Advantages of the CROP Technology in Aprilis Photopolymer Recording Media for High Performance Holographic Storage Systems

Contribution from
Aprilis, Inc.

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Acknowledgment

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Testing of Media at Independent Laboratories

Holoplex
HRP Laboratories
IBM
MetroLaser
Rockwell International
Samsung
Siros Technologies
Wavefront Research

University of Arizona
California Institute of Technology
De Monfort University
Stanford University
Technical University of Berlin

Imaging Challenges for Recording Medium

- **Modulation of Refractive Index**
  - **$\Delta n \geq 0.004$ at 0.2 % transverse shrinkage**
- **Record Wide Range of Spatial Frequencies**
  - $0.1\ \mu \sim< \Lambda < \sim 10\ \mu$
- **Record Wide Range of Fringe Visibilities**
  - $0.09 \sim< V < \sim 1.0$
  - $500 \sim> (I_r/I_o) > 1.0$
- **Media Thickness $\geq 500\ \mu m$**
- **Good Recording Sensitivity Without Reciprocity Failure**
  - **$S \sim\geq 500$ cm/J For Intensity Range of mW to 5×10^5W**
- **Low Exposure Threshold**
  - $\sim < 25\ mJ/cm^2$
- **Stable Image for Low Diffraction Efficiencies**
- **Good Angular Selectivity**
  - $\eta_{pk}/\eta_{sat} \sim > 10$, ***low Background Uplift, ~ no Asymmetry***
- **Small Angular Deviations from Bragg Matching Condition**
  - ***Volume Shrinkage*** **~ < 0.1 %**
- **Low Scattering; $\leq$ 1E-4/steradian, $\cong 10^{-6}\ \eta$**
- **Low Absorbance After Recording: $(\alpha L) < 0.05$**
- **Phase Uniformity/homogeneity: $< \pi/5$**
- **Dry Process**
- **Lifetime (after recording): > 10 years**
- **Pre-recording Shelf Life: > 1 year**

Conventional Photopolymers

- Based on free radical polymerization of vinyl monomers
  [Lucent 2-Chemistry System, Dupont HRF, DMP-128]
- Inhibited by oxygen
- Suffer from significant volume shrinkage
- Exhibit high intensity reciprocity failure
- High exposure threshold
- Performance drop for low spatial frequencies

Aprilis Holographic Recording Technology

- Photopolymer System Comprising:

›› Cationic ring-opening polymerization (CROP) monomers

›› Cyclohexene oxide groups with siloxane spacers

›› Multifunctional low shrinkage monomers

›› High-n_D siloxane binders support cationic polymerization

›› Iodonium salt photoacid generators (PAG)

›› Polynuclear aromatic photosensitizing dyes
⇒ sensitized to visible laser lines

Cationic Versus Radical Polymerization Rates

Propagation rate constants for free ions ≥ radical propagating species

Free ion concentration increases with increasing solvating power

Ion pair propagation rate constants typically < radical propagating species

Closely associated ion pair changes to solvent-separated ion pair with increased solvating power

Large and less tightly bound gegenion increases reactivity of ion pair towards propagation

$$R_p \sim \frac{k_p}{k_t^{1/2}} \quad \text{in Radical Polymerization}$$

$$R_p \sim \frac{k_p}{k_t} \quad \text{in Cationic Polymerization}$$

$$\frac{k_p}{k_t} >> \frac{k_p}{k_t^{1/2}} \quad \text{by as much as four orders of magnitude}$$

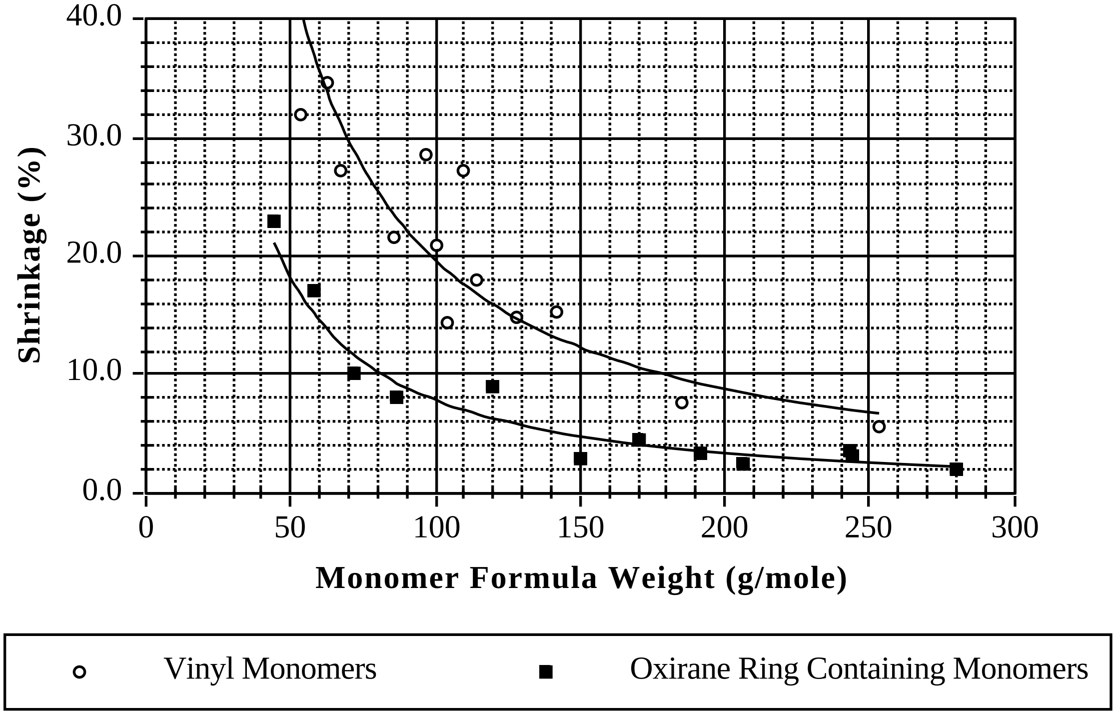
{ Termination in Radical Polymerization is Fast Relative to Propagation}

Concentration of Reactive Chain End

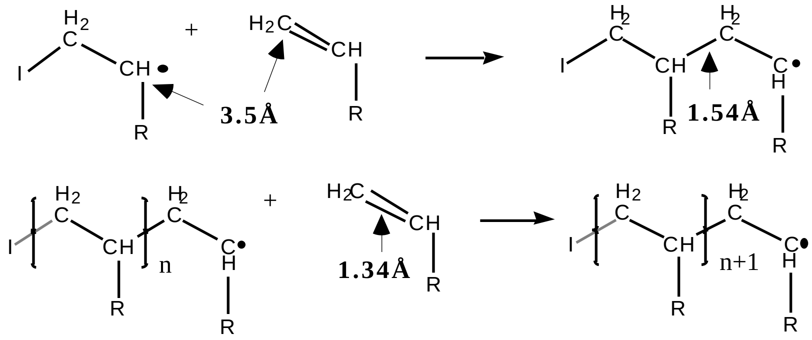
Concentration of propagating species in Cationic Polymerization is typically much higher than in Radical Polymerization for both free ions and ion pairs.

