~ on the following date(s) by the
    following applicant~~(s)~~ namely:-

Country, filing date and name of Applicant(s) for the or each basic application

in United States of America on January 15,   19 88
by Dalen Eugene Keys and William Karl Smothers

3. The said basic application(s) was/~~were~~ the first
    application~~(s)~~ made in a Convention country in respect
    of the invention the subject of the application.

Name(s) and address(es) of the or each actual inventor

4. The actual inventor(s) of the said invention is/are
    Dalen Eugene Keys and William Karl Smothers, of R. D. #5,
    Box 260A2, Towanda, Pennsylvania 18848, (formerly of:
    4 Butternut Court, Wilmington, Delaware 19810); and
    R. D. #2, Box 103, Old Public Road, Hockessin, Delaware
    19707, respectively, United States of America

See reverse side of this form for guidance in completing this part

5. The facts upon which the applicant(s) is/are entitled
    to make this application are as follows:-

    The applicant is the assignee of the actual inventors

DECLARED at_Wilmington,____this_12th_ day of_December____19_88_
            Delaware, USA

[signature: James Joseph Flynn]

This form may be completed and filed after the filing of a patent
~~...~~ after it has been

(57) Claim

1.   A process for forming a reflection hologram wherein a reference beam of coherent actinic radiation and an object beam of the same coherent actinic radiation enter a layer of recording medium from opposite sides to create an interference pattern in the medium that forms the hologram, characterised in that the medium is a substantially solid, photopolymerizable layer consisting essentially of:

(a)   a polymeric binder selected from the group consisting of polyvinyl acetate, polyvinyl butyral, polyvinyl acetal, polyvinyl formal, interpolymers containing major segments thereof, and mixtures thereof;

(b)   an ethylenically unsaturated monomer selected from the group consisting of carbazole containing monomers and liquid monomers containing one or more moieties selected from the group consisting of (1) phenyl, (2) phenoxy, (3) naphthyl, (4) naphthyloxy, (5) heteroaromatic groups containing up to three aromatic rings, (6) chlorine

...../2

and (7) bromine and

      (c)   a photoinitiator system activatable by the actinic radiation.

9.   A process for forming and enhancing a reflection hologram in a substantially solid photopolymerizable recording medium the process comprising:

    A.   Projecting a reference beam of coherent actinic radiation on a first side of the recording medium which consists essentially of:

        (1)   a polymeric binder selected from the group consisting of polyvinyl acetate, polyvinyl butyral, polyvinyl acetal, polyvinyl formal, interpolymers containing major segments thereof and mixtures thereof:

        (2)   an ethylenically unsaturated monomer selected from the group consisting of carbazole containing monomers and liquid monomer containing one or more moieties selected from the group consisting of (a) phenyl, (b) phenoxy, (c) naphthyl, (d) naphthyloxy, (e) heteroaromatic group containing up to three aromatic rings, (f) chlorine and (g) bromine and

        (3)   a photoinitiator system activatable by the actinic radiation;

    B.   Projecting an object beam of the same coherent actinic radiation approximately in an opposite direction to the reference beam onto a second side of the photopolymerizable layer so as to intersect with the reference beam in a plane within the layer whereby a reflection hologram is formed;

    C.   Irradiating the imaged photopolymerizable layer with uniform source of actinic radiation; and

    D.   Treating the irradated reflection hologram with a liquid enhancing agent which is a swelling agent for the photopolymerized layer.

AUSTRALIA

PATENTS ACT 1952

Form 10

COMPLETE SPECIFICATION

(ORIGINAL)

608403

FOR OFFICE USE

Short Title:

Int. Cl:

Application Number:
          Lodged:

Complete Specification-Lodged:
                Accepted:
                  Lapsed:
              Published:

Priority:

Related Art:

TO BE COMPLETED BY APPLICANT

Name of Applicant:
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Actual Inventor:

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                Australia.

Complete Specification for the invention entitled:
        PROCESS OF FORMING REFLECTION HOLOGRAMS IN
              PHOTOPOLYMERIZABLE LAYERS

The following statement is a full description of this invention
including the best method of performing it known to me:-

<u>TITLE</u>   IM-0066

PROCESS OF FORMING REFLECTION

HOLOGRAMS IN PHOTOPOLYMERIZABLE LAYERS

5   <u>Field of the Invention</u>

This invention relates to imaging systems in which the imaged layer contains image areas having an index of refraction which is different from that of non-image areas. More particularly this invention

10 relates to such systems wherein the refractive index image is a reflection hologram.

<u>Discussion of the Background and Prior Art</u>

The term "image recording" is conventionally

15 taken to mean a process which produces a spatial pattern of optical absorption in the recording medium. Photographic processes are well known examples of this type of process.

In a broader sense, however, the word

20 "image" means a spatial variation of the optical properties of a sample in such a way as to cause a desired modification of a beam of light passing through the sample. Refractive index images in general and holograms in particular, which modulate

25 the phase, rather than the amplitude, of the beam passing through them are usually referred to as phase holograms. Phase holographic image recording systems produce a spatial pattern of varying refractive index rather than optical absorption in the recording

30 medium and, thus, can modulate a beam of light without absorbing it.

This type of refractive index image also includes a number of optical elements or devices which superficially bear little resemblance to

35

absorption images. Examples are holographic lenses,
gratings, mirrors, and optical waveguides.

Holography is a form of optical information
storage. The general principles are described in a
5 number of references, e.g., "Photography by Laser" by
E. N. Leith and J. Upatnieks in SCIENTIFIC AMERICAN
212, No. 6,24-35 (June, 1965). In brief, the object
to be photographed or imaged is illuminated with
coherent light, e.g., from a laser, and a light
10 sensitive recording medium, e.g., a photographic
plate, is positioned so as to receive light reflected
from the object. Each point on the object reflects
light to the entire recording medium, and each point
on the medium receives light from the entire object.
15 This beam of reflected light is known as the object
beam. At the same time, a portion of the coherent
light is beamed by a mirror directly to the medium,
bypassing the object. This beam is known as the
reference beam. What is recorded on the recording
20 medium is the interference pattern that results from
the interaction of the reference beam and the object
beam impinging on the medium. When the processed
recording medium is subsequently illuminated and
observed appropriately, the light from the
25 illuminating source is diffracted by the hologram to
reproduce the wave-front that originally reached the
medium from the object, so that the hologram
resembles a window through which the virtual image of
the object is observed in full three-dimensional
30 form, complete with parallax.

Holograms that are formed by allowing the
reference and object beams to enter the recording
medium from the same side are known as transmission
holograms. Interaction of the object and reference
35 beams in the recording medium forms fringes of

material with varying refractive indices which are
approximately normal to the plane of the recording
medium. When the hologram is played back by viewing
with transmitted light, these fringes refract the

5   light to produce the viewed virtual image. Such
transmission holograms may be produced by methods
which are well known in the art such as disclosed in
U.S. Patent 3,506,327; U.S. Patent 3,838 903 and U.S.
Patent 3,894,787.

10   A diffraction grating is the simplest
possible transmission hologram. It is the hologram
of two coherent plane waves. It can be created by
splitting a single laser beam and recombining the
beams at the recording medium.

15   The interference pattern produced by two
plane waves which are coherent and are not polarized
perpendicular to each other is a set of uniformly
spaced fringes with a sinusoidal intensity
distribution. When incident on a recording medium

20   they produce a set of uniformly spaced fringes which
have a sinusoidal variation in refractive index,
generally referred to as a grating, oriented parallel
to the bisector of the angle between the two beams.
If the two waves are incident at equal angles with

25   respect to the surface of the recording medium and
are both incident on the same side of the recording
medium, the fringes are perpendicular to the surface
of the medium and the grating is said to be
unslanted. The hologram grating produced is said to

30   be a transmission grating since light passing through
it is diffracted. The grating is said to be thick if
it is much thicker than the distance between the
fringes, generally referred to as the grating spacing.
        A diffraction grating can be characterized

35   by its diffraction efficiency, that is the percent of

incident radiation which is diffracted, and by its
thickness. A simple but useful theory for thick
hologram gratings, generally known as the "coupled
wave theory", has been developed by Kogelnik (H.

5 Kogelnik, Coupled wave theory for thick hologram
gratings, Bell Syt. Tech. J., 48, 2909-2947, 1969).
This theory treats the relationship between
diffraction efficiency, grating thickness, wavelength
of incident radiation, and the angle of incident

10 radiation. A useful discussion of this theory in
regard to refractive index recording systems has been
presented in Section II of an article by Tomlinson
and Chandross (W. J. Tomlinson and E. A. Chandross,
Organic photochemical refractive-index image

15 recording systems, Adv. in Phot.chem., Vol. 12, J. N.
Pitts, Jr., G. S. Hammond, and K. Gollinick, eds.,
Wiley-Interscience, New York, 1980, pp. 201-281).
        Holograms formed by allowing the reference
and object beams to enter the recording medium from

20 opposite sides, so that they are traveling in
approximately opposite directions are known as
reflection holograms. Interaction of the object and
reference beams in the recording medium forms fringes
of material with varying refractive indices which

25 are, approximately, planes parallel to the plane of
the recording medium. When the hologram is played
back these fringes act as mirrors reflecting incident
light back to the viewer. Hence, the hologram is
viewed in reflection rather than in transmission.

30 Since the wavelength sensitivity of this type of
hologram is very high, white light may be used for
reconstruction.
        Reflection holograms may be produced by an
in-line or on-axis method wherein the beam of

35 coherent radiation is projected through the recording

medium onto an object therebehind. In this instance, the reflected object beam returns and intersects with the projected beam in the plane of the recording medium to form fringes substantially parallel to the

5   plane of the medium. Reflection holograms also may be produced by an off-axis method wherein a reference beam is projected on one side of the recording medium and an object beam is projected on the reverse side of the medium. In this instance the object beam is

10 formed by illuminating the object with coherent radiation which does not pass through the recording medium. Rather, the original beam of coherent radiation is split into two portions, one portion being projected on the medium and the other portion

15 being manipulated to project on the object behind the medium. Reflection holograms produced by an off-axis process are disclosed in U.S. Patent 3,532,406.

A holographic mirror is the simplest possible reflection hologram. It is the hologram of

20 two coherent plane waves intersecting in a recording medium from substantially opposite directions. It can be created by splitting a single laser beam and recombining the beams at the recording medium, or the unsplit laser became can be projected through the

25 medium onto a plane mirror therebehind. As with transmission halograms, a set of uniformly spaced fringes with a sinusoidal intensity distribution is formed which are oriented parallel to the bisector of the obtuse angle between the two projected beams. If

30 the obtuse angle is 180° and the projected beams are normal to the plane of the medium, the fringes will be parallel to the plane of the medium. If the obtuse angle is less than 180° or if both beams are not normal to the plane of the medium, reflective

35 fringes will be formed which will be slanted at an

acute angle relative to the plane of the medium. The
holographic mirror can be characterized by its
reflection efficiency, that is the percent of
incident radiation which is reflected, and by the
spectral bandwidth and character of the reflected
radiation.

The substantially horizontal fringes which
form reflection holograms are much more difficult to
record than the perpendicular fringes which form
transmission holograms for two reasons. The first
reason is the need for higher resolution, i.e., the
need for more fringes per unit length, and thus a
smaller fringe spacing. Horizontal reflection
holograms require about 3X to 6X more fringes per
unit length than do transmission holograms. The
second reason is the sensitivity of horizontal
fringes to shrinkage of the recording medium. Any
shrinkage of the recording medium during exposure
will tend to wash out the fringes and, if severe,
will prevent a hologram from being formed. This is
in contract to the transmission hologram case, where
shrinkage has little or no effect if the fringes are
perpendicular to the plane of the medium, and
produces only relatively minor image distortion if
the transmission fringes are slanted more than 45°
from the plane of the medium.

