

AD-A216 124

Fourth Quarterly Technical Report

Analysis and Evaluation of Technical Data
on the
Photochromic and Non-Linear Optical
Properties of Materials

December 18, 1989

George Mason University

Robert F. Cozzens, Principal Investigator

ARPA Order#: 6631

Contract #: DAAB07-89-C-F404

Project#: CJ829178CJCA

Program Code#: 8E20

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BACKGROUND

The principle goal of this relatively small contractual effort is to provide technical assistance to the DARPA Program Director in evaluating data on materials, especially polymers, that may be useful in the development of limiters and switches for the protection of eyes and electro-optic sensors from exposure to damaging levels of laser radiation. A principle task is to assist in the development of a predicative capability in assessing the viability of various approaches and devices and to assess those theoretical limitations which may exist in the use of organic materials as optical switches and limiters.

PROGRESS TO DATE

A search of the literature has been completed for the purpose of gathering into one table the non-linear optical properties, especially values reported for Chi-3, of various organic materials. The first quarterly technical report (March 1989) included a partial list of references being reviewed. The second quarterly report included a lengthy table of organic systems and their reported NLO properties. The third quarterly report was accompanied by a copy of a Naval Research Laboratory report (NRL Memorandum Report #6482) containing an extensive listing of materials and their reported NLO properties. The Principal Investigator is also employed at the Naval Research Laboratory as an intermittent employee, GM 15. Activities associated with this project have been coordinated with NRL in an attempt to minimize duplication of effort.

The third quarterly report, September 1, 1989, also included an attached Working Draft Paper evaluating the feasibility of developing an ablative mirror-fuse system to be placed at the focal plane of an optical device. This paper proposed the use of a thermally unstable material, probably a polymer in order to maintain optical flatness, under a thin front surface reflective layer. This thin backing layer would serve as a thermochemical enhancer for lowering the threshold for mirror-fuse activation. Further analysis of this concept is underway. Submission of a research proposal, separate from this contract, is being considered.

The Principal Investigator is also considering the possibility as to whether the linear photochromic response of a traditional photochromic material has any possibility for use in a realistic eye/sensor protection system. Theoretical limitations on switching speed and degree of opacity provided when switched as well as ambient transparency are controlled by basic photophysical properties. The beginning of detailed analysis is presented in the attached appendix to this report as a Working Draft Paper entitled "Limitations on Photochromic Techniques for Optical Protection of Eyes and Sensors."

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TECHNICAL ADVISORY COMMITTEE

The Principal Investigator was appointed by Dr. Frank Patten (DARPA), the former Program Manager, to an ad hoc Technical Advisory Committee to assess the feasibility of a variety of materials and systems associated with the eye/sensor hardening program. This committee did not formally meet during this quarter, but informal discussions were held at the Program Review Dec 4-5, 1989.

Attachment: Working Draft Paper: "Limitations on Photochromic Techniques for Optical Protection of Eyes and Sensors"

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Working Draft Paper
December 18, 1989

LIMITATIONS ON LINEAR PHOTOCHROMIC TECHNIQUES
FOR THE
PROTECTION OF EYES AND SENSORS
FROM
INTENSE LIGHT SOURCES

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Working Draft Paper
December 18, 1989

LIMITATIONS ON LINEAR PHOTOCHROMIC TECHNIQUES
FOR THE
PROTECTION OF EYES AND SENSORS
FROM
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INTRODUCTION

There is increasing interest within the scientific community to develop systems to protect eyes and electro-optic sensors from fixed wavelength and frequency agile laser devices. Damage thresholds for the human eye is quite low, where visible laser radiation with an irradiance of 0.5 J/cm^2 for a nanosecond results in irreversible damage to the retina. Damage thresholds for electro-optic sensors are higher and can be extended further by electronic hardening techniques. Relatively high-energy laser devices are available over a wide frequency range. NdYAG lasers with outputs in excess of a megawatt per square centimeter with nanosecond pulse widths are common in laboratory and field testing environments. Laser range finders and other devices currently in use both in the field and in the laboratory have intensities able to produce extensive eye damage if misdirected.