Radical; ~ 10^{-7} to 10^{-9} M **Cationic; ~ 10^{-3} to 10^{-5} M**

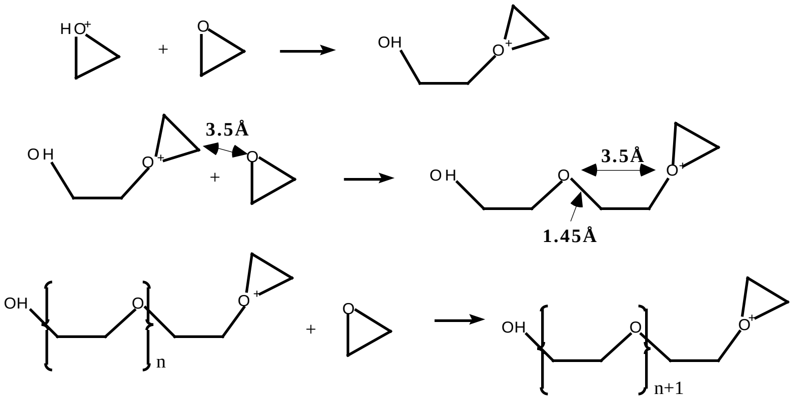
Comparison of Shrinkage From Polymerization of Vinyl Monomers versus Ring Opening Oxirane Monomers



Vinyl Free Radical



Cationic Ring Opening



Dynamic Range of Holographic Recording Medium

Determination of n_1 for thick media

Single Transmission Recording to High Diffraction Efficiency
Overmodulation when T > 50 µm for ULSH photopolymer

Cumulative Grating Strength

Multiple Co-locational Recordings, Each to Low Diffraction Efficiency (~0.1%)

$$\nu_M = \sum_{i=1}^{M} \sqrt{(\eta_i)} \quad \textit{for} \quad M \text{ Multiplexed Holograms}$$

where $\sqrt{\eta_i} = \sin \nu_i \cong \nu_i$ for case of low diffraction efficiency

where $\nu_i(\lambda) = \dfrac{\pi\, n_1(\lambda) T}{\lambda \cos\theta_{\mathrm{int}}}$ for intensity based diffraction efficiency
where refractive index modulation exhibits dispersion
n_1 can be dependant upon grating angle and period
ν is grating angle and period dependant

More Holograms per Location as Thickness T Increases

Exposure Scheduling

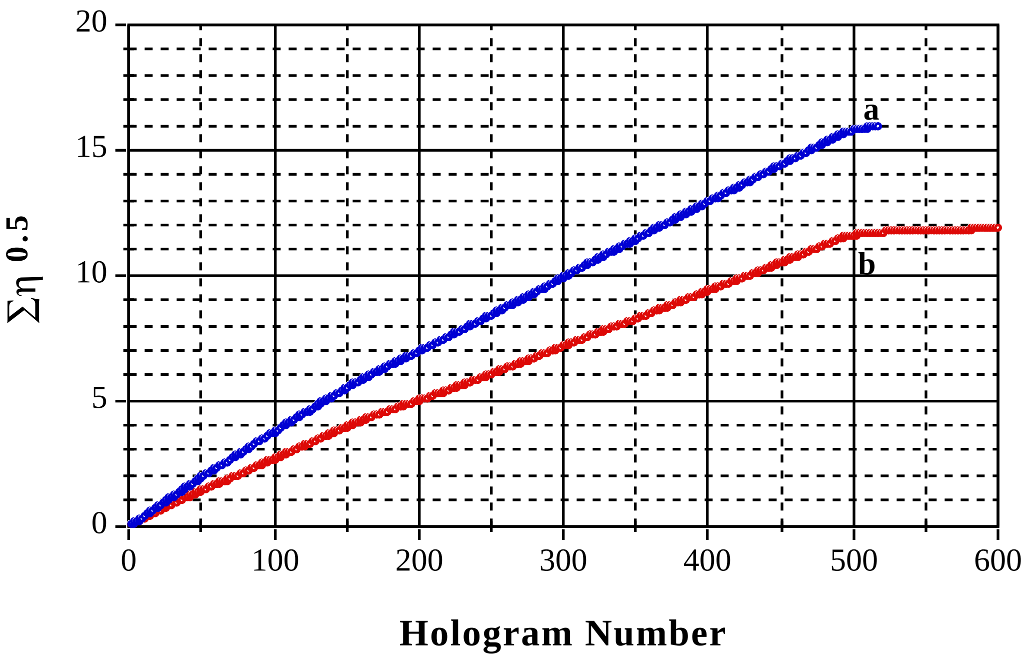
Allocates a grating strength of $\dfrac{\nu_N}{M}$ for each of M holograms
and individual diffraction efficiencies scale as $\eta_i \sim \dfrac{1}{M^2}$

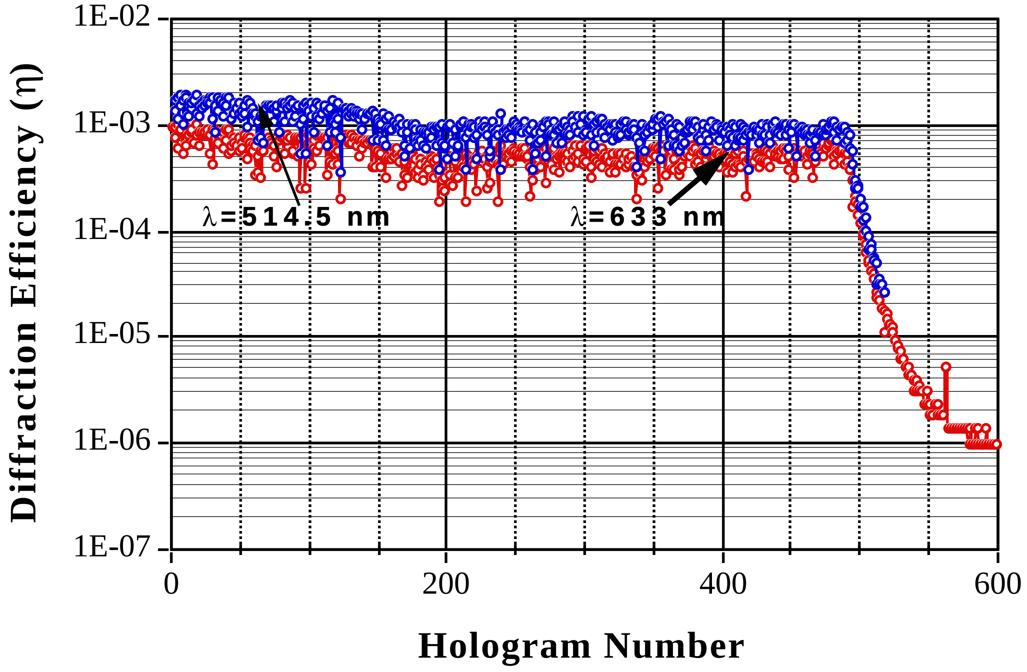
As photopolymerization proceeds the amount of available monomer and photoinitiator diminishes and the physical state of the material approaches vitrification ⇒ Exposure energy must increase with M.