A variety of materials have been used to
record volume holograms. Among the more important
are: silver halide emulsions, hardened dichromated
gelatin, ferroelectric crystals, photopolymers,
photochromics and photodichromics. Characteristics
of these materials are given in Volume Holography and
Volume Gratings, Academic Press, New York, 1981
Chapter 10, pp. 254-304 by L. Solymar and D. J. Cook.

Dichromated gelatin is the material most widely used for recording volume holograms. This material has become the popular choice because of its high diffraction efficiency and low noise

5   characteristics. However, dichromated gelatin has poor shelf life and requires wet processing. Plates must be freshly prepared, or prehardened gelatin must be used. Wet processing means that an additional step is required in hologram preparation and may also

10   cause the hologram to change due to swelling and then shrinkage of the gelatin during processing. The requirement that plates by freshly prepared each time a hologram is made plus the problems associated with wet processing make reproducibly extremely difficult

15   to achieve with dichromated gelatin.

While early holograms where prepared from silver halide or dichromated colloids which required several processing steps, photopolymerizable elements were introduced which require only a single process

20   step. U.S. Patent 3,658,526, incorporated herein by reference, discloses preparation of stable, high-resolution holograms from solid, photopolymerizable layers by a single step-process wherein a permanent refractive index image is

25   obtained by a single imagewise exposure of the photopolymerizable layer to actinic radiation bearing holographic information. The holographic image formed is not destroyed by subsequent uniform actinic exposure, but rather is fixed or enhanced.

30   In spite of their many advantages, however, the solid photopolymerizable layers proposed by Haugh had limited response to visible radiation and reflection holograms produced therefrom have been poor at best, with little or no reflection

35   efficiency. Thus, there has been a need for an

improved process and composition for the preparation of reflection holograms.

SUMMARY OF THE INVENTION

This invention attempts to provide an improved process for forming reflection holograms of improved reflection efficiency and increment spectral bandwidth through use of certain storage stable, solid, photopolymerizable elements as the recording medium. According to one embodiment of the present invention there is provided a process for forming a reflection hologram wherein a reference beam of coherent actinic radiation and an object beam of the same coherent actinic radiation enter a layer of recording medium from opposite sides to create an interference pattern in the medium that forms the hologram, characterised in that the medium is a substantially solid, photopolymerizable layer consisting essentially of:

(a)   a polymeric binder selected from the group consisting of polyvinyl acetate, polyvinyl butyral, polyvinyl acetal, polyvinyl formal, interpolymers containing major segments thereof, and mixtures thereof;

(b)   an ethylenically unsaturated monomer selected from the group consisting of carbazole containing monomers and liquid monomers containing one or more moieties selected from the group consisting of (1) phenyl, (2) phenoxy, (3) naphthyl, (4) naphthyloxy, (5) heteroaromatic groups containing up to three aromatic rings, (6) chlorine and (7) bromine and

(c)   a photoinitiator system activatable by the actinic radiation.

In a preferred embodiment the liquid monomer is phenoxyethyl acrylate.   In a still more preferred

embodiment the ethylenically unsaturated monomer is a
mixture of N-vinyl carbazole and phenoxyethyl
acrylate.

5   It also has been found, surprisingly, that
the reflection hologram formed in the recording
medium is enhanced if the recording medium
subsequently is treated with a liquid enhancing agent
or is subsequently heated at a temperature of at
least 50°C. Thus, in another embodiment, this

10   invention also provides a process for forming and
enhancing a reflection hologram in a substantially
solid, photopolymerizable recording medium comprising:

A)   Projecting a reference beam of coherent actinic
       radiation on a first side of the recording medium

15   which consists essentially of:

       (1)   a polymeric binder selected from the group
               consisting of polyvinyl acetate, polyvinyl
               butyral, polyvinyl acetal, polyvinyl formal,
               interpolymers containing major segments

20   thereof and mixtures thereof;

       (2)   an ethylenically unsaturated monomer
               selected from the group consisting of
               carbazole containing monomers and a liquid
               monomer containing one or more phenyl,

25   phenoxy, naphthyl, naphthyloxy,
               heteroaromatic group containing up to three
               aromatic rings, chlorine and bromine and

       (3)   a photoinitiator system activatable by the
               actinic radiation.

30 B)   Projecting an object beam of the same coherent
       actinic radiation approximately in an opposite
       direction to the reference beam onto a second
       side of the photopolymerizable layer so as to
       intersect with the reference beam in a plane

35

within the layer whereby a reflection hologram is formed;

C)   Irradiating the imaged photopolymerizable layer with a uniform source of actinic radiation; and

5   D)   either treating the irradiated reflection hologram with a liquid enhancing agent which is a swelling agent for the photopolymerized layer, or heating the irradiated reflection hologram at a temperature of at least 50°C for a period of time
10   to enhance the reflectivity of the hologram.

Detailed Description of the Invention

In the process of this invention, reflection holograms are prepared using a substantially solid,
15   photopolymerizable recording medium which comprises a transparent, dimensionally stable substrate having thereon a thin layer, typically between about 10 and 100 micrometers thick, of a unique, substantially solid, photopolymerizable composition.
20   In the instance of the "in-line" or "on-axis" mode of the process, a uniform, coherent beam of laser radiation, e.g., a collimated 488 nm argon-ion laser beam, is projected onto a first surface of the photopolymerizable layer typically at
25   an angle of up to 70° from the normal to the plane of the layer. The collimated beam functions in part as a "reference beam" while a portion of the collimated beam which is transmitted through the layer and transparent substrate illuminates an object behind
30   the layer. The portion of the transmitted laser radiation which is reflected by the object forms an "object beam" which projects back onto the rear second surface of the layer and interacts with the reference beam in the plane of the layer to form
35   fringes which are oriented parallel to the bisector

of the obtuse angle between the reference and object beams.
The assembly of fringes in the plane of the layer forms a
reflection hologram when viewed with radiation projected on
the front surface of the layer. A potential difficulty with
5   this mode of operation results when the media layer absorbs a
substantial portion of the incident collimated beam so that
the reflected object beam is too weak to form a satisfactory
hologram. The unique formulations of this invention can be
easily adjusted to minimize these potential problem.

10   In the instance of the "off-axis" mode of this process
the potential difficulty is partially obviated by splitting
the uniform, coherent beam of laser radiation. One of the
split beams is projected onto the first front surface as a
reference beam and the second split beam is manipulated to
15   bypass the photopolymerizable layer and directly illuminate
the object behind the layer. The reflected radiation forms
an object beam which can be adjusted in intensity by simply
adjusting the intensity ratio of the split radiation beams.

The object to be illuminated to form the object beam may
20   be a real three dimensional object or it may itself be a
reflection or transmission hologram. When a hologram is used
as the object, a virtual image in reconstructed to form the
object beam. In the instance when a reflection hologram is
used as the object, it simply may be placed behind the
25   photopolymerizable layer and reproduced by the in-line mode
of operation. In the instance when a transmission hologram
is used as the object, a manipulated split beam illuminates
the hologram at the Bragg Angle to reconstruct the virtual
image and form the object beam.

For the purpose of evaluating materials useful in the processes of this invention holographic mirrors are prepared and reflection efficiency, spectral bandwidth and wavelength of maximum

5

reflection are determined. A film element is prepared comprising, in order: a 0.1 mm thick clear polyethylene terephthalate film support; a dried, coated photopolymerizable layer between about 15 and 35 micrometers thick; and a 0.023 mm thick

10

polyethylene terephthalate cover sheet.

Coated film is cut into uniform sections, the cover sheet is removed, and the film then mounted by hand laminating the tacky coating directly to either the glass back of an aluminum front-surface

15

mirror or to a glass plate. Typically, the film support is left in place on the laminate and serves to protect the layer during exposure and handling operations.

For coatings mounted on front surface

20

mirrors, holographic mirrors are formed by actinic exposure under the same exposure conditions to a collimated 488 nm argon-ion laser beam, TEM_{oo} mode, oriented perpendicular to the film plane and reflecting back on itself. After recording

25

holographic mirrors, film samples are overall exposed to ultraviolet and visible light. The film support and coating are then removed from the front surface mirror and transmission spectra of the unprocessed holographic mirrors are recorded at 400-500 nm using

30

a conventional spectrophotometer. Maximum reflection efficiency, wavelength, and bandwidth at half maximum (fwhm) are measured from the transmission spectra. The holographic mirrors are then thermally processed by heating to 80 or 150°C for 30 minutes in a

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convection oven, cooled to room temperature, and

analyzed again by recording and measuring their
transmission spectra.

    Coatings mounted on glass plates are exposed
to form holographic mirrors in the same manner as
5 those mounted on front surface mirrors, except that
each plate is tightly clamped to a front surface
aluminum mirror which reflect the laser beam back
onto itself. Coating samples with holographic
mirrors are overall exposed as described above.
10 Generally, the film support is then removed, leaving
the coating on the glass plate. Unprocessed
holographic mirrors are analyzed by recording and
measuring their transmission spectra, after which
they are thermally processed by heating to 150°C in a
15 convection oven, cooled to room temperature, and
analyzed again.

    Reflection efficiencies using prior art
solid formulations typically are less than 10%
whereas reflection efficiencies of as high as 99% can
20 be achieved using the processes of this invention.

    The improved photopolymerizable compositions
used in the processes of this invention are
substantially solid and are typically used as a layer
applied to a permanent substrate. The composition
25 may be directly coated onto the substrate by any
conventional method or may be laminated thereto as a
storage stable, preformed element comprising the
photopolymerizable layer releasably adhered to a
temporary support film which is dimensionally stable
30 and, preferably, transparent to actinic radiation,
e.g., of polyethylene terephthalate. The other side
of the supported photopolymerizable layer may have a
temporary protective coversheet releasably adhered
thereto, e.g., polyethylene, polypropylene, etc.
35 Typically the coversheet has the weaker adherence to

the photopolymerizable layer and the permanent
substrate has the stronger adherence. Conventional
intermediate layers or coatings may be used to
facilitate the adhesive and/or release

5   characteristics needed for the preformed element.
        The photopolymerizable layer is a
thermoplastic composition which upon exposure to
actinic radiation forms crosslinks or polymers of
higher molecular weight to change the refractive

10 index and rheological character of the composition.
Preferred photopolymerizable compositions are
compositions wherein free radical addition
polymerization and crosslinking of a compound
containing one or more ethylenically unsaturated

15 groups, usually in a terminal position, hardens and
insolubilizes the composition. The sensitivity of
the photopolymerizable composition is enhanced by the
photoinitiating system which may contain a component
which sensitizes the composition to practical

20 radiation sources, e.g., visible light.
Conventionally a binder is the most significant
component of a substantially dry photopolymerizable
film or layer in terms of what physical properties
the film or laminate will have while being used in

25 the invention. The binder serves as a containing
medium for the monomer and photoinitiator prior to
exposure, provide the base line refractive index, and
after exposure contributes to the physical and
refractive index characteristics needed for the

30 reflection hologram or refractive index image
formed. Cohesion, adhesion, flexibility,
miscibility, tensil strength, in addition to index of
refraction, are some of the many properties which
determine if the binder is suitable for use in a

35 refractive index medium.

While the photopolymerizable layer is a
solid sheet of uniform thickness it is composed of at
least three major components: a solid, solvent
soluble, preformed, polymeric material; at least one
5   ethylenically unsaturated monomer capable of addition
polymerization to produce a polymeric material with a
refractive index substantially different from that of
the preformed polymeric material; and a
photoinitiator system activatable by actinic
10   radiation. Although the layer is a solid
composition, components interdiffuse before, during
and after imaging exposure until they are fixed or
destroyed by a final uniform treatment, usually by a
further uniform exposure to actinic radiation or by
15   thermal treatment at elevated temperatures.
Interdiffusion may be further promoted by
incorporation into the composition of an otherwise
unreactive plasticizer. Typically, the composition
contains a liquid monomer, but it may contain solid
20   monomer components, either individually or in
combination with the liquid monomer, which are
capable of interdiffusing in the solid composition
and reacting to form a polymer or copolymer with a
refractive index shifted from that of the preformed
25   polymeric material.
Preformed polymeric materials useful in
solid, photopolymerizable layers for forming high
reflectivity reflection holograms are polyvinyl
acetate, polyvinyl formal, polyvinyl acetal,
30   polyvinyl butyral, and mixtures thereof. Also useful
are interpolymers containing within their structure
major segments or portions of the aforementioned
polymers. By the use of these particular preformed
polymeric materials it is possible to form and
35   enhance reflection holograms as contrasted to
previously used solid photopolymerizable layers.