APPROACHES TO HARDENING

To prevent damaging levels of laser radiation from reaching the eye or electro-optic sensor, the incoming beam must either be absorbed, reflected, refracted to a harmless location or defocused to a lower irradiance level. A successful protection system must be effective over a wide range of wavelengths and intensities. Narrow band interference filters are useful at only fixed wavelengths and thus are not effective against frequency agile threat. Absorption of radiation may be accomplished by inducing electronic transitions in a molecular species or by

producing a chemical transformations resulting in the formation of new absorbing species. If an incoming beam passes through a focal plane, it is possible to disrupt the optical transparency at the focus by producing scattering centers (bubbles, etc.) resulting from large thermal gradients around absorbing particulates or clusters of molecules in a colloidal suspension. Light or thermally induced changes in index of refraction may be used to produce frequency agile interference filters or Bragg cells, assuming the light to be sufficiently coherent (a questionable situation under realistic long range field conditions) or to change the focus or alignment of an incoming beam. Optical properties such as the absorption coefficient and index of refraction of many materials may have a component which is intensity dependent. These non-linear optical properties may be used to amplify those phenomena required to make the hardening system sufficiently effective under high intensity radiation.

PHOTOCHROMIC BEHAVIOR

Photochromic materials are those which increase their optical absorption when exposed to light. These may respond in either a linear or non-linear manner relative to the intensity of incoming light. A small amount of light absorbed by a photochromic material results in the formation of a highly absorbing short lived species. Commercially available eyeglasses which darken in bright light but remain highly transparent in dim light is an example of a commercial use of photochromic behavior. These are generally relatively slow to respond. In order to use this approach to protect eyes and sensors against laser radiation, it is necessary that the switching time be short (of the order of a nanosecond) and the degree of darkening be large (an absorbance or optical density increase of at least 4). For practical application, the material must be acceptably transparent at low light intensities, absorbing under 25% of the ambient light. These are some of the boundary conditions for an acceptable photochromic material.

The switching or response time of a photochromic material is a function of the optical properties of the material in both its dark and illuminated state and the intensity of the incoming radiation responsible for the switching process. The following is a first approximation derivation and interpretation of this relationship.

DERIVATION OF PHOTOCHROMIC RELATIONSHIP - FIRST APPROXIMATION

To a first approximation, the absorption of a photon of light by a linearly absorbing material is described by the Beer-Lambert relationship

$$1) \log(I_0/I) = \epsilon c l$$

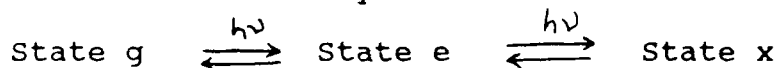
or

$$\ln(I_0/I) = \alpha c l$$

$$\text{where } \alpha = 2.303 \epsilon$$

where I_0 is the intensity of the incident light, I is the intensity of the light transmitted by the system, ϵ is the molar absorptivity (an intrinsic property of the absorber and a function of wavelength), C is the concentration of the absorber and l is the pathlength of light through the absorbing system. The term $\log(I_0/I)$ is referred to as absorbance (A) or optical density (OD). An optical density of 1.0 absorbs 90% of the incident light, an optical density of 2.0 absorbs 99%, and so on.

A photochromic process requires that a species (here after referred to as ground state "g") absorb a photon of incident radiation, from which you wish to protect an eye or sensor, and produce a second or excited species (here after referred to as state "e") with a much larger absorptivity at the wavelength of interest than that of state "g". Some light must be absorbed by "g" in order to trigger the formation of "e" which in turn absorbs the remaining (up to the dark OD of the system) light. The boundary conditions stated above limit initial absorption of "g" to less than 25%, while "e" must be a much stronger absorber at the same wavelength. To be effective, the process must occur in a sufficiently short period of time (nanosecond) and produce sufficient absorption (OD 4 or greater) to prevent damaging levels of radiation from reaching the eye or sensor. This process is described by



where states g, e and x may be either different chemical species (dimers, radicals, isomers, etc.) or different electronic states of the same species.

The protective device must be acceptably transparent under ambient light conditions and sufficiently opaque under high intensity radiation. The following parameters control the photophysics involved in the switching process:

- I_0 = irradiance of incident laser radiation in Watts/cm²
- I = intensity of transmitted radiation
- T_g = transmittance under ambient light (I/I_0)
- A_g = absorbance (optical density) under ambient light (i.e. switch "on" or transparent mode)
- ϵ_g = molar absorptivity of state g in liters/mole-cm
- ϵ_e = molar absorptivity of state e in liters/mole-cm
- A_e = absorbance (optical density) under intense laser radiation (i.e. switch "off" or opaque mode)
- C_g = concentration of state g under ambient light in moles/liter
- C_e = concentration of state e under intense radiation in moles/liter
- l = thickness of absorbing layer in cm
- N_a = number of incident photons per cm² produced by the potentially damaging laser