Finite Dynamic Range: More Holograms, Smaller n_1 per Hologram

Growth in Cumulative Grating Strength and Diffraction Efficiency of 600 Sequentially Recorded Plane-wave Holograms Imaged Co-locationally in ULSH-500- 6A using Peristrophic and Angle Multiplexing

$\Delta\phi$ = 1.5° for 5 Different Grating Angles (ϕ_i = -9.8°, -6.2°, -2.5°, +1.2°, +5.0°)


Reconstruction at (a) λ = 514.5 nm and (b) λ = 632.8 nm



Diffraction Efficiency of Plane-Wave Transmission Hologram Recorded During Peristrophic Angle Multiplexing, and Calculated Refractive Index Modulation, versus Reconstruction Wavelength

Effect of Dispersion in Refractive Index

Formulation: ULSH-500 Dual Monomer/Binder with Reactive Copolymer

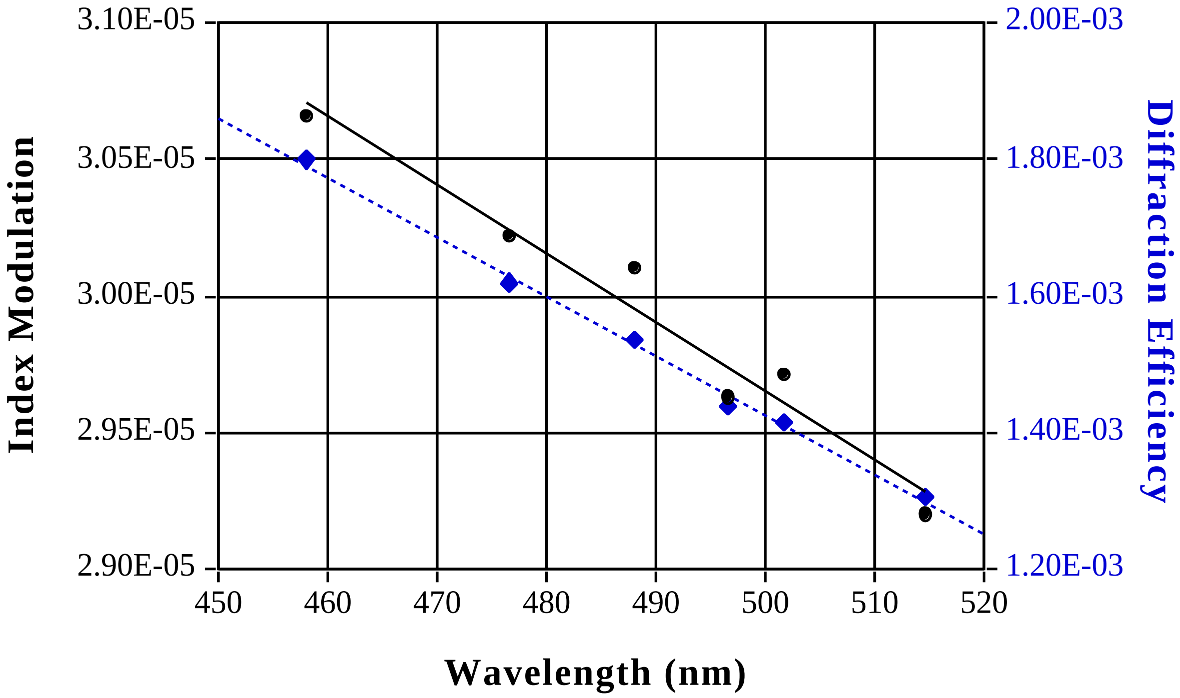
Plane-Wave Recording Geometry: $\Phi_{int} = 6.2°$ ***at*** $\lambda_W = 514.5$ ***nm***
Read Wavelength; $\lambda_R = 514.5, 501.7, 496.5, 488.0, 476.5, 457.9$ ***nm***

$$\nu_i(\lambda) = \frac{\pi n_1(\lambda) T}{\lambda \cos\theta_{\mathrm{int}}}$$

$$\frac{n_{1(632.8)}}{n_{1(514.5)}} = 0.89$$ **(Experimental values for n_{D}, $\Omega_{1_{ext}}$, $\Omega_{2_{ext}}$, η_i)**

$= 0.90$ **(Calculated from Extrapolation of Ar^+ data)**

$$\sum n_{1(632.8)} = 1.141E-2 \qquad \sum n_{1(514.5)} = 1.283E-2$$



y = -2.516E-08x + 4.223E-05 $r^2 = 9.587E-01$

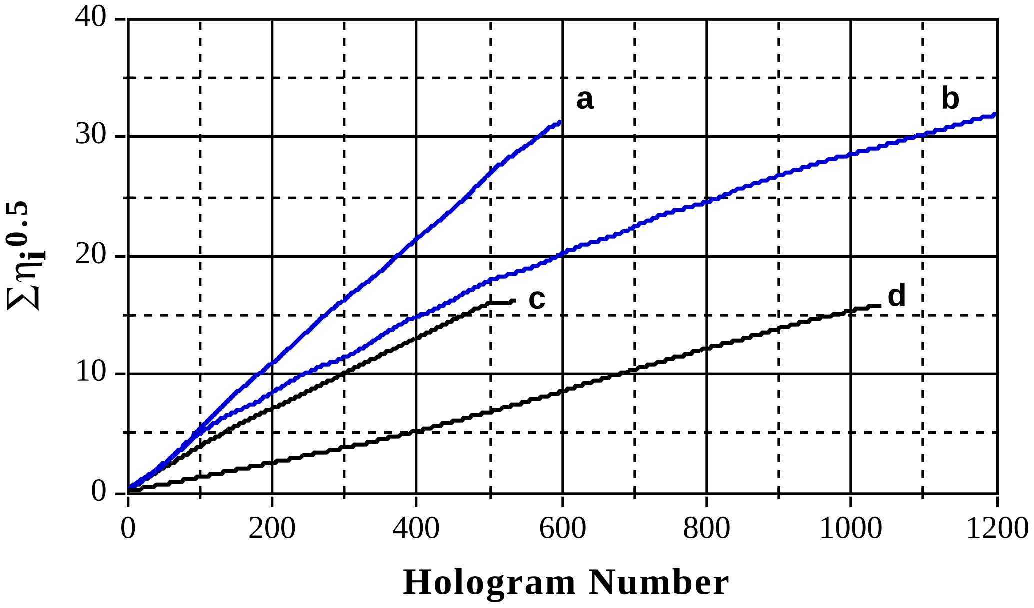
Growth in Cumulative Grating Strength for Plane-wave Holograms Recorded Sequentially and Co-locationally in ULSH-500-6 and ULSH-500- 7 CROP Media Using Peristrophic and Angle Multiplexing

(a); (b); ULSH-500-7C in 500 µmThickness
(c); (d); ULSH-500- 6A in 200 µmThickness

$\Delta\phi = 1.5°$ for Sample Plane Angles of (a), (c) θ = -16, -10°, -4°, +2°, +8°
(b) θ = -17, -11°, -5°, +1°, +7°, +13°, +17°, +3°, +9°, +15°
$\Delta\phi = 1.2°$ for Sample Plane Angles of (d) θ = -16, -11°, -6°, -1°, +4, +9°, +14°