Ethylenically unsaturated monomers useful in
the practice of this invention are ethylenically
unsaturated carbazole monomers, e.g., N-vinyl
carbazole and/or a liquid, ethylenically unsaturated

5   compound capable of addition polymerization and
having a boiling point above 100°C. The monomer
contains either a phenyl, phenoxy, naphthyl,
naphthyloxy, heteroaromatic group containing up to
three aromatic rings, chlorine or bromine. The

10   monomer contains at least one such moiety and may
contain two or more of the same or different moieties
of the group, provided the monomer remains liquid.
Contemplated as equivalent to the groups are
substituted groups where the substitution may be

15   lower alkyl, alkoxy, hydroxy, carboxy, carbonyl,
amino, amido, imido or combinations thereof provided
the monomer remains liquid and diffusable in the
photopolymerizable layer. Suitable monomers which
can be used as the sole monomer or in combination

20   with liquid monomers of this type include but are not
limited to styrene, 2-chlorostyrene, 2-bromostyrene,
methoxystyrene, phenyl acrylate, ρ-chlorophenyl
acrylate, 2-phenylethyl acrylate, 2-phenoxyethyl
acrylate, 2-phenoxyethyl methacrylate, phenol

25   ethoxylate monoacrylate, 2-(ρ-chlorophenoxy)ethyl
acrylate, benzyl acrylate, 2-(1-naphthyloxy)ethyl
acrylate, 2,2-di(ρ-hydroxy phenyl)-propane
diacrylate or dimethacrylate,
2,2-di-(p-hydroxyphenyl)-propane dimethacrylate,

30   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

35

bisphenol-A, ethyoxylated bisphenol-A diacrylate,
di(3-methacryloxy-2-hydroxpropyl) ether of
tetrachloro-bisphenol-A, di-(2-methacryloxyethyl)
ether of tetrachloro-bisphenol-A,
5 di-(3-methacryloxy-2-hydroxypropyl) ether of
tetrabromo-bisphenol-A, di-(2-methacryloxyethyl)
ether of tetrabromo-bisphenol-A,
di-(3-methacryloxy-2-hydroxypropyl) ether of
diphenolic acid, 1,4-benzenediol dimethacrylate
10 1,4-diisopropenyl benzene, 1,3,5-triisopropenyl
benzene, hydroquinone methyl methacrylate, and
2-[B-(N-carbazoyl)propionyloxy]ethyl acrylate.

Preferred liquid monomers for use in this
invention are 2-phenoxyethyl acrylate, 2-phenoxyethyl
15 methacrylate, phenol ethoxylate monoacrylate,
2-(p-chlorophenoxy)ethyl acrylate, p-chlorophenyl
acrylate, phenyl acrylate, 2-phenylethyl acrylate,
di(2-acryloxyethyl)ether of bisphenol-A, ethoxylated
bisphenol-A diacrylate and 2-(1-naphthyloxy)ethyl
20 acrylate.

Ethylenically unsaturated carbazole monomers
having ethylenic substitution on the nitrogen atom of
the carbazole moiety typically are solids. Suitable
monomers of this type include N-vinyl carbazole and
25 3,6-dibromo-9-vinyl carbazole. Of these N-vinyl
carbazole is preferred.

A particularly preferred ethylenically
unsaturated monomer comprises N-vinyl carbazole used
in combination with the above preferred liquid
30 monomers and, in particular, with 2-phenoxyethyl
acrylate, phenol ethoxylate monoacrylate, ethoxylated
bisphenol-A diacrylate, or mixtures thereof.

While monomers useful in this invention are
liquids, they may be used in admixture with one or
35 more ethylenically unsaturated solid monomers such as

the ethylenically unsaturated carbazole monomers
disclosed in _Journal of Polymer Science: Polymer
Chemistry Edition_, Vol. 18, pp. 9-18 (1979) by H.
Kamogawa et al.; 2-naphthyl acrylate;
5 pentachlorophenyl acrylate; 2,4,6-tribromophenyl
acrylate; bisphenol-A diacrylate;
2-(2-naphthyloxy)ethyl acrylate; and N-phenyl
maleimide.

      In the embodiment of this invention where
10 crosslinking is desirable, e.g., during thermal
enhancement and curing, up to about 5 weight per cent
of at least one multifunctional monomer containing
two or more terminal ethylenically unsaturated groups
typically is incorporated into the photopolymerizable
15 layer. Suitable such multifunctional monomers are
the acrylic adducts of bisphenol-A ethers identified
above and acrylate and methacrylate esters such as:
1,5-pentanediol diacrylate, ethylene glycol
diacrylate, 1,4-butanediol diacrylate, diethylene
20 glycol diacrylate, hexamethylene glycol diacrylate,
1,3-propanediol diacrylate, decamethylene glycol
diacrylate, decamethylene glycol dimethacrylate, 1,
4-cyclohexanediol diacrylate, 2,2-dimethylolpropane
diacrylate, glycerol diacrylate, tripropylene glycol
25 diacrylate, glycerol triacrylate, trimethylolpropane
triacrylate, pentaerythritol triacrylate,
polyoxyethylated trimethylolpropane triacrylate and
trimethacrylate and similar compounds as disclosed in
U.S. Patent 3,380,831, pentaerythritol tetraacrylate,
30 triethylene glycol diacrylate, triethylene glycol
dimethacrylate, polyoxypropyltrimethylol propane
triacrylate (462), ethylene glycol dimethacrylate,
butylene glycol dimethacrylate, 1,3-propanediol
dimethacrylate, 1,2,4-butanetriol trimethacrylate,
35 2,2,4-trimethyl-1,3-pentanediol dimethacrylate,

pentaerythritol trimethacrylate, pentaerythritol
tetramethacrylate, trimethylolpropane
trimethacrylate, 1,5-pentanediol dimethacrylate,
diallyl fumarate.

5   Preferred multifunctional monomers include a
diacrylate or dimethacrylate of a bisphenol-A epoxy
adduct such as di(2-acryloxyethyl) ether of
bisphenol-A, ethoxylated bisphenol-A diacrylate,
di(3-acryloxy-2-hydroxyphenyl) ether of bisphenol-A,
10   and di(2-acryloxyethyl) ether of
tetrabromo-bisphenol-A.

          Photoinitiator systems useful in practicing
this invention typically will contain a
photoinitiator and a sensitizer which extends the
15   spectral response into regions having special
utility, e.g., the near U.V. region, and the visible
and near infrared spectral regions where lasers emit.

          Suitable free radical-generating addition
polymerization initiators activatable by actinic
20   light and thermally inactive at and 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, 1-chloroanthraquinone,
25   2-chloroanthraquinone, 2-methylanthraquinone,
2-ethylanthraquinone, 2-tert-butylanthraquinone,
octamethylanthraquinone, 1,4-naphthoquinone
9,10-phenanthrenequinone, 1,2-benzanthraquinone,
2,3-benzanthraquinone, 2-methyl-1,4-naphthoquinone,
30   2,3-dichloronaphthoquinone,
1,4-dimethylanthraquinone, 2,3-dimethylanthraquinone,
2-phenylanthraquinone, 2-3-diphenylanthraquinone,
sodium salt of anthraquinone alpha-sulfonic acid,
3-chloro-2-methylanthraquinone, retenequinone,
35   7,8,9,10-tetrahydronaphthacenequinone, and

1,2,3,4-tetrahydrobenz(a)anthracene-7,12-dione.
Other photoinitiators which are also useful, even
though some may be thermally active at temperatures
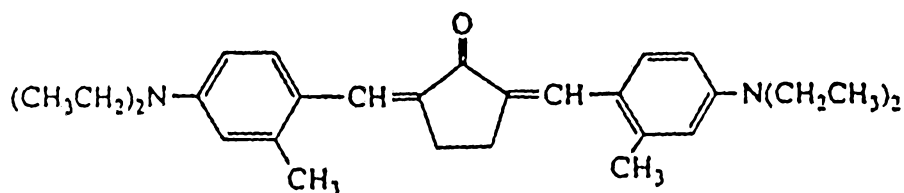as low as 85°C, are described in U.S. Patent

5   2,760,863 and include vicinal ketaldonyl alcohols,
such as benzoin, pivaloin, acyloin ethers, e.g.,
benzoin methyl and ethyl ethers,
α-hydrocarbon-substituted aromatic acyloins,
including α-methylbenzoin, α-allylbenzoin and

10 α-phenylbenzoin.

        Photoreducible dyes and reducing agents such
as those disclosed in U.S. Patents: 2,850,445;
2,875,047; 3,097,096; 3,074,974; 3,097,097;
3,145,104; and 3,579,339; as well as dyes of the

15 phenazine, oxazine, and quinone classes; Michler's
ketone, benzophenone, 2,4,5-triphenylimidazolyl
dimers with hydrogen donors, and mixtures thereof as
described in U.S. Patents: 3,427,161; 3,479,185;
3,549,367; 4,311,783; 4,622,286; and 3,784,557 can be

20 used as initiators. A useful discussion of dye
sensitized photopolymerization can be found in "Dye
Sensitized Photopolymerization" by D. F. Eaton in
Adv. in Photochemistry, Vol. 13, D. H. Volman, G. S.
Hammond, and K. Gollinick, eds., Wiley-Interscience,

25 New York, 1986, pp. 427-487. Similarly, the
cyclohexadienone compounds of U.S. Patent No.
4,341,860 are useful as initiators.

        Preferred photoinitiators include CDM-HABI,
i.e., 2-(o-chlorophenyl)-4,5-bis(m-methoxyphenyl)-

30 imidazole dimer; o-Cl-HABI, i.e., 1,1'-biimidazole,
2,2'-bis (o-chlorophenyl)-4,4'5,5'-tetraphenyl-; and
TCTM-HABI, i.e., 1H-imidazole, 2,5-bis(o-chloro-
phenyl)-4-[3,4-dimethoxyphenyl]-, dimer, each of
which is typically used with a hydrogen donor, e.g.,

35 2-mercaptobenzoxazole. Sensitizers useful with

photoinitiators include methylene blue and those
disclosed in U.S. Patents 3,554,753; 3,563,750;
3,563,751; 3,647,467; 3,652,275; 4,162,162;
4,268,667; 4,351,893; 4,454,218; 4,535,052; and
5 4,565,769. 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}; and
10 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]-.
which have the following structures respectively:

15

$(CH_3CH_2)_2N$ —⟨ring⟩— CH= ⟨cyclopentanone with O⟩ =CH —⟨ring⟩— $N(CH_2CH_3)_2$
CH_3 CH_3

DBC

20

$(CH_3CH_2)_2N$ —⟨ring⟩— CH= ⟨cyclopentanone with O⟩ =CH —⟨ring⟩— $N(CH_2CH_3)_2$

DEAW

25

30

CH_3O— / CH_3O— ⟨indanone with O⟩ =CH— ⟨tetrahydrobenzoquinolizine with N⟩
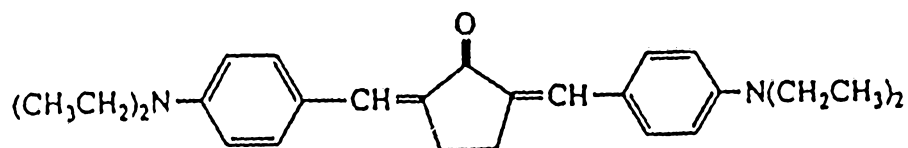
Dimethoxy-JDI