N_e = moles per cm^3 of state e under intense irradiation
 N_A = Avagadro's number (6.02×10^{23})
 λ = wavelength of laser threat in meters
 c = speed of light 3.0×10^8 meters/sec
 t = switching time (time to change absorbance from A_g to A_e)
 n = net quantum efficiency of switching process
 h = Planck's Constant (6.62×10^{-34} J-sec)

The acceptable ambient light absorbance, according to Beer's law is described by

$$(2) \quad A_g = \epsilon_g C g l$$

while the absorbance under high intensity radiation is

$$(3) \quad A_e = \epsilon_e C e l$$

The number of moles of species e per cm^3 of absorber (N_e) responsible for the strong absorption under irradiated conditions is a function of the intensity of the incident radiation which is absorbed by state g, the quantum efficiency for formation of state e, the species responsible for the high intensity absorption, and the molar absorptivity of species (g). This relationship is described

$$(4) \quad N_e = \frac{n N_A (1 - T_g)}{N o l}$$

where N_A is the number of incident photons per cm^2 , $1 - T_g$ is the fraction of photons absorbed by g which produce e, and n is the efficiency of the process. N_A is described by

N_A = incident irradiance multiplied by the switching or response time Δt and divided by the energy per photon

or

$$(5) \quad N_A = \frac{I_o \Delta t}{hc/\lambda} = \frac{I_o \Delta t \lambda}{hc}$$

Substitution into (4) results in the number of species e per cm^3 available to absorb light during intense irradiation

$$(6) \quad N_e = \frac{n I_o \Delta t \lambda (1 - T_g)}{hc N o l}$$

Converting to molar concentration C_e

$$(7) \quad C_e = N_e(1000) = \frac{1000 \, n_{Io} \Delta t \, \lambda (1-T_g)}{hc N_{oI}}$$

where the 1000 converts cm^3 to liters and N_o converts number of absorber molecules e to moles of absorber.

Equation (3) shows that

$$(8) \quad C_e = A_e / \epsilon_{el}$$

and

$$(9) \quad C_g = A_g / \epsilon_{gl}$$

Substitution of equations 8 and 9 into 7 and solving for Δt gives

$$(10) \quad \Delta t = \frac{A_e hc N_{oI}}{\epsilon_{el} (1000) n_{Io} \lambda (1-T_g)} = \frac{A_e hc N_o}{1000 \epsilon_{en} n_{Io} \lambda (1-T_g)}$$

The term $(1-T_g)$ is the optical transparency of the system under ambient light conditions. If desired, $(1-T_g)$ or the fraction of light absorbed under ambient light conditions, may be replaced by $(1-10^{-A_g})$.

Equation 10 shows the relationship between the switching time of a photochromic system and the variables that describe the system and the damaging source of radiation.

REALISTIC SWITCHING TIMES

The following are ideal, yet realistic values which may be substituted into equation 10 to calculate, to a first approximation, the theoretical limits on switching time of a linearly responding photochromic material:

Laser threat wavelength = 500nm (mid-visible)

Laser irradiance = 1.0 megawatt/cm²

C_g under ambient light conditions = 10 moles/liter

(Note: This would be approximately the concentration of benzene chromophores in pure solid polystyrene, about as high as is reasonable for any system. Polymers doped with small molecules would have a lower concentration.)

A_g ambient light = 0.125 (i.e. 25% ambient light absorption)

(Note: A_g of 0.125 corresponds to $T_g = 0.75$)

A_e under laser irradiation = 4 (i.e. OD switched on=4)

(Note: 99.99% of the harmful radiation is absorbed)

Quantum efficiency = 1

(Note: the "best case" scenario without chain reaction type steps. In the real world this value could be less than 1.0)

Molar absorptivity (ϵ_g) of state g = 0.0125 lit/mol-cm

(Note: this corresponds to an absorbing thickness of 1.0 cm for $A_g = 0.125$. This path length is a variable that may be changed, but being linear, its effect is small)

Molar absorptivity (ϵ_e) of state e = 100,000 lit/mol-cm

(Note: Benzene at 185 nm is 100,000. Only a few specialized systems have significantly higher absorptivities, such as certain metal chelates and charge transfer complexes, and large ring systems such as phthalocyanines.)

Substitution of these values into equation 10 results in a first approximation of switching time of 3.8×10^{-8} sec, probably too slow to protect the eye from a pulsed laser with a wavelength of 500 nm and an irradiance of 1.0 megawatt/cm². All of the terms in equation 10 are a linear function of Δt . Thus to decrease Δt by 2 orders of magnitude requires an appropriate 2 orders of magnitude change in some combination of the parameters on the right side of equation 10.