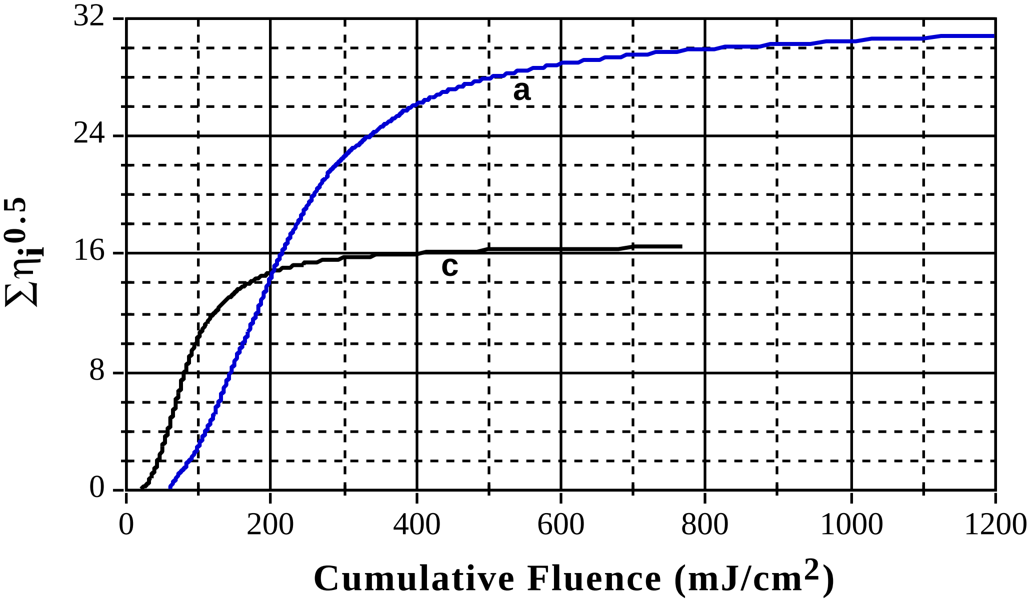
Pre-imaging Exposure Fluence = (a) 60 , (b) 80 mJ/cm^2 at 0.8 mW/cm^2 at λ = 514.5 nm
Exposure Irradiance = 12.1 mW/cm^2, Reconstruction at λ = 514.5 nm

Pre-imaging Exposure Fluence = (c), (d) 20 mJ/cm^2 at 0.4 mW/cm^2 at λ = 514.5 nm
Exposure Irradiance = 4.85 mW/cm^2, Reconstruction at λ = 514.5 nm



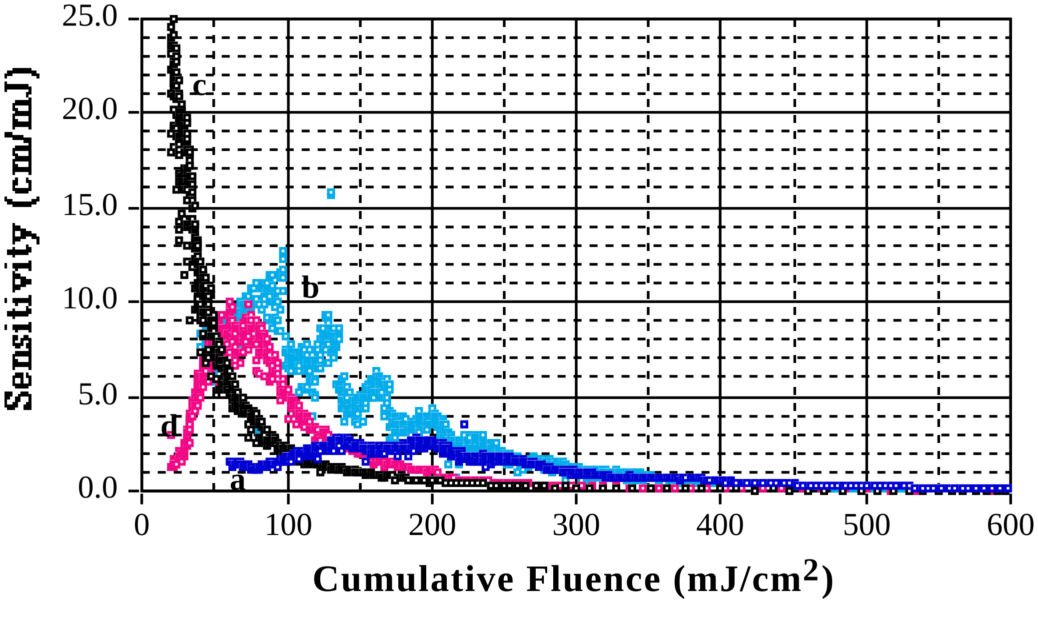
Cumulative Grating Strength versus Cumulative Fluence for 600 Plane-wave Holograms Recorded Sequentially and Co-locationally Using Peristrophic and Angle Multiplexing in ULSH CROP Media

(a) ULSH-500-7C [500 µm]   (c) ULSH-500- 6A [200 µm]



Recording Sensitivity versus Cumulative Fluence

(a), (c) as above; (b) ULSH-500-14B [500 µm]; (d) ULSH-500-7A [200 µm]



Growth in Cumulative Grating Strength and Sensitivity of Recording Medium as a Function of Cumulative Fluence for Plane-wave Holograms Recorded Sequentially and Co-locationally in 200 μm Thickness of ULSH-500-7A Using Peristrophic and Angle Multiplexing

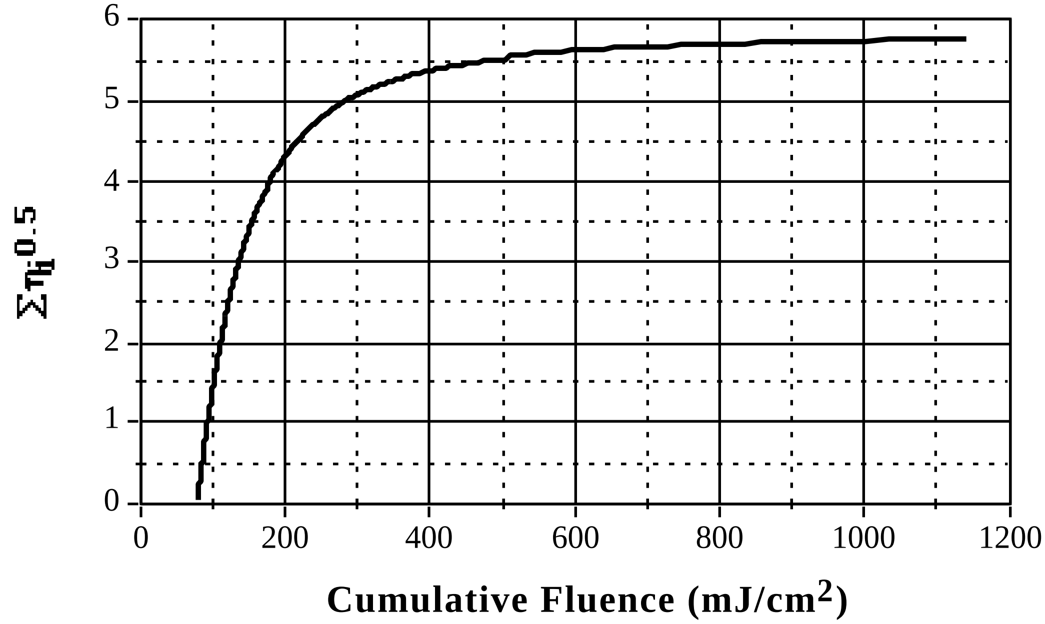
Formulation Comprising Increased Equiv. Wt. Multifunctional Monomer