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The solid photopolymerizable compositions of this invention may contain a plasticizer to enhance the refractive index modulation of the imaged composition. Plasticizers of this invention may be used in amounts varying from about 2% to about 25% by weight of the composition preferably 5 t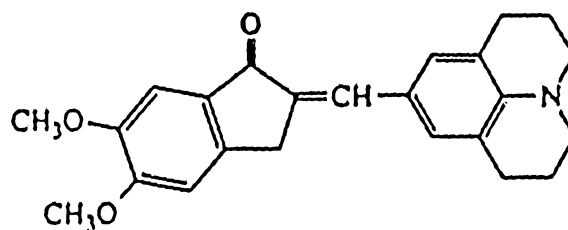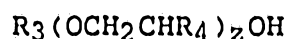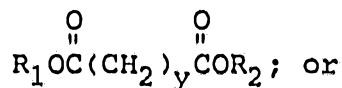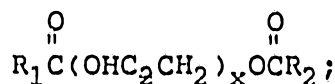o about 15 wt.%. Suitable plasticizers include triethylene glycol, triethylene glycol diacetate, triethylene glycol dipropionate, triethylene glycol dicaprylate, triethylene glycol dimethyl ether, triethylene glycol bis(2-ethylhexanoate), tetraethylene glycol diheptanoate, poly(ethylene glycol), poly(ethylene glycol) methyl ether, isopropylnaphthalene, diisopropylnaphthalene, poly(propylene glycol), glyceryl tributyrate, diethyl adipate, diethyl sebacate, dibutyl suberate, tributyl phosphate, tris(2-ethylhexyl) phosphate, and compounds having the general formula:

$$R_1 \overset{O}{\overset{\|}{C}}(OHC_2CH_2)_x \overset{O}{\overset{\|}{O}}CR_2;$$

$$R_1 O\overset{O}{\overset{\|}{C}}(CH_2)_y \overset{O}{\overset{\|}{C}}OR_2; \text{ or}$$

$$R_3(OCH_2CHR_4)_zOH$$

wherein R_1 and R_2 each is an alkyl group of 1 to 10 carbon atoms, R_3 is H or an alkyl group of 8 to 16 carbon atoms, R_4 is H or CH_3, x is 1-4, y is 2-20, and z is 1-20, examples of these compounds being Brij 30 $[C_{12}H_{25}(OCH_2CH_2)_4OH]$, and Brij 35 $[C_{12}H_{25}(OCH_2CH_2)_{20}OH]$. Particularly preferred plasticizers for use in these systems are triethylene glycol dicaprylate and tetraethylene glycol diheptanoate. Similarly, triethylene glycol dicaprylate and tetraethylene glycol diheptanoate are preferred for use with solid carbazole monomers in the absence of any second liquid monomers.

Other components in addition to those described above can be present in the photopolymerizable compositions in varying amounts. Such components include: optical

brighteners, ultraviolet radiation absorbing material,
thermal stabilizers, hydrogen donors and release agents.

Optical brighteners useful in the process of the
invention include those disclosed in Held U.S. Patent
3,854,950. A preferred optical brightener is
7-(4'chloro-6'-diethylamino-1',3',5'-triazine-4'-yl)

amino 3-phenyl coumarin. Ultraviolet radiation
absorbing materials useful in the invention are also
disclosed in Held U.S. Patent 3,854,950.

Useful thermal stabilizers include:
5 hydroquinone, phenidone, p-methoxyphenol, alkyl and
aryl-substituted hydroquinones and quinones,
tert-butyl catechol, pyrogallol, copper resinate,
naphthylamines, beta-naphthol, cuprous chloride,
2,6-di-tert-butyl p-cresol, phenothiazine, pyridine,
10 nitrobenzene, dinitrobenzene, p-toluquinone and
chloranil. The dinitroso dimers described in Pazos
U.S. Patent 4,168,982, are also useful. Normally a
thermal polymerization inhibitor will be present to
increase stability in the storage of the
15 photopolymerizable composition.

Hydrogen donor compounds useful as chain
transfer agents in the photopolymer compositions
include: 2-mercaptobenzoxazole, 2-mercaptobenzothia-
zole, 4-methyl-4H-1,2,4,triazole-3-thiol, etc.; as
20 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 3,390,996.
25 Suitable hydrogen donor compounds for use in systems
containing both biimidazole type initiator and N-vinyl
carbazole are 5-chloro-2-mercaptobenzothiazole;
2-mercaptobenzothiazole; 1H-1,2,4-triazole-3-thiol;
6-ethoxy-2-mercaptobenzothiazole; 4-methyl-4H-1,2,4-
30 triazole-3-thiol; 1-dodecanethiol; and mixtures
thereof. Compounds which have been found useful as
release agents are described in Bauer U.S. Patent
4,326,010. A preferred release agent is
polycaprolactone.
35

Amounts of ingredients in the photopolymerizable compositions will generally be within the following percentage ranges based on total weight of the photopolymerizable layer: monomer, 5-60%, preferably 15-50%; initiator 0.1-10%, preferably 1-5%: binder, 25-75%, preferably 45-65%; plasticizer, 0-25%, preferably 5-15%; other ingredients 0-5%, preferably 1-4%.

Reflection holograms formed using the unique solid photopolymerizable compositions of this invention have improved reflection efficiency, typically between about 15% to over 60%. Surprisingly, when such holograms are further treated with a particular class of liquids which swell the hologram, the reflection efficiency irreversibly jumps to 70% and above with no apparent detrimental effects. Concurrent with the reflection efficiency increase is an increase in the bandwidth as well.

The class of liquids which are particularly effective in enhancing reflection holograms are polar organic liquids which may swell the hologram. The polar organic liquid may be selected from the group consisting of alcohols, ketones, aldehydes, glycol alkyl ethers, esters, liquid monomers and mixtures thereof. Use of one or more such enhancing agents is generally all that is required to effect an equilibrated image enhancement. The enhancing agent may be a single liquid or a mixture of such liquids of varying activity. Diluents, e.g. water, hydrocarbon solvents, can be present to decrease the concentration of the enhancing agent. Diluents are "inert solvents" which, when they are applied along to the hologram surface, have substantially no effect on reflection efficiency. Diluted enhancing agents are used in the instance when limited equilibrated enhancement is desired at lower than maximum reflectance, or when use of the enhancing agent alone

causes some dissolving of the hologram. Additional treatment of such limited equilibrated enhancement is possible with a more concentrated or more active enhancing agent.

5   Enhancing agent typically is applied after the reflection hologram has been fixed by uniform actinic exposure. The reflection hologram may be immersed in the enhancing agent or may be applied by other means.

10   The procedure for applying the swelling agent to the imaged holographic recording medium generally may be controlled to obtain a uniform enhancement of the reflection hologram and to prevent damage to the polymeric image, which is softened by

15   the swelling action of the enhancing agent. Ideally, just sufficient enhancing agent is needed to uniformly wet the image surface without either flooding it or applying tangential or compressive forces. However, since the rate of enhancement of

20   the diluted agents of this invention is slower and can be repeated, uniformity can be insured by multiple applications. Any method may be used to uniformly apply the swelling agent to the hologram provided the method does not entail abrasive or

25   compressive forces which would distort or mar the image.

A satisfactory method of applying the enhancing agent is by lightly drawing across the image area the edge of a paint brush or other

30   applicator such as a foraminous wick, soaked in enhancing agent. If the image area is small this procedure might be accomplished with a small brush or a felt-tip pen. If the image area is large, a felt-edged squeegee of sufficient length might be

35   used. In either case the enhancing agent is supplied

uniformly from the applicator to the hologram and is absorbed into the hologram to increase its reflection efficiency. In place of felt, any foraminous material may be used such as paper, and woven and nonwoven fabrics. Similarly, the enhancing agent may be applied as a mist, e.g., using an airbrush; or carefully coated as a liquid film. Excess enhancing agent that may be present is removed from this hologram by known means. Normal evaporation or speeded evaporation by air impingement using air at ambient temperature or elevated temperature are useful in removing excess enhancing agent. The enhancing agent may also be removed by treating with diluent nonenhancing agent.

Enhancing agents useful in this invention include; glycol alkyl ethers, e.g. 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol; alochols, e.g., methanol, ethanol, butanol, 1- or 2-propanol; ketones, e.g., acetone, methyl ethyl ketone, cyclohexanone, etc.; esters, e.g. ethyl acetate, butyl benzoate, etc.; aldehydes, e.g. benzaldehyde, etc.; as well as other enhancing agents, e.g. phenoxyethyl acrylate, phenol ethoxylate acrylate, ethoxylated bisphenol-A diacrylate, etc.; and mixtures thereof.

Diluents that may be present with the aforementioned enhancing agent include: water; inert hydrocarbon solvent, e.g., Soltrol®50, a mixture of C_{8-10} iso-paraffins with a boiling point range of 116 -149°C, a product of Philips Petroleum; hexane; cyclohexane; heptane; 1,2-dichloroethane; trichlorotrifluoroethane; and the like.

Typically, maximum enhancement of the entire reflection hologram is desired, requiring full strength treatment of the hologram by a highly active agent for a duration to reach an increased equilibrated reflection efficiency. Surprisingly, the reflection efficiency remains at the equilibrated value even after the agent has been substantially

removed. In those instances where immersion is not
used or where isolated areas of the hologram are to
be enhanced, controlled methods of application
identified above may be used to prevent flooding of
5   the hologram surface and retain the agent in the
desired isolated area.

Reflection holograms formed using the unique
solid photopolymerizable compositions of this
invention may be thermally treated to enhance
10   reflection efficiency up to about 100%. In this
embodiment, a reflection hologram is first formed in
the photopolymerizable layer of this invention and is
then heated to a temperature above 50°C and
preferably between 100 and 160°C for a commensurate
15   time period to maximize enhancement. Thermal
enhancement treatment may be carried out either
before or after any actinic radiation fixing step.
Typically it is carried out before any fixing step
and may be used to concurrently fix the enhanced
20   hologram by thermally hardening or polymerizing the
photopolymerizable material in the hologram. After
thermal enhancement is complete, the enhanced
hologram may be fixed, if needed, by uniform
irradiation with a source of actinic radiation. Both
25   the rate of thermal enhancement and and the rate of
thermal hardening increase with increasing
temperature.

In the practice of this embodiment of the
invention, the reflection hologram once formed may be
30   heated by any conventional method to enhance its
reflection efficiency. The hologram may be heated in
a single convection oven, irradiated with infrared or
microwave radiation or contact heated on a hot shoe
or in a lamination press. Whichever means is used,
35

care is needed to prevent distortion or damage to the
photopolymer layer containing the reflection hologram.

    A particular useful application of thermal
enhancement embodiment is in the preparation of
5   "head-up" displays for use in windshields and other
such glass laminate structures. In this instance, a
glass sheet has applied thereto a polymeric
reflection hologram of this invention. The
reflection hologram may be formed directly in a
10 photopolymerized layer previously applied to the
glass sheet, or it may be preformed in a
photopolymerizable element containing a temporary
support and then laminated to a glass sheet, In the
latter preformed mode of operation sufficient heat
15 may be used during lamination to the glass sheet to
thermally enhance the reflection hologram. After
removal of the temporary support the laminated glass
sheet may be used as a head-up display. More
preferably, a glass sheet with the photopolymer
20 reflection hologram thereon is placed in a lamination
press along with a second mating glass sheet with a
Butacite®/polymer sheet there between so that the
photopolymer hologram is in face to face contact with
the Butacite® interleaf. Heat and pressure are
25 applied to the glass-sandwich structure, e.g., about
150°C, whereby the reflection hologram is enhanced
and fixed concurrently with forming a glass
laminate. Surprisingly, a safety glass laminate is
formed having therein a reflection hologram
30 substantially free of distortion due to the
lamination process. The safety glass laminate can be
used as a "head-up" display. While glass typically
is used in such displays, other transparent sheet
material may also be used, e.g., quartz, polymethyl
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28

methacrylate, polycarbonate, polystyrene, and the like.

The advantages of the embodiments of this invention can be observed by reference to the following examples.