The only realistic way to decrease Δt is to increase ϵ_e . A molar absorptivity of state e greater than 100,000 lit/mol-cm is reasonable only with molecular systems which are very conjugated, involve electron transfer processes or contain unique metal chelates.

The use of materials which have a non-linear component of molar absorptivity will lead to a decrease in Δt at high I_0 . A 100 fold increase in ϵ_e seems unreasonable. Most non-linear effects are relatively small at irradiances as low as 1.0 megawatt/cm². Systems could be designed with a quantum efficiency (η) greater than one, however, a 1 or 2 order of magnitude increase in η may be unrealistic.

The above first approximation assumes Beer's law behavior which is, of course, not totally valid under conditions of high illumination. However, one would not expect 1 or 2 orders of magnitude improvement in Δt simply from deviations in Beer's law behavior, except in the case of very non-linear absorbers.

From the above simplified calculations, it does not appear trivial to protect the human eye or most electro-optic sensors from damaging levels of laser radiation by a simple, linear photochromic process. Any proposed research to use photochromic materials should address the issues herein noted and document what unique and novel techniques or material property is being studied or developed by the research that would shorten switching time. The introduction of a focal plane increases I_0 and may make a protective device possible. Extremely non-linear optical properties may provide enhancement of the photochromic behavior of some materials, but probably not without a focal plane to increase irradiance and amplify non-linear behavior. Optical "tricks" which take advantage of refractive properties or the thermal production of light scattering centers such as bubbles (probably requiring a focal plane) or liquid crystals are not at all considered in the above discussion, which is limited to the simple linear photochromic behavior of materials.

Attached is a set of calculations demonstrating the effect of varying several parameters on the right side of equation 10. Graphical demonstration of these effects are also attached.

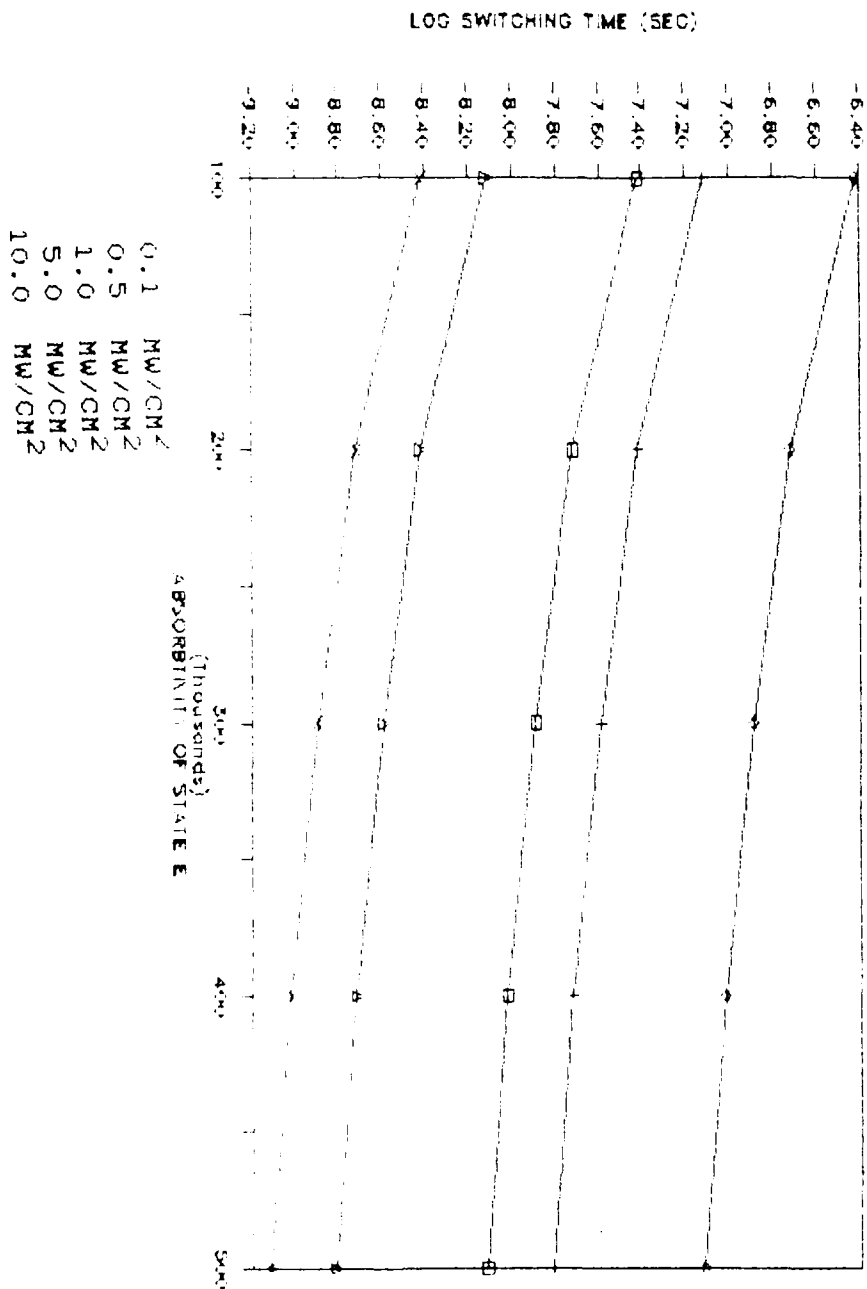
EYE/SENSOR PROTECTION BY DIRECT PHOTOCHROMIC PROCESS