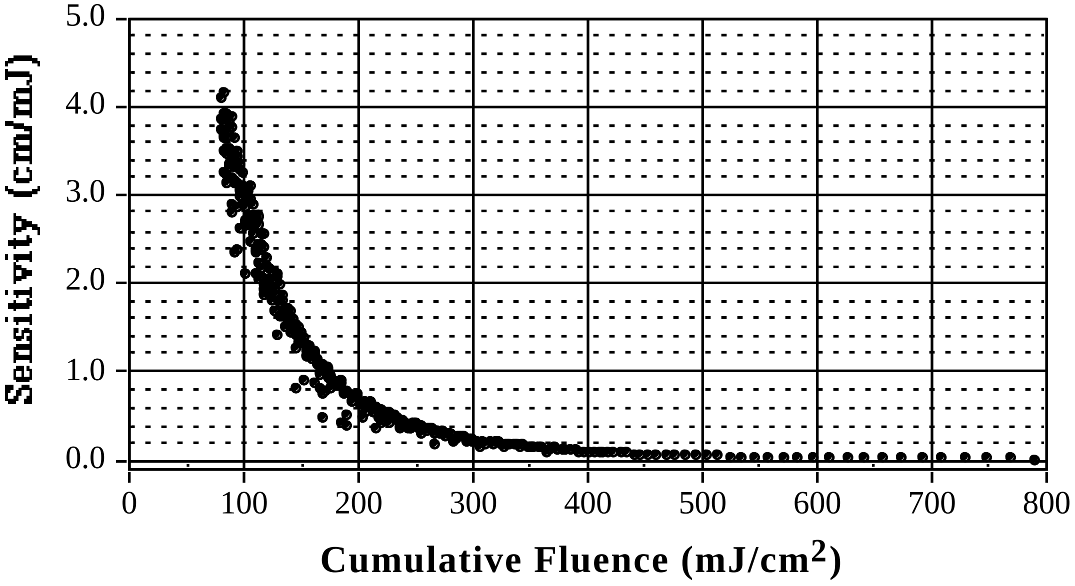
$\Delta\phi$ = 1.5° for 3 Different Grating Angles (θ = -15°, -8°, -1°)

Pre-imaging Exposure Fluence = 80.5 mJ/cm^2 [Volume Shrinkage Reduced to ~ 0.2%]

I_{Wr} = 4.85 mW/cm^2

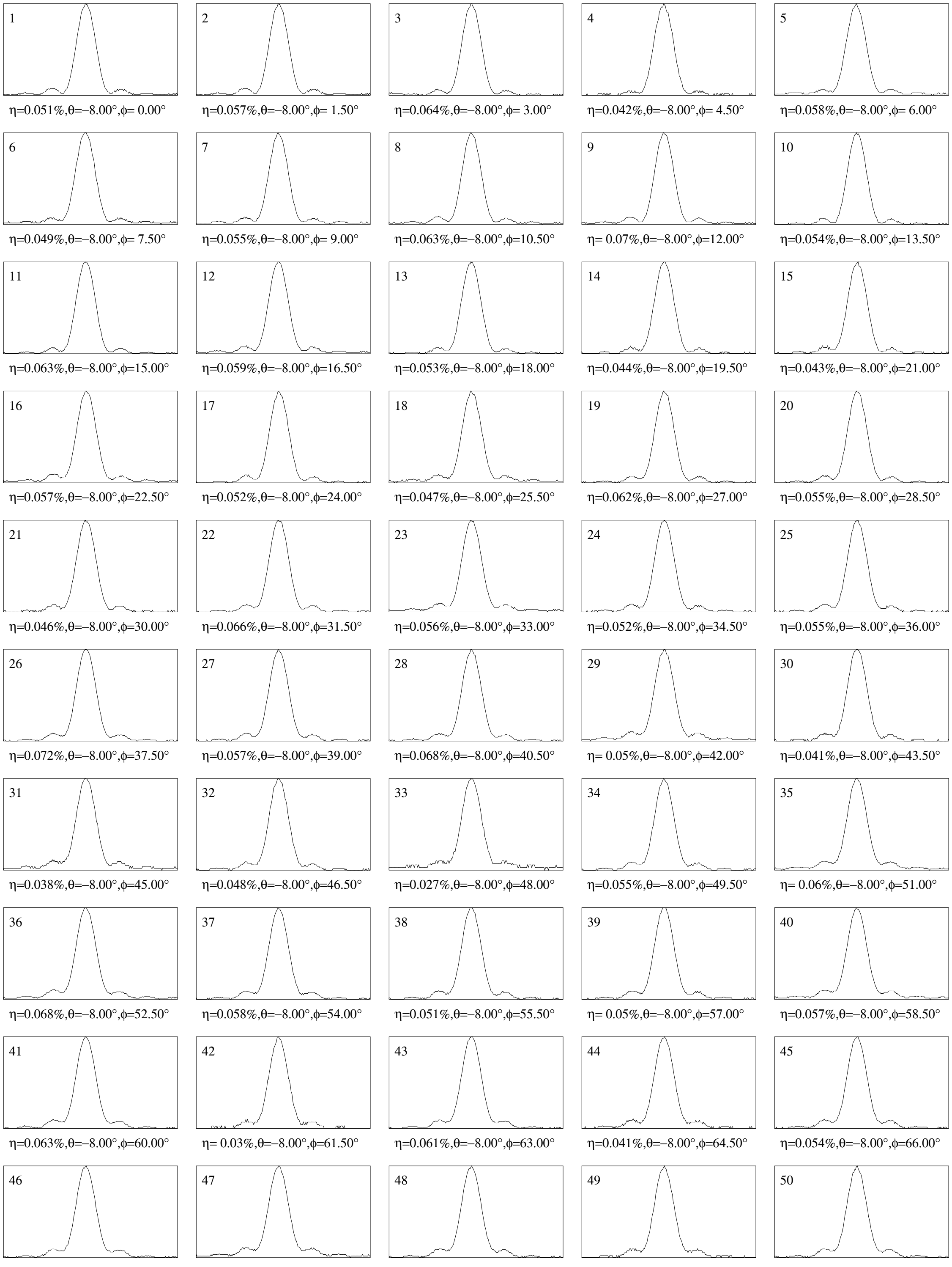
Reconstruction at λ = 514.5 nm





Angle Selectivity Profiles, Obtained at 514.5 nm With Read Irradiance of 5 mW/cm^2, After Co-locational Multiplexing in ULSH-500-7A CROP medium of 200 μm Thickness pre-exposed to Diminish Cumulative Volume Shrinkage to ~ 0.2%

[First 50 of 360 Sequentially Recorded Plane-Wave Holograms]