GENERAL PROCEDURES

Sample Preparation

Coating solutions without visible sensitizer, DEAW, were prepared under yellow or red light. After addition of DEAW, all operations on solutions and their resulting coatings were performed under red light only. To further protect them from actinic light, all solutions were prepared and stored in amber bottles. Solutions were prepared by adding components to the solvent and mixing with a mechanical stirrer until they completely dissolved. The solvent was a mixture of dichloromethane (90-95% by weight) and methanol (5%), ethanol (10%), or 2-propanol (10%) unless otherwise specified. Solution components were used as received from the manufacturer without purification, except for o-Cl-HABI and POEA which were chromatographed on aluminum oxide (activity-1) prior to use.

Solutions were coated onto a 4-mil clear film support of polyethylene terephthalate at a speed of 4 to 8 fpm using a Talboy coater equipped with a 6-8 mil doctor knife, 12 ft drier set at 40-50°C, and a laminator station. A cover sheet 1 mil polyethylene terephthalate was laminated to the coatings after drying. Coating samples were stored in black polyethylene bags at room temperature until used.

Sample Evaluation

Coated film was cut into 4x5-inch sections, the cover sheet was removed, and the film then

mounted by hand laminating the tacky coating directly
to either the glass back of an aluminum front-surface
mirror or to a glass plate. The film support was
left in place during exposure and initial handling
5 operations.

Coatings mounted on front surface mirrors
were evaluated by recording holographic mirrors and
determining their reflection efficiency, bandwidth,
and wavelength of maximum reflection. The
10 holographic mirrors were formed by actinic exposure
to a collimated 488 nm argon-ion laser beam, TEM_{oo}
mode, oriented perpendicular to the film plane and
reflecting back on itself. The beam had a 2.5-3.0 cm
diameter and an intensity of 10-54 mW/cm^2. Laser
15 exposure times ranged from 5-10 seconds,
corresponding to 200-270 mJ/cm^2 total exposure.
After recording holographic mirrors, film samples
were overall exposed to ultraviolet and visible light
using a Douthitt type DCOP-X exposure unit equipped
20 with a mercury arc photopolymer lamp
(Theimer-Strahler #5027). The film support and
coating were then removed from the front surface
mirror and transmission spectra of the unprocessed
holographic mirrors were recorded at 400-550 nm using
25 a Hitachi Perkin-Elmer model 330 spectrophotometer.
Maximum reflection efficiency, wavelength, and
bandwidth at half maximum (fwhm) were measured from
the transmission spectra. In examples 28-53 the
holographic mirrors were then thermally processed by
30 heating to 80 or 150°C for 30 minutes in a convection
oven, cooled to room temperature, and analyzed again
by recording and measuring their transmission spectra.

Coatings mounted on glass plates were
exposed to form holographic mirrors, as described
35 above, except each plate was tightly clamped to a

front surface aluminum mirror having the plate orientated such that the beam, in order, passes through the glass, the coating, and the film support, and then reflects back on itself. Coating samples
5 with holographic mirrors were overall exposed using the Douthitt exposure unit described above. Generally, the film support was then removed, leaving the coating on the glass plate. Unprocessed holographic mirrors were analyzed by recording and
10 measuring their transmission spectra, after which they were thermally processed by heating to 150°C in a convection oven, cooled to room temperature, and analyzed again. In some cases, the film support was left in place over the coating during thermal
15 processing and evaluation.

Coating thicknesses were measured on photocured samples by scratching through the coating to the glass plate, then measuring the profile using a Sloan DEKTAK 3030 surface profile monitoring system.
20

GLOSSARY OF CHEMICAL NAMES

BHT	2,6-Di-_tert_-butyl-4-methylphenol; CAS 128-37-0
Butacite®B140C	Poly(vinylbutyral), plasticized with 4G7
CAB 531-1	Cellulose acetate butyrate, Eastman type 531-1, CAS 9004-36-8
DEA	Diethyladipate
DEAW	Cyclopentanone, 2,5-bis[[4-(diethylamino)-phenyl]-methylene] CAS 38394-53-5
EBPDA	Ethoxylated bisphenol-A diacrylate; CAS 24447-78-7
4G7	Tetraethylene glycol diheptanoate; HATCOL 5147

2-HPA	2-Hydroxypropyl acrylate; propyleneglycol monoacrylate
MMT	4-Methyl-4H-1,2,4-triazole-3-thiol; CAS 24854-43-1
5 NVC	N-Vinyl carbazole; 9-Vinyl carbazole; CAS 1484-13-5
o-Cl-HABI	2,2'-Bis(o-chlorophenyl)-4,4',5,5'-tetraphenyl-1,1'-biimidazole; CAS 1707-68-2
10 POEA	2-Phenoxyethyl acrylate; CAS 48145-04-6
PVB	Poly(vinylbutyral), Aldrich, average M.W. 36,000; CAS 63148-65-2
TDA	Triethylene glycol diacrylate; CAS 1680-21-3
15 TDC	Triethylene glycol dicaprylate
TMPTA	Trimethylolpropane triacrylate: 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate; CAS 15625-89-5
20 Vinac B-15	Poly(vinylacetate), Air Products, M.W. 90,000; CAS 9003-20-7
Vinac B-100	Poly(vinylacetate), Air Products, M.W. 500,000; CAS 9003-20-7

CONTROL EXAMPLES A-B; EXAMPLES 1-2

25   Prior art control Examples A and B with
either NVC or POEA as monomer and CAB as binder
either were inoperative or had poor reflection
efficiency and spectral bandwidth. Useful coatings
were achieved using poly(vinyl acetate) binder.

30   The formulations shown below were prepared
and coated with a Talboy coater equipped with a 7 mil
doctor knife. All quantities are in grams, unless
otherwise indicated. The film in control example A
was not imaged since it was opaque with crystals as
35 coated. The film from Example 1 also formed crystals

but slowly enough to allow imaging of the film.
Plates were prepared and holographic mirror imaged as
described above except that the 514 nm beam of an
argon ion laser was used at a power of about 10 mW.

5 Film thicknesses, reflection efficiencies, and
spectral bandwidths are reported below.

	Example Number			
	A	B	1	2
Vinac B-15	–	–	14.16	14.25
CAB 531-1	14.22	14.25	–	–
NVC	9.04	–	9.04	–
POEA	–	9.06	–	9.04
o-Cl-HABI	0.74	0.74	0.74	0.73
MMT	0.251	0.250	0.251	0.250
DEAW	0.012	0.012	0.012	0.012
BHT	0.001	0.001	0.001	0.001
Methanol	12.2	12.2	12.2	12.2
Methylene Chloride	110.3	109.9	110.1	109.8
Film Thickness, micron –	–	17.1	16.0	18.9
Reflection Efficiency, %	–	3	15	27
Spectral Bandwidth, nm	–	5	5	7

The holographic mirrors were then processed
in a bath composed of 3% cyclohexanone in
isopropanol. The mirrors were immersed in the bath

25 for two minutes, air dried for about five minutes,
immersed in the developer bath for another two
minutes, and air dried overnight. After drying, %
transmission spectra were obtained. The bandwidth
for Example 1 could not be measured due to the low

30 reflection efficiency and width of the transmission
band. The film from Example B wrinkled during
development and a reflection could not be detected.
Data obtained is given below.

35

	A	B	1	2
Reflection Efficiency, %	–	–	3	78
Spectral Bandwidth, nm	–	–	–	18

EXAMPLE 3

This example shows good performance using poly(vinylbutyral), particularly compositions combining NVC and POEA liquid monomer.

The following formulation was prepared:

Butacite B140C	179.8 g
POEA	54.9 g
NVC	37.6 g
o-Cl-HABI	2.5 g
MMT	2.5 g
BHT	0.025 g
DEAW	0.509 g
Methanol	554 g
Tetrahydrofuran	554 g

The formulation was hand coated onto 4 mil polyethylene terephthalate film through a 1 mil doctor knife. The film was air dried at room temperature before applying a 1 mil polyethylene terephthalate film as coversheet. Plates were prepared and holographic mirrors imaged as described above. Each plate was exposed for 90 seconds with the 488 nm beam with a power of about 30 mW. The plate and mirror combination were oriented at either normal to or 40° off normal to the incident laser beam. Exposures made at normal to the incident beam will be referred to as "0°" and those at 40° off

normal will be referred to as "40°". The following
results were obtained:

Angle	Measured Reflection Efficiency
40°	13%
40°	12%
0°	18%
0°	20%

EXAMPLES 4-6

A stock formulation was prepared using 75 g
of Butacite B140C, 6.25 g o-Cl-HABI, 2.5 g MMT,
0.125 g DEAW, and 500 g 10% methanol/90% methylene
chloride. From this stock formulation three separate
film formulations were prepared using 117 g portions
for each formulation and adding to each formulation a
total of 8 g of monomer. Each formulation was coated
as described above. Film samples were mounted on
glass plates and holographic mirrors prepared as in
Example 3. The plate and mirror combination was
oriented normal to the incident laser beam. Results
are shown below.

Example Number	Monomer(s)	Reflection Efficiency
4	100% POEA	2%
5	100% NVC	4%
6	40.6% NVC, 59.4% POEA	15%

EXAMPLES 7-11

These are useful compositions similar to the
poly(vinylbutyral) Examples 3-6 and also show that
good results can be obtained by including a liquid
plasticizer.

The formulations listed below were coated as
described above. All quantities are in grams, unless
otherwise indicated. Plates were prepared as
described above and holographic mirrors generated by

splitting the 488 nm beam from an Argon ion laser and
impinging the collimated coherent beams onto opposite
sides of the plate with the angle between them about
180°. All films were exposed for 90 seconds.
Reflection efficiencies and film thicknesses are
given below.

	Example Number				
	7	8	9	10	11
Polyvinyl Butyral, Aldrich	10.6	10.6	10.6	13.1	10.6
NVC	5.20	5.19	5.19	5.20	6.99
POEA	2.08	2.08	2.08	2.08	2.79
TDC	2.51	-	-	-	-
DEA	-	2.67	-	-	-
4G7	-	-	2.56	-	-
o-Cl-HABI	0.643	0.642	0.642	0.643	0.643
MMT	0.209	0.209	0.209	0.209	0.209
DEAW	0.011	0.011	0.011	0.011	0.011
BHT	0.001	0.001	0.001	0.001	0.001
Methanol	10.4	10.4	10.4	10.4	10.4
Methylene Chloride	93.5	93.4	93.4	93.5	93.5
Film Thickness, micron	20.6	20.5	20.5	19.8	19.0
Reflection Efficiency,%	21	27	20	28	19

EXAMPLES 12 AND 13

These are useful compositions with
poly(vinylacetate) binder, combined with a mixture of
NVC and POEA monomer and TDC plasticizer. The
formulations listed below were coated and holographic

mirrors imaged as described in Example 7 except that exposure times for both films were 60 seconds. Film thicknesses and reflection efficiencies are reported below.

5

		Example Number	
		12	13
	Vinac B15	12.6	15.1
10	NVC	6.18	2.47
	POEA	2.55	6.1
	TDC	2.56	-
	o-Cl-HABI	0.75	0.76
15	MMT	0.26	0.25
	DEAW	0.012	0.012
	BHT	0.0013	0.0016
	Methanol	12.3	12.3
20	Methylene Chloride	110.2	110.2
	Film Thickness, micron	18.6	18.6
	Reflection Efficiency, %	22	22

EXAMPLES 14-20

25   Additional useful compositions prepared from poly(vinylacetate) showing the advantage of using NVC/POEA mixtures are shown below. The listed formulations were coated and holographic mirrors 30 imaged as described in Example 7. Reflection efficiencies and film thicknesses are reported below.

35

<div align="center">Example Number</div>

	14	15	16	17
Vinac B-15	12.5	12.5	12.5	12.5
NVC	–	2.53	3.51	1.54
POEA	7.85	5.30	4.23	6.24
TDC	–	–	–	–
o-Cl-HABI	0.617	0.617	0.617	0.617
MMT	0.209	0.209	0.209	0.209
DEAW	0.010	0.010	0.010	0.010
BHT	0.001	0.001	0.001	0.001
Methanol	10.2	10.2	10.2	10.2
Methylene Chloride	91.5	91.4	91.4	91.4
Film Thickness, micron	–	15.0	13.1	12.8
Reflection Efficiency, %	4	38	13	18

<div align="center">Example Number</div>

	18	19	20
Vinac B-15	14.0	12.5	14.0
NVC	–	1.51	–
POEA	6.23	5.45	4.23
TDC	–	1.02	1.10
o-Cl-HABI	0.617	0.617	0.617
MMT	0.209	0.209	0.209
DEAW	0.010	0.010	0.010
BHT	0.001	0.001	0.001
Methanol	10.2	10.2	10.2
Methylene Chloride	91.4	91.4	91.4
Film Thickness, micron	14.2	15.3	13.5
Reflection Efficiency, %	11	28	4

EXAMPLES 21-23

These examples illustrate useful results can be obtained independent of poly(vinylacetate) molecular weight. The listed formulations were coated and holographic mirrors imaged as in Examples 7. Reflection efficiencies and film thicknesses are reported below.

	Example Number		
	21	22	23
Polyvinyl Acetate, Low MW, Aldrich	37.4	-	-
Polyvinyl Acetate, Medium MW, Aldrich	-	37.4	-
Polyvinyl Acetate, High MW, Aldrich	-	-	37.4
NVC	7.63	7.62	7.56
POEA	16.0	16.0	15.9
o-Cl-HABI	1.86	1.86	1.87
MMT	0.625	0.625	0.627
DEAW	0.031	0.030	0.033
BHT	0.004	0.003	0.003
Methanol	25.1	25.2	25.2
Methylene Chloride	241.2	227.1	226.7
Film Thickness, micron	21.9	22.5	19.0
Reflection Efficiency, %	49	49	49

EXAMPLE 24

This example shows a useful poly(vinylformal) composition. The formulation below was coated and a

holographic mirror imaged as described in Example 7
except that a 30 second exposure was used.

Vinac B15	37.4
NVC	7.57
POEA	15.9
o-Cl-HABI	1.87
MMT	0.626
DEAW	0.030
BHT	0.003
Methanol	25.1
Methylene Chloride	226.1
Film Thickness, micron	16.7
Reflection Efficiency, %	20

EXAMPLE 25

This and Examples 26 and 27 show a
substantial reflection efficiency increase from
treating the holographic mirror with a swelling
solvent, whereas the prior art control compositions
do not.

The formulation below was coated through a 6
mil doctor knife applicator. Plates were prepared
and holographic mirrors imaged as described in the
general procedures. Film thickness and reflection
efficiency are reported below.

Vinac B15	37.5
NVC	7.64
POEA	15.9
o-Cl-HABI	1.86
MMT	0.625
DEAW	0.035
BHT	0.004
Methanol	25.2
Methylene Chloride	226.7

Film Thickness, micron   16.9
Reflection Efficiency, % 44
Spectral Bandwidth, nm   6

After obtaining the above data the holographic mirror was processed by gently wiping over the mirror a cotton swab containing acetone. After air drying for about 30 minutes a % transmission spectrum was recorded. The reflection efficiency had increased to 62% and the spectral bandwidth had increased to 35 nm.

EXAMPLE 26

The formulation shown below was coated with a 7 mil doctor knife applicator. Plates were prepared and holographic mirrors imaged as described in the general procedures. Film thickness, reflection efficiency and spectral bandwidth are listed below.

Vinac B15	37.5
NVC	7.55
POEA	15.9
5 o-Cl-HABI	1.83
MMT	0.623
DEAW	0.017
BHT	0.004
10 Methanol	25.1
Methylene Chloride	225.8
Film Thickness, micron	25.8

Reflection Efficiency, % 48 (average 8 mirrors - all imaged
15 identically)

Spectral Bandwidth, nm 6-7 (average 8 mirrors - all imaged
identically)

20 The holographic mirrors were then processed in a bath composed of 800 ml water and 600 ml acetone. The mirrors were immersed in the bath for 30 seconds, then water washed for 30 seconds, and then air dried. After drying, % transmission spectra were obtained. Data obtained is given below.

25 Reflection Efficiency, % 77 (average 3 mirrors - all imaged and processed identically)

Spectral Bandwidth, nm 22-28 (average 3 mirrors - all imaged and
30 processed identically)

EXAMPLE 27 AND CONTROL EXAMPLES C-E

The formulations below were coated through a
35 7 mil doctor knife applicator. Plates were prepared

and used at a power of about 10 nW. Results are reported below.

5

		Example Number		
		27	C	D	E

	27	C	D	E
Vinac B-15	14.2	–	14.2	–
CAB 531-1	–	14.2	–	14.1
TDA	–	–	9.04	9.04
NVC	2.50	2.50	–	–
POEA	6.49	6.50	–	–
o-Cl-HABI	0.73	0.73	0.74	0.74
MMT	0.249	0.249	0.260	0.260
DEAW	0.012	0.012	0.012	0.012
BHT	0.001	0.001	0.001	0.001
Methanol	12.2	12.2	12.3	12.3
Methylene Chloride	109.8	110.0	110.2	110.1
Film Thickness, micron	16.9	17.7	17.0	16.4
Reflection Efficiency, %	23	10	1	0
Spectral Bandwidth, nm	6	6	–	–

10

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The holographic mirrors were then processed in a bath composed of 3% cyclohexanone in 2-propanol. The mirrors were immersed in the bath for two minutes, air dried for about five minutes, immersed in the developer bath for another two minutes, and air dried overnight. After drying, % transmission spectra were obtained. Data obtained is given below.

25

30

	Example Number			
	27	C	D	E
Reflection Efficiency, %	75	6	–	–
Spectral Bandwidth, nm	14	–	–	–

35

EXAMPLES 28-31

These are useful compositions containing
Vinac B-15, a low molecular weight poly(vinylacetate)
binder and various crosslinking monomers. Reflection
holograms recorded in these compositions can be
thermally processed to obtain greater reflection
efficiency and bandwidth.

Four formulations were prepared, each
containing a crosslinking acrylate monomer, with or
without POEA, as described below, and each containing
14.2 g Vinac B-15 (56.96% by weight of total solids),
3.0 g NVC (12%), 1.0 g o-Cl-HABI (4.0%), 0.50 g MMT
(2.0%), 0.0075 g DEAW (0.03%), 71.25 g
dichloromethane, and 3.75 g methanol. The
formulations were coated on polyethylene
terephthalate film, mounted on the back of a
front-surface mirror, exposed, and evaluated
according to the general procedures given above. The
reflection efficiency, bandwidth, and wavelength of
maximum reflection are presented below.

Example Number

		28	29	30	31
POEA, grams (wt%)		–	3.75 (15)	5.00 (20)	5.00 (20)
EBPDA, grams (wt%)		6.25 (25)	2.50 (10)	–	–
TDA, grams (wt%)		–	–	1.25 (5)	–
TMPTA, grams (wt%)		–	–	–	1.25 (5)
Thickness, microns		24.8	27.4	27.2	28.0

Unprocessed mirrors

	28	29	30	31
Reflection Efficiency, %	67.5	61.0	46.0	47.0
fwhm, nm	5	5	5	5
λ_{max}, nm	476.5	478.5	476.5	477.0

Thermally processed: 80°C, 30 minutes, mirrors on polyethylene terephthalate film

	28	29	30	31
Reflection Efficiency, %	91	91	93	92
fwhm, nm	11	27	23	27
λ_{max}, nm	472	466	465	467

Thermally processed: 150°C, 30 minutes, mirrors on polyethylene terephthalate film

	28	29	30	31
Reflection Efficiency, %	84.0	99.8	99.6	99.9
fwhm, nm	31	25	25	26
λ_{max}, nm	453	447	447	449

EXAMPLES 32-35

These are useful compositions containing a
low molecular weight poly(vinylacetate) binder, TMPTA
crosslinking monomer, and varied amounts of POEA and
NVC. Reflection holograms recorded in these
compositions can be thermally processed to obtain
greater reflection efficiency and bandwidth.

Four formulations were prepared, each
containing TMPTA and POEA with or without NVC, as
described in the following table, and each containing
28.48 g Vinac B-15 (56.96% by weight of total
solids), 2.0 g o-Cl-HABI (4.0%), 1.0 g MMT (2.0%),
0.015 g DEAW (0.03%). 0.005 g BHT (0.01%), 7.5 g
methanol, and 142.5 g dichloromethane. The
formulations were coated on film support, mounted on
glass plates, exposed, and evaluated according to the
general procedures given above. The reflection
efficiency, bandwidth, and wavelength of maximum
reflection are presented below.

EXAMPLE 36

This is a useful composition containing a
low molecular weight poly(vinylacetate) binder, TMPTA
crosslinking monomer, and 4G7 plasticizer.
Reflection holograms recorded in this composition can
be thermally processed to obtain greater reflection
efficiency and bandwidth.

A formulation was prepared containing POEA,
TMPTA, NVC, and 4G7, as described below, and
containing 14.24 g Vinac B-15 (56.06% by weight of
total solids), 1.0 g o-Cl-HABI (4.0%), 0.5 g MMT
(2.0%), 0.0075 g DEAW (0.03%), 0.0025 g BHT (0.01%),
3.75 g methanol, and 71.25 g dichloromethane. The
formulation was coated and evaluated as in Examples
32-35. The reflection efficiency, bandwidth, and
wavelength of maximum reflection are presented below.

Example Number

	32	33	34	35	36
TMPTA, grams (wt%)	2.5 (5)	2.5 (5)	2.5 (5)	2.5 (5)	1.25 (5)
POEA, grams (wt%)	16.0 (32)	13.0 (26)	10.0 (20)	8.0 (16)	3.75 (15)
NVC, grams (wt%)	–	3.0 (6)	6.0 (12)	8.0 (16)	3.0 (12)
4G7, grams (wt%)	–	–	–	–	1.25 (5)
Thickness, microns	22.3	21.6	24.2	24.5	22.4

Unprocessed mirrors

Reflection Efficiency, %	32	51	64	66	58
fwhm, nm	6	5	5	5	6
λ_{max}, nm	476	477	477	478	478

Thermally processed: 150°C, 90 minutes, mirrors on film support

Reflection Efficiency, %	56	89	99.9	99.8	99.4
fwhm, nm	22	32	30	30	30
λ_{max}, nm	464	458	447	437	437

Thermally processed: 150°C, 90 minutes, mirrors on film support

Reflection Efficiency, %	56	80	99.9	99.2	84
fwhm, nm	16	25	30	42	35
λ_{max}, nm	467	471	470	476	462

EXAMPLE 37

This is a useful composition containing a low molecular weight poly(vinylacetate) binder, but no crosslinking monomer. Reflection holograms recorded in this composition can be thermally processed, without degradation, at temperatures of about 80°C or less, to obtain greater reflection efficiency and bandwidth.

A formulation was prepared containing POEA and NVC, as described below, and containing 284.8 g Vinac B-15 (56.96% by weight of total solids), 20.0 g o-Cl-HABI (4.0%), 10.0 g MMT (2.0%), 0.15 g DEAW (0.03%), 0.05 g BHT (0.01%), 75 g methanol, and 1,425 g dichloromethane. The formulation was coated and evaluated as described in Examples 28 and 32, except an extrusion-die coating bar attached to the Talboy coater was used instead of a doctor knife. The reflection efficiency, bandwidth, and wavelength of maximum reflection are presented below.

Examples 38-41

These are useful compositions containing a low molecular weight poly(vinylacetate) binder and varied amounts of TMPTA crosslinking monomer. Reflection holograms recorded in these compositions can be thermally processed to obtain greater reflection efficiency and bandwidth.