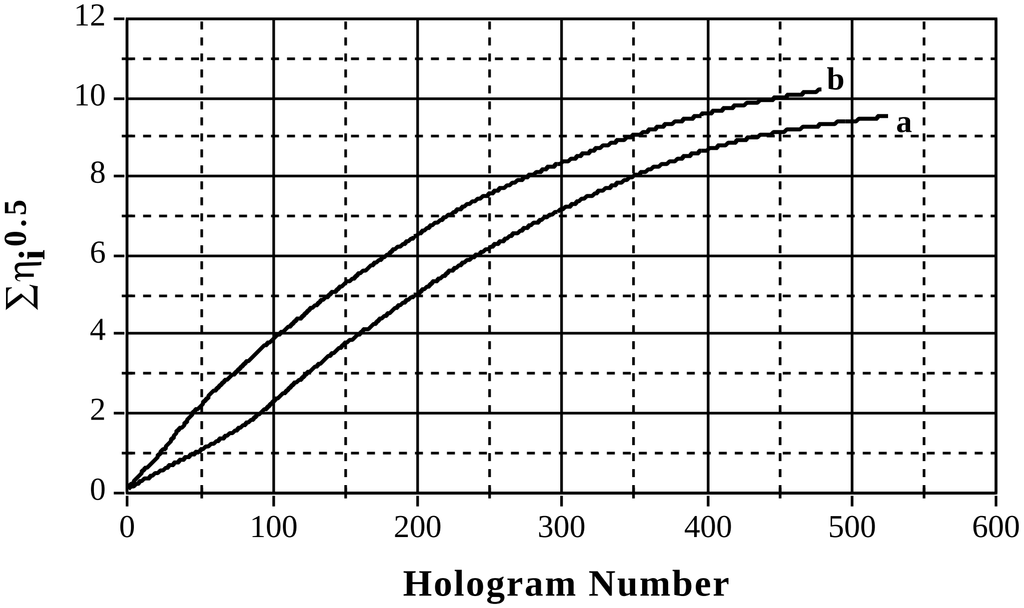


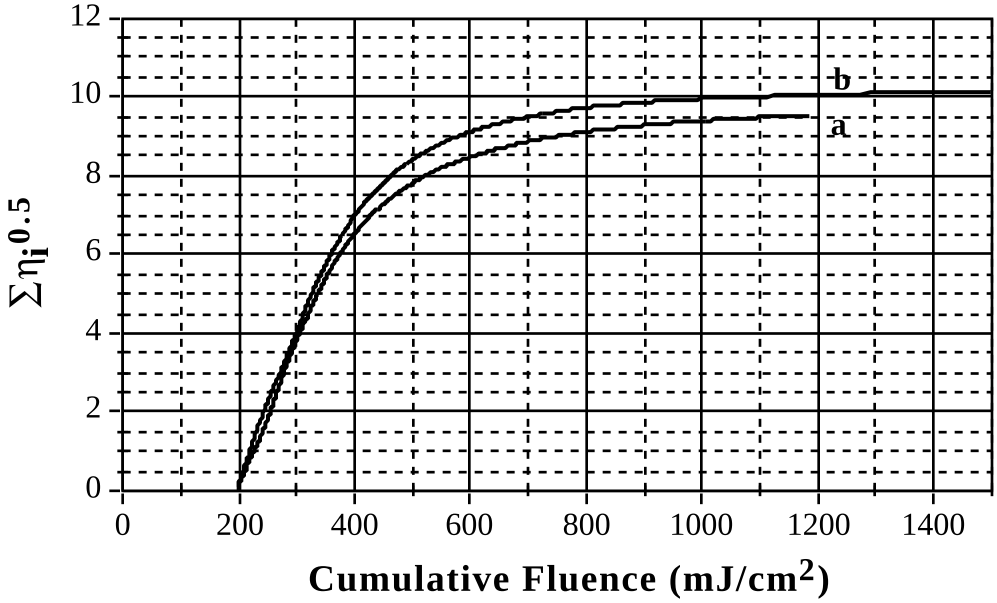
$\eta=0.051\%, \theta=-8.00^\circ, \phi= 0.00^\circ$
$\eta=0.057\%, \theta=-8.00^\circ, \phi= 1.50^\circ$
$\eta=0.064\%, \theta=-8.00^\circ, \phi= 3.00^\circ$
$\eta=0.042\%, \theta=-8.00^\circ, \phi= 4.50^\circ$
$\eta=0.058\%, \theta=-8.00^\circ, \phi= 6.00^\circ$
$\eta=0.049\%, \theta=-8.00^\circ, \phi= 7.50^\circ$
$\eta=0.055\%, \theta=-8.00^\circ, \phi= 9.00^\circ$
$\eta=0.063\%, \theta=-8.00^\circ, \phi=10.50^\circ$
$\eta= 0.07\%, \theta=-8.00^\circ, \phi=12.00^\circ$
$\eta=0.054\%, \theta=-8.00^\circ, \phi=13.50^\circ$
$\eta=0.063\%, \theta=-8.00^\circ, \phi=15.00^\circ$
$\eta=0.059\%, \theta=-8.00^\circ, \phi=16.50^\circ$
$\eta=0.053\%, \theta=-8.00^\circ, \phi=18.00^\circ$
$\eta=0.044\%, \theta=-8.00^\circ, \phi=19.50^\circ$
$\eta=0.043\%, \theta=-8.00^\circ, \phi=21.00^\circ$
$\eta=0.057\%, \theta=-8.00^\circ, \phi=22.50^\circ$
$\eta=0.052\%, \theta=-8.00^\circ, \phi=24.00^\circ$
$\eta=0.047\%, \theta=-8.00^\circ, \phi=25.50^\circ$
$\eta=0.062\%, \theta=-8.00^\circ, \phi=27.00^\circ$
$\eta=0.055\%, \theta=-8.00^\circ, \phi=28.50^\circ$
$\eta=0.046\%, \theta=-8.00^\circ, \phi=30.00^\circ$
$\eta=0.066\%, \theta=-8.00^\circ, \phi=31.50^\circ$
$\eta=0.056\%, \theta=-8.00^\circ, \phi=33.00^\circ$
$\eta=0.052\%, \theta=-8.00^\circ, \phi=34.50^\circ$
$\eta=0.055\%, \theta=-8.00^\circ, \phi=36.00^\circ$
$\eta=0.072\%, \theta=-8.00^\circ, \phi=37.50^\circ$
$\eta=0.057\%, \theta=-8.00^\circ, \phi=39.00^\circ$
$\eta=0.068\%, \theta=-8.00^\circ, \phi=40.50^\circ$
$\eta= 0.05\%, \theta=-8.00^\circ, \phi=42.00^\circ$
$\eta=0.041\%, \theta=-8.00^\circ, \phi=43.50^\circ$
$\eta=0.038\%, \theta=-8.00^\circ, \phi=45.00^\circ$
$\eta=0.048\%, \theta=-8.00^\circ, \phi=46.50^\circ$
$\eta=0.027\%, \theta=-8.00^\circ, \phi=48.00^\circ$
$\eta=0.055\%, \theta=-8.00^\circ, \phi=49.50^\circ$
$\eta= 0.06\%, \theta=-8.00^\circ, \phi=51.00^\circ$
$\eta=0.068\%, \theta=-8.00^\circ, \phi=52.50^\circ$
$\eta=0.058\%, \theta=-8.00^\circ, \phi=54.00^\circ$
$\eta=0.051\%, \theta=-8.00^\circ, \phi=55.50^\circ$
$\eta= 0.05\%, \theta=-8.00^\circ, \phi=57.00^\circ$
$\eta=0.057\%, \theta=-8.00^\circ, \phi=58.50^\circ$
$\eta=0.063\%, \theta=-8.00^\circ, \phi=60.00^\circ$
$\eta= 0.03\%, \theta=-8.00^\circ, \phi=61.50^\circ$
$\eta=0.061\%, \theta=-8.00^\circ, \phi=63.00^\circ$
$\eta=0.041\%, \theta=-8.00^\circ, \phi=64.50^\circ$
$\eta=0.054\%, \theta=-8.00^\circ, \phi=66.00^\circ$
$\eta= 0.06\%, \theta=-8.00^\circ, \phi=67.50^\circ$
$\eta=0.048\%, \theta=-8.00^\circ, \phi=69.00^\circ$
$\eta=0.051\%, \theta=-8.00^\circ, \phi=70.50^\circ$
$\eta=0.038\%, \theta=-8.00^\circ, \phi=72.00^\circ$
$\eta=0.051\%, \theta=-8.00^\circ, \phi=73.50^\circ$