Four formulations were prepared, each containing TMPTA, POEA, and NVC, as described below, and each containing 289.5 g Vinac B-15 (56.96 by weight of total solids), 2.0 g o-Cl-HABI (4.0%), 1.0 g MMT (2.0%), 0.015 g DEAW (0.03%), 0.005 g BHT (0.01%), 7.5 g methanol, and 142.5 g dichloromethane. The formulations were coated and evaluated as described in Example 32. The reflection efficiency,

bandwidth, and wavelength of maximum reflection are
presented below.

5

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	Example Number				
	37	38	39	40	41
TMPTA, grams (wt%)	–	0.5 (1)	1.0 (2)	3.5 (7)	4.5 (9)
POEA, grams (wt%)	125 (25)	12.0 (24)	11.5 (23)	9.0 (18)	8.0 (16)
NVC, grams (wt%)	60 (12)	6.0 (12)	6.0 (12)	6.0 (12)	6.0 (12)
Thickness, microns	26.1	20.6	27.0	26.7	23.2

Unprocessed mirrors

Reflection Efficiency, %	57	67	72	50	53
fwhm, nm	5	5	5	5	5
λ_{max}, nm	476	478	478	477	477

Thermally processed: 80°C, 30 minutes, mirrors on film support

Reflection Efficiency, %	62	–	–	–	–
fwhm, nm	40	–	–	–	–
λ_{max}, nm	464	–	–	–	–

Thermally processed: 150°C, 90 minutes, mirrors on glass, film support removed

Reflection Efficiency, %	0[a]	0[a]	99.9	99.4	98.7
fwhm, nm	–	–	33	27	22
λ_{max}, nm	–	–	448	444	443

Thermally processed: 150°C, 90 minutes,
<u>mirrors between glass and film support</u>

Reflection

Efficiency, %	0^a	99.9	99.9	99.6	99.8
fwhm, nm	–	37	37	31	25
λ_{max}, nm	–	469	469	472	472

---

[a] Coating hazy, hologram destroyed or very weak.

EXAMPLES 42-43

These are examples of a low molecular weight poly(vinylacetate) based compositions for recording reflection holograms and use of these compositions to
5　produce automobile windshield safety glass with a reflection hologram internally mounted (as might be used for head-up displays).

Two formulations were prepared, each containing Vinac B-15, TMPTA, POEA, and NVC, as
10　described below, and each containing 2.0 g o-Cl-HABI (4.0%), 1.0 g MMT (2.0%), 0.015 g DEAW (0.03%), 0.005 g BHT (0.01%), 7.5 g methanol, and 142.5 dichloromethane. The formulations were coated on polyethylene terephthalate film support mounted on
15　glass plates and exposed as described in the general procedures.

Unprocessed holographic mirrors on glass, film support removed, were analyzed by recording and measuring their transmission spectra; results are
20　given below. A sheet of 30-mil Butacite® @140C was then placed over each holographic mirror and a second piece of glass placed on the opposite side of the @140C Butacite® @140C thus forming glass-hologram-Butacite® glass composite structures which were clamped tightly
25　together and heated to 150°C under vacuum for 60 minutes. The (safety) glass composite structures were then removed from the vacuum oven, allowed to cool to room temperature, and analyzed by recording and measuring their transmission spectra. Results
30　are presented below.

EXAMPLE 44

This is an example of a low molecular weight poly(vinylacetate) based composition containing
35　2-HPA, and its use to produce safety glass with an internally mounted reflection hologram.

A formulation was prepared containing Vinac B-15, TMPTA, POEA, NVC, and 2-HPA, as described below, and containing 1.0 g o-Cl-HABI (4.0%), 0.5 g MMT (2.0%), 0.0075 g DEAW (0.03%), 0.0025 g BHT (0.01%), 3.75 g methanol, and 71.25 g dichloromethane. The formulation was coated and evaluated as in Example 42. Results are presented below.

EXAMPLE 45

This is a useful composition containing Vinac B-100, a high molecular weight poly(vinylacetate) binder, and TMPTA crosslinking monomer. Reflection holograms recorded in this composition can be thermally processed to obtain greater reflection efficiency and bandwidth. This composition is also useful for producing safety glass with internally mounted reflection holograms.

A formulation was prepared containing Vinac B-100, TMPTA, POEA, NVC, and 2-HPA, as described below, and containing 0.75 g o-Cl-HABI (3.0%), 0.25 g MMT (1.0%), 0.010 g DEAW (0.04%), 0.0025 g BHT (0.01%), 3.75 g methanol, and 71.25 g dichloromethane. The formulation was coated and evaluated as in Example 42, except exposure was with a 514 nm argon ion laser beam, the holographic mirror was thermally processed before making the safety glass composite, and a longer heating cycle was used in making the safety glass composite, as shown in the table below.

Example Number

	42	43	44	45
Vinac B-15, grams (wt%)	28.48 (57)	28.48 (57)	14.24 (57)	–
Vinac B-100, grams (wt%)	–	–	–	14.73 (59)
TMPTA, grams (wt%)	2.50 (5)	4.50 (9)	1.25 (5)	1.75 (7)
POEA, grams (wt%)	10.00 (20)	8.00 (16)	3.75 (15)	3.25 (13)
NVC, grams (wt%)	6.00 (12)	6.00 (12)	3.00 (12)	3.00 (12)
2-HPA, grams (wt%)	–	–	1.25 (5)	1.25 (5)
Thickness, microns	24.2	23.2	21.5	22.4

Unprocessed mirrors

	42	43	44	45
Reflection Efficiency, %	65	57	50	32
fwhm, nm	4	4	4	5
λ_{max}, nm	477	476	477	503

Thermally processed: 150°C, 60 minutes, mirrors between glass and Butacite®

	42	43	44	45
Reflection Efficiency, %	84	80	85	–
fwhm, nm	50	33	55	–
λ_{max}, nm	498	503	510	–

Thermally processed: 100°C, 30 minutes,
then 150°C, 60 min., mirrors on glass

Reflection
Efficiency, %   —   —   —   73

fwhm, nm   —   —   —   20

λ_{max}, nm   —   —   —   493

(Process continued) then 150°C, 90 min.,
mirrors between glass and Butacite®

Reflection
Efficiency, %   —   —   —   72

fwhm, nm   —   —   —   15

λ_{max}, nm   —   —   —   562

EXAMPLES 46-47

These are useful compositions containing
high molecular weight poly(vinylacetate) binder with
and without a crosslinking monomer. Reflection
holograms recorded in these compositions can be
thermally processed to obtain greater reflection
efficiency and bandwidth.

Two formulations were prepared as listed
below. The formulations were coated as in the
general procedures given above, except an
extrusion-die coating bar was used rather than a
doctor knife, and the drier was set at 50-60°C.
Coatings were mounted on glass plates, exposed and
evaluated according to the general procedure, except
total laser exposure for each mirror was 300
mJ/cm^2. Results are presented below.

	Example Number	
	46	**47**
Vinac B-100, grams (wt%)	374.75 (59.96)	365.00 (56.96)
POEA, grams (wt%)	93.75 (15.0)	156.25 (25.0)
NVC, grams (wt%)	68.75 (11.0)	75.00 (12.0)
TMPTA, grams (wt%)	31.25 (5.0)	-
2-HPA, grams (wt%)	25.00 (4.0)	-
o-Cl-HABI, grams (wt%)	18.75 (3.0)	25.00 (4.0)
MMT, grams (wt%)	12.50 (2.0)	12.50 (2.0)
DEAW, grams (wt%)	0.188 (0.03)	0.188 (0.03)
BHT, grams (wt%)	0.063 (0.01)	0.063 (0.01)
Methanol, grams	93.8	93.8
Dichloromethane, grams	1781.2	1781.2
Thickness, microns	14.4	17.4
Unprocessed mirrors		
Reflection Efficiency,%	28	53
fwhm, nm	5	5
λ_{max}, nm	479	479

Thermally processed: 100°C, 30 minutes, mirrors between glass and film support

Reflection Efficiency,%	75	99
fwhm, nm	8	13
λ_{max}, nm	479	479

EXAMPLE 48

This is a useful composition containing poly(vinylbutyral) binder and TDC plasticizer, but no crosslinking monomer. Reflection holograms recorded in this composition can be thermally processed, without degradation, at temperatures of about 80°C or less to obtain greater reflection efficiency and bandwidth.

A formulation was prepared containing POEA, NVC, and TDC, as described below and containing 25.4 g PVB (50.93%), 1.0 g o-Cl-HABI (2.0%), 1.0 g MMT (2.0), 0.030 g BHT (0.01%), 20.0 g 2-propanol, and 180 g dichloromethane. The formulation was coated on film support mounted on the back of a front-surface mirror, exposed, and evaluated according to the general procedures given above. Results are presented below.

EXAMPLES 49-51

These are useful compositions containing poly(vinylbutyral) binder and TMPTA crosslinking monomer. Reflection holograms recorded in these compositions can be thermally processed to obtain greater reflection efficiency and bandwidth.

Three formulations were prepared, each containing TMPTA, POEA, and NVC, as described below, and each containing 21.6 g PVB (53.96%), 1.6 g o-Cl-HABI (4.0%), 0.80 g MMT (2.0%), 0.012 g DEAW (0.03%), 0.0040 g BHT (0.01%), 16.0 g ethanol, and 144.0 g dichloromethane. The formulations were coated, exposed, and evaluated as in Example 48. Results are presented below.

EXAMPLE 52

This is a useful composition containing poly(vinylbutyral) binder, TMPTA crosslinking monomer, and 4G7 plasticizer. Reflection holograms recorded in this composition can be thermally processed to obtain greater reflection efficiency and bandwidth.

A formulation was prepared containing TMPTA, POEA, NVC, and 4G7, as described below and containing 17.96 g PVB (53.96), 1.33 g $\underline{o}$-Cl-HABI (4.0%), 0.67 g MMT (2.0%), 0.010 g DEAW (0.03%), 0.0033 g BHT (0.01%), 13.3 g ethanol, and 119.8 g dichloromethane. The formulation was coated, exposed, and evaluated as in Example 48. Results are presented below.

Example Number

	48	49	50	51	52
TMPTA, grams (wt%)	–	2.0 (5)	2.0 (5)	2.0 (5)	1.67 (5)
POEA, grams (wt%)	5.0 (10)	4.0 (10)	10.0 (25)	14.0 (35)	3.3 (10)
NVC, grams (wt%)	12.5 (25)	10.0 (25)	4.0 (10)	–	4.7 (15)
4G7, grams (wt%)	–	–	–	–	3.3 (10)
Thickness, microns	24.5	23.9	26.1	24.1	26.7

Unprocessed mirrors

	48	49	50	51	52
Reflection Efficiency, %	49	49	48	20	43
fwhm, nm	6	4	5	5	4
λ_{max}, nm	474	478	476	477	477

Thermally processed: 45°C, 12 hours, mirrors on film support

	48	49	50	51	52
Reflection Efficiency, %	63	54	51	19	53
fwhm, nm	8	4	5	8	5
λ_{max}, nm	455	476	474	472	470

Thermally processed: 45°C, 12 hours, then 80°C, 30 minutes, mirrors on film support

	48	49	50	51	52
Reflection Efficiency, %	77	63	55	26	63
fwhm, nm	27	7	7	8	5
λ_{max}, nm	448	473	472	470	468

Thermally processed: 150°C, 30 minutes, mirrors on film support

Reflection					
Efficiency, %	0^a	75	90	58	82
fwhm, nm	–	11	9	8	17
λ_{max}, nm	–	424	447	457	440

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[a] Coating hazy/cloudy, hologram destroyed.

EXAMPLE 53

This is a useful composition coated on aluminized polyethylene terephthalate film.