Growth in Cumulative Grating Strength for Plane-wave Holograms Recorded Sequentially and Co-locationally in 500 µm Thickness of ULSH-500-7B Using Peristrophic and Angle Multiplexing

Formulation Comprises Increased Equiv. Wt. Multifunctional Monomer

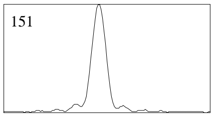
$\Delta\phi$ = 1.5° for 5 Different Grating Angles (where θ = -16, -10°, -4°, +2°, +8°)
Pre-imaging Exposure Fluence = 200 mJ/cm^2 [Volume Shrinkage Reduced to ~ 0.25%]
Exposure Irradiance = (a) 8.0 mW/cm^2 (b) 13.6 mW/cm^2
Average Recording Sensitivity = (b) 350 cm/J for 95% of growth in grating strength
Reconstruction at λ = 514.5 nm



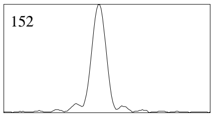


Angle Selectivity Profiles, Obtained at 514.5 nm With Read Irradiance of 5 mW/cm^2, After Co-locational Multiplexing in ULSH-500-7B CROP medium of 500 μm Thickness pre-exposed to Diminish Cumulative Volume Shrinkage to ~ 0.25%

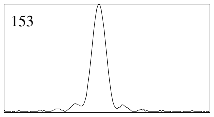
[#151 to #200 Sequentially Recorded Plane-Wave Holograms]



$\eta=0.064\%,\theta=-10.00^\circ,\phi=45.00^\circ$



$\eta=0.093\%,\theta=-10.00^\circ,\phi=46.50^\circ$



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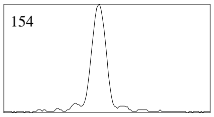

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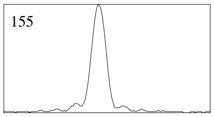
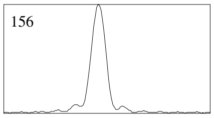
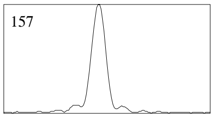


$\eta=0.059\%,\theta=-10.00^\circ,\phi=51.00^\circ$



$\eta=0.075\%,\theta=-10.00^\circ,\phi=52.50^\circ$



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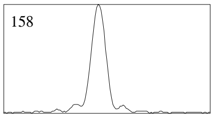
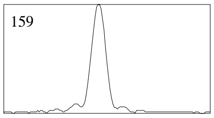
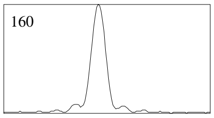


$\eta=0.065\%,\theta=-10.00^\circ,\phi=55.50^\circ$



$\eta= 0.05\%,\theta=-10.00^\circ,\phi=57.00^\circ$



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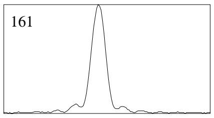
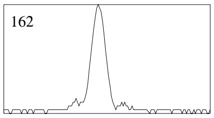
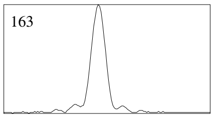


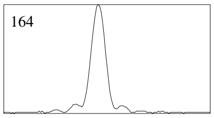
$\eta=0.083\%,\theta=-10.00^\circ,\phi=60.00^\circ$



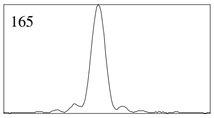
$\eta=0.019\%,\theta=-10.00^\circ,\phi=61.50^\circ$



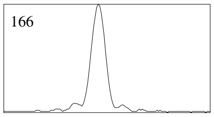
$\eta=0.072\%,\theta=-10.00^\circ,\phi=63.00^\circ$



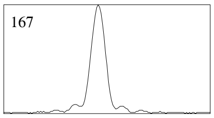
$\eta=0.062\%,\theta=-10.00^\circ,\phi=64.50^\circ$



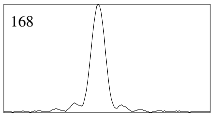
$\eta=0.081\%,\theta=-10.00^\circ,\phi=66.00^\circ$



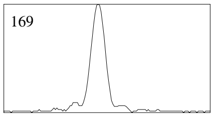
$\eta=0.061\%,\theta=-10.00^\circ,\phi=67.50^\circ$



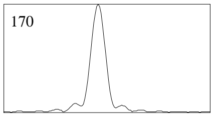
$\eta=0.064\%,\theta=-10.00^\circ,\phi=69.00^\circ$



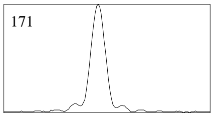
$\eta=0.074\%,\theta=-10.00^\circ,\phi=70.50^\circ$



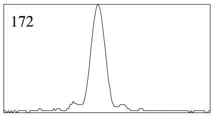
$\eta=0.047\%,\theta=-10.00^\circ,\phi=72.00^\circ$



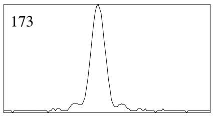
$\eta=0.087\%,\theta=-10.00^\circ,\phi=73.50^\circ$



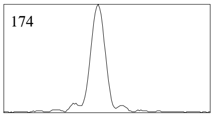
$\eta=0.079\%,\theta=-10.00^\circ,\phi=75.00^\circ$



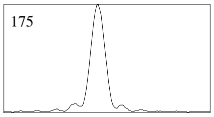
$\eta=0.035\%,\theta=-10.00^\circ,\phi=76.50^\circ$



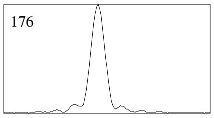
$\eta=0.036\%,\theta=-10.00^\circ,\phi=78.00^\circ$



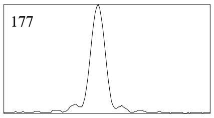
$\eta=0.076\%,\theta=-10.00^\circ,\phi=79.50^\circ$



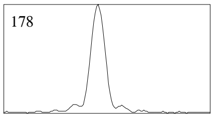
$\eta=0.071\%,\theta=-10.00^\circ,\phi=81.00^\circ$



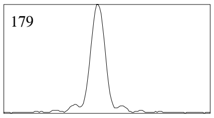
$\eta=0.076\%,\theta=-10.00^\circ,\phi=82.50^\circ$



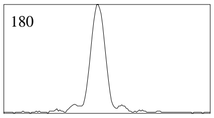
$\eta=0.072\%,\theta=-10.00^\circ,\phi=84.00^\circ$



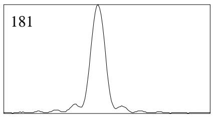
$\eta=0.066\%,\theta=-10.00^\circ,\phi=85.50^\circ$



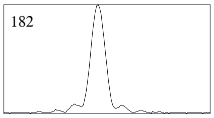
$\eta=0.073\%,\theta=-10.00^\circ,\phi=87.00^\circ$



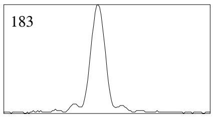
$\eta=0.064\%,\theta=-10.00^\circ,\phi=88.50^\circ$



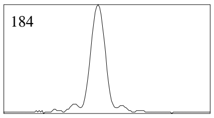
$\eta=0.085\%,\theta=-10.00^\circ,\phi=90.00^\circ$



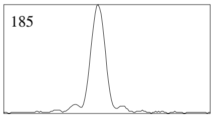
$\eta=0.069\%,\theta=-10.00^\circ,\phi=91.50^\circ$



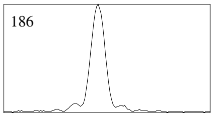
$\eta= 0.05\%,\theta=-10.00^\circ,\phi=93.00^\circ$



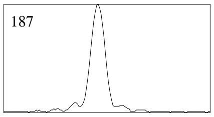
$\eta=0.051\%,\theta=-10.00^\circ,\phi=94.50^\circ$



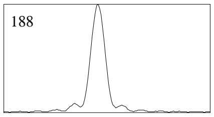
$\eta=0.065\%,\theta=-10.00^\circ,\phi=96.00^\circ$



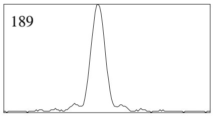
$\eta=0.064\%,\theta=-10.00^\circ,\phi=97.50^\circ$



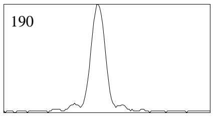
$\eta=0.055\%,\theta=-10.00^\circ,\phi=99.00^\circ$



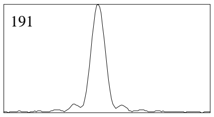
$\eta=0.086\%,\theta=-10.00^\circ,\phi=100.50^\circ$



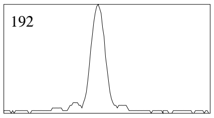
$\eta=0.051\%,\theta=-10.00^\circ,\phi=102.00^\circ$



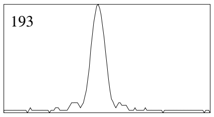
$\eta=0.042\%,\theta=-10.00^\circ,\phi=103.50^\circ$



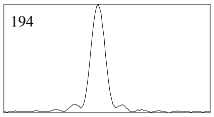
$\eta=0.076\%,\theta=-10.00^\circ,\phi=105.00^\circ$



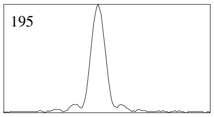
$\eta=0.028\%,\theta=-10.00^\circ,\phi=106.50^\circ$



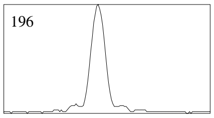
$\eta=0.029\%,\theta=-10.00^\circ,\phi=108.00^\circ$



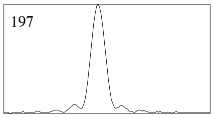
$\eta= 0.07\%,\theta=-10.00^\circ,\phi=109.50^\circ$



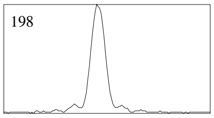
$\eta=0.067\%,\theta=-10.00^\circ,\phi=111.00^\circ$



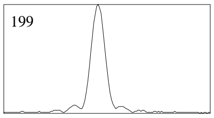
$\eta=0.043\%,\theta=-10.00^\circ,\phi=112.50^\circ$



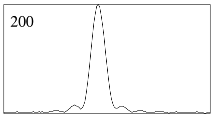
$\eta=0.069\%,\theta=-10.00^\circ,\phi=114.00^\circ$



$\eta=0.059\%,\theta=-10.00^\circ,\phi=115.50^\circ$



$\eta=0.071\%,\theta=-10.00^\circ,\phi=117.00^\circ$



$\eta=0.079\%,\theta=-10.00^\circ,\phi=118.50^\circ$

Recording Characteristics of Aprilis Cationic Ring Opening Polymerization Holographic Recording Medium

Fluid Coatings Can be Prepared With Thickness of $25\ \mu\text{m} \le t \le 1000\ \mu\text{m}$

Pre-Imaging Shelf Life (>1.0 yr)

No Post Imaging Chemical Processing or UV Fixing Requirement
Diffraction Efficiency and Angular Selectivity Stable With Time and Temperature

High Sensitivity **$(0.2 \le S \le 28.0\ \text{cm / mJ})$**
S; Maximum Slope From a Plot of $de^{1/2}$ Versus Exposure Energy

Refractive Index Modulation $(1.0\text{E-}5 \le n_1 \le 1.5\text{E-}2)$
Calculated From the Measured Diffraction Efficiency and Hologram Thickness

Reciprocity; No Decline for $0.5\ \text{mW/cm}^2 \le I_{Wr} \le 5\ \text{W/cm}^2$

Low Shrinkage in Lateral and Transverse Directions for Plane-Wave Slant Fringe Holograms $\{\phi_{int} = 5° \text{ to } 45°\}$ With Low η When Pre-exposed With Modest Fluence or Thermal Treatment

Small Grating Period Achievable (~ 244 nm)

Demonstrated Recording of Megapixel Pages (Raw BER ~1E-3)

Demonstrated Read Rate of 110 MB/sec

Small Pre-imaging Exposure for Multiplexing with Good Angular Selectivity

Co-locational Angle Multiplexing With Holograms of Low DE (~0.1%)
Cumulative Grating Strength; **$\Sigma\, \eta^{1/2} \ge 19$ in 200 μ thickness**
$\Sigma\, \eta^{1/2} \ge 32$ in 500 μ thickness

Scattering; **$\eta_{scatt} =$ ~3E-6 at Bragg Condition**

Raw Bit-Error Rate; **{1E-7 to 1E-5; 256Kbit Holographic Images}**

Background Uplift In Regions of First Minima Can be Reduced by Either Altering Composition of Formulation or Exposure Conditions

Post-Imaging Lifetime (>3 yr)

Aprilis, Inc. and Polaroid Corporation Information 033000