A formulation identical to Example 34 was prepared and coated on 4-mil aluminized polyethylene terephthalate film using a 6-mil doctor knife. The drier temperature was 40-50°C. After drying, a cover sheet of silicon release polyethylene terephthalate film was laminated to the coating. A 4x5-inch section of coating was stripped of its cover sheet, mounted on a glass plate, and then exposed and evaluated according to the general procedure described above, except a front surface mirror was not clamped to the plate since the aluminized polyethylene terephthalate film served to reflect the incident radiation. After exposure, the aluminized polyethylene terephthalate film was removed leaving the holographic mirrors mounted on glass. Results before and after thermal processing follow:

	Unprocessed Mirror	Processed:150°C, 90 min., on glass
Reflection Efficiency, %	54	82
fwhm, nm	4	30
λ_{max}, nm	477	444

Having described the invention, we claim:

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1.   A process for forming a reflection hologram wherein
a reference beam of coherent actinic radiation and an
object beam of the same coherent actinic radiation enter a
layer of recording medium from opposite sides to create an
interference pattern in the medium that forms the hologram,
characterised in that the medium is a substantially solid,
photopolymerizable layer consisting essentially of:
        (a) a polymeric binder selected from the group
consisting of polyvinyl acetate, polyvinyl butyral,
polyvinyl acetal, polyvinyl formal, interpolymers
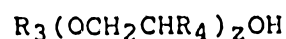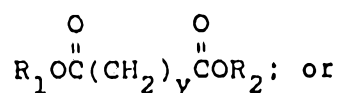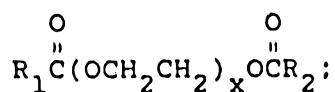containing major segments thereof, and mixtures thereof;
        (b) an ethylenically unsaturated monomer selected
from the group consisting of carbazole containing monomers
and liquid monomers containing one or more moieties
selected from the group consisting of (1) phenyl, (2)
phenoxy, (3) naphthyl, (4) naphthyloxy, (5) heteroaromatic
groups containing up to three aromatic rings, (6) chlorine
and (7) bromine and
        (c) a photoinitiator system activatable by the
actinic radiation.

2.   The process of claim 1 wherein the liquid monomer
is selected from the group consisting of phenoxyethyl
acrylate, phenol ethoxylate monoacrylate, the
di(2-acryloxyethyl) ether of bisphenol-A, ethoxylated
bisphenol-A diacrylate, 2-(1-napthyloxy) ethyl acrylate,
and mixtures thereof.

3. The process of claim 2 wherein the ethylenically unsaturated monomer is a mixture of a solid monomer selected from the group consisting of N-vinyl carbazole, 3,6-dibromo-9-vinyl carbazole, 2,4,6-tribromophenyl acrylate or methacrylate, pentachlorophenyl acrylate or methacrylate, 2-naphthyl acrylate or methacrylate, 2-(2-naphthyloxy)ethyl acrylate or methacrylate, the di-(2-acryloxyethyl)ether of tetrabromo-bisphenol-A and mixtures thereof; and a liquid monomer selected from the group consisting of phenoxyethyl acrylate, phenol ethoxylate acrylate, the di(2-acryloxyethyl ether) of bisphenol-A, ethoxylated bisphenol-A diacrylate, 2-(1-naphthyloxy)ethyl acrylate, and mixtures thereof.

4. The process of claim 1 in which a plasticizer is also present, which plasticizer is selected from the group consisting of tris(2-ethylhexyl)phosphate, glyceryl tributyrate, and a compound having the general formula:

$$R_1 \overset{\overset{O}{\|}}{C}(OCH_2CH_2)_x O\overset{\overset{O}{\|}}{C}R_2;$$

$$R_1 O\overset{\overset{O}{\|}}{C}(CH_2)_y \overset{\overset{O}{\|}}{C}OR_2; \text{ or}$$

$$R_3(OCH_2CHR_4)_zOH$$

wherein R_1 and R_2 each is an alkyl group of 1 to 10 carbon atoms, R_3 is H or an alkyl group of 8 to 16 carbon atoms, R_4 is H or CH_3, x is 1-4, y is 2-20, and z is 1-20.

5.   The process of claim 4 wherein the plasticizer
     is selected from the group consisting of
     triethylene glycol dicaprylate, triethylene
     glycol bis(2-ethylhexanoate), diethyl adipate,
 5   dibutyl adipate, tetraethylene glycol
     diheptanoate, dibutyl suberate, diethyl
     sebacate, tris(2-ethylhexyl)phosphate, and
     glyceryl tributyrate.

10
6.   The process of claim 4 in which said plasticizer
     is substituted for ~~at least~~ a portion of the
     liquid ethylenically unsaturated monomer.

7.   The process of claim 1 wherein the solid
15   photopolymerizable layer contains an added
     crosslinking monomer containing two or more
     terminal ethylenically unsaturated groups.

8.   The process of claim 7 wherein the crosslinking
20   monomer is diacrylate or dimethacrylate of a
     bisphenol-A epoxy adduct.

9.   A process for forming and enhancing a reflection
     hologram in a substantially solid
25   photopolymerizable recording medium the process
     comprising:
     A.   Projecting a reference beam of coherent
          actinic radiation on a first side of the
          recording medium which consists essentially
30   of:
          (1) a polymeric binder selected from the
               group consisting of polyvinyl acetate,
               polyvinyl butyral, polyvinyl acetal,
               polyvinyl formal, interpolymers
35   containing major segments thereof and
               mixtures thereof:

> (2)   an ethylenically unsaturated monomer
>   selected from the group consisting of
>   carbazole containing monomers and liquid
>   monomer containing one or more moieties
>   selected from the group consisting of (a)
>   phenyl, (b) phenoxy,(c) naphthyl, (d)
>   naphthyloxy, (e) heteroaromatic group
>   containing up to three aromatic rings, (f)
>   chlorine and (g) bromine and
>
> (3)   a photoinitiator system activatable by the
>   actinic radiation;

B.   Projecting an object beam of the same coherent
        actinic radiation approximately in an opposite
        direction to the reference beam onto a second side
        of the photopolymerizable layer so as to intersect
        with the reference beam in a plane within the layer
        whereby a reflection hologram is formed;

C.   Irradiating the imaged photopolymerizable layer
        with uniform source of actinic radiation; and

D.   Treating the irradated reflection hologram with a
        liquid enhancing agent which is a swelling agent
        for the photopolymerized layer.

10.   A process of claim 9 wherein the liquid enhancing
agent contains a polar organic liquid selected from the
group consisting of an alcohol, a ketone, an aldehyde, a
glycol alkyl ether, an ester, a liquid monomer and mixtures
thereof.

11. The process of claim 10 wherein the liquid
    enhancing agent is selected from the group
    consisting of 1-propanol, methanol, ethanol,
    2-propanol, acetone, methyl ethyl ketone,

5   cyclohexanone, benzaldehyde, ethyl acetate,
    butyl benzoate, phenoxyethyl acrylate, phenol
    ethoxylate acrylate, ethoxylated bisphenol-A
    diacrylate, and mixtures thereof.

10 12. The process of claim 9 wherein the liquid
    enhancing agent contains a substantially inert
    liquid diluent.

13. The process of claim 12 wherein the liquid
15 diluent is selected from the group consisting of
    water, inert hydrocarbon solvents,
    1,2-dichloroethane, and trichlorotrifluoroethane.

14. The process of claim 9 wherein the swelling
20 agent is removed from the treated layer by
    evaporation.

15. The process of claim 9 wherein each projected
    beam subtends an angle up to 70° from the normal
25 to the plane of the layers sides.

16. A process for forming and enhancing a reflection
    hologram in a substantially solid
    photopolymerizable recording medium comprising:
30 A. Projecting a reference beam of coherent
        actinic radiation on a first side of the
        recording medium which consists essentially
        of:
        (1) a polymeric binder selected from the
35   group consisting of polyvinyl acetate,
            polyvinyl butyral, polyvinyl acetal,
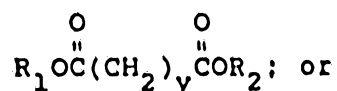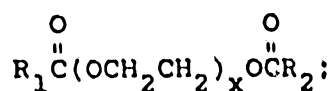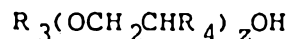   polyvinyl formal, interpolymers

containing major segments thereof and
mixtures thereof:

(2)   an ethylenically unsaturated monomer
        selected from the group consisting of
        carbazole containing monomers and a liquid
        monomer containing one or more moieties
        selected from the group consisting of (a)
        phenyl, (b) phenoxy, (c) naphthyl, (d)
        naphthyloxy, (e) heteroaromatic group
        containing up to three aromatic rings, (f)
        chlorine and (g) bromine and

(3)   a photoinitiator system activatable by the
        actinic radiation;

B.   Projecting an object beam of the same coherent
        actinic radiation approximately in an opposite
        direction to the reference beam onto a second side
        of the photopolymerizable layer so as to intersect
        with the reference beam in a plane within the layer
        whereby a reflection hologram is formed;

C.   Irradiating the imaged photopolymerizable layer
        with uniform source of actinic radiation; and

D.   Heating the irradiated reflection hologram at a
        temperature of at least 50°C for a period of time
        to enhance the reflectivity of the hologram.

17.   The process of claim 16 wherein the solid recording
medium contains an added crosslinking monomer containing at
least two terminal ethylenically unsaturated groups.

18.   The process of claim 17 wherein the crosslinking
monomer is diacrylate or dimethacrylate of a bisphenol-A
epoxy adduct.

19. The process of claim 16 wherein the unsaturated monomer is a phenoxyalkyl acrylate or methacrylate, a phenol ethoxylate acrylate or methacrylate, a phenyl alkyl acrylate or methacrylate, 2-(1-naphthyloxy)ethyl acrylate, the di(2-acryloxyethyl)ether of bisphenol-n, or ethoxylated bisphenol-A diacrylate.

20. A process of claim 16 wherein the ethylenically unsaturated monomer is a mixture of a solid monomer selected from the group consisting of N-vinyl carbazole, 3,6-dibromo-9-vinyl carbazole, 2,4,6-tribromophenyl acrylate or methacrylate, pentachlorophenyl acrylate or methacrylate, 2-naphthyl acrylate or methacrylate, 2-(2-naphthyloxy)ethyl acrylate or methacrylate, the di-(2-acryloxyethyl)ether of tetrabromo-bisphenol-A, and mixtures thereof and a liquid monomer selected from the group consisting of phenoxyethyl acrylate, phenol ethoxylate acrylate, the di(2-acryloxyethyl ether) of bisphenol-A, ethoxylated bisphenol-A diacrylate, 2-(1-naphthyloxy)ethyl acrylate, and mixtures thereof.

21. The process of claim 16 in which a plasticizer is also present, which plasticizer is selected from the group consisting of tris(2-ethylhexyl)-phosphate, glyceryl tributyrate, and a compound having the general formula:

$$R_1\overset{\overset{O}{\|}}{C}(OCH_2CH_2)_x\overset{\overset{O}{\|}}{O}CR_2;$$

$$R_1O\overset{\overset{O}{\|}}{C}(CH_2)_y\overset{\overset{O}{\|}}{C}OR_2; \text{ or}$$

$$R_3(OCH_2CHR_4)_zOH$$

wherein R_1 and R_2 each is an alkyl group of 1 to 10 carbon atoms. R_3 is H or an alkyl group of 8 to 16 carbon atoms. R_4 is H or CH_3, x is 1-4, y is 2-20, and z is 1-20.

22.   The process of claim 21 wherein the plasticizer is selected from the group consisting of triethylene glycol dicaprylate, triethyleneglycol bis(2-ethylehexanote), diethyl adipate, dibutyl adipate, tetraethylene glycol diheptanoate, dibutyl suberate, diethyl sebacate, tris(2-ethylhexyl)phosphate, and glyceryl tributyrate.

23.   The process of claim 21 in which said plasticizer is substituted for a portion of the liquid ethylenically unsaturated monomer.

24.   A process for forming a reflection hologram according to claim 1 and substantially as hereinbefore described.

25.   A process for forming and enhancing a reflection hologram according to claim 9 or 16, and substantially as hereinbefore described.

DATED THIS 2ND DAY OF JANUARY, 1991.

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Fellows Institute of Patent
Attorneys of Australia.