RELATIONSHIP BETWEEN PHOTOCHROMIC SWITCHING TIME AND OPTICAL PROPERTIES OF MATERIALS

TIME sec	Eg/Ec	LASER POWER watts	WAVELENGTH meters	Cg mol/L	OD on opaque	OD off clear	TRANS off clear	EFFIC. n	ODon/ODoff	Eg	Ec	THICKNESS cm	LOG TIME
3.82E-08	1.25E-07	1.00E+06	5.00E-07	10	4	0.125	0.75	1	32	0.0125	100000	1	-7.42
1.91E-08	6.25E-08	1.00E+06	5.00E-07	10	4	0.125	0.75	1	32	0.0125	200000	1	-7.72
1.27E-08	4.17E-08	1.00E+06	5.00E-07	10	4	0.125	0.75	1	32	0.0125	300000	1	-7.89
9.56E-09	3.13E-08	1.00E+06	5.00E-07	10	4	0.125	0.75	1	32	0.0125	400000	1	-8.02
7.65E-09	2.50E-08	1.00E+06	5.00E-07	10	4	0.125	0.75	1	32	0.0125	500000	1	-8.12
7.65E-08	1.25E-07	5.00E+05	5.00E-07	10	4	0.125	0.75	1	32	0.0125	100000	1	-7.12
3.82E-08	6.25E-08	5.00E+05	5.00E-07	10	4	0.125	0.75	1	32	0.0125	200000	1	-7.42
2.55E-08	4.17E-08	5.00E+05	5.00E-07	10	4	0.125	0.75	1	32	0.0125	300000	1	-7.59
1.91E-08	3.13E-08	5.00E+05	5.00E-07	10	4	0.125	0.75	1	32	0.0125	400000	1	-7.72
1.53E-08	2.50E-08	5.00E+05	5.00E-07	10	4	0.125	0.75	1	32	0.0125	500000	1	-7.82
3.82E-07	1.25E-07	1.00E+05	5.00E-07	10	4	0.125	0.75	1	32	0.0125	100000	1	-6.42
1.91E-07	6.25E-08	1.00E+05	5.00E-07	10	4	0.125	0.75	1	32	0.0125	200000	1	-6.72
1.27E-07	4.17E-08	1.00E+05	5.00E-07	10	4	0.125	0.75	1	32	0.0125	300000	1	-6.89
9.56E-08	3.13E-08	1.00E+05	5.00E-07	10	4	0.125	0.75	1	32	0.0125	400000	1	-7.02
7.65E-08	2.50E-08	1.00E+05	5.00E-07	10	4	0.125	0.75	1	32	0.0125	500000	1	-7.12
7.65E-09	1.25E-07	5.00E+06	5.00E-07	10	4	0.125	0.75	1	32	0.0125	100000	1	-8.12
3.82E-09	6.25E-08	5.00E+06	5.00E-07	10	4	0.125	0.75	1	32	0.0125	200000	1	-8.42
2.55E-09	4.17E-08	5.00E+06	5.00E-07	10	4	0.125	0.75	1	32	0.0125	300000	1	-8.59
1.91E-09	3.13E-08	5.00E+06	5.00E-07	10	4	0.125	0.75	1	32	0.0125	400000	1	-8.72
1.53E-09	2.50E-08	5.00E+06	5.00E-07	10	4	0.125	0.75	1	32	0.0125	500000	1	-8.82
3.82E-09	1.25E-07	1.00E+07	5.00E-07	10	4	0.125	0.75	1	32	0.0125	100000	1	-8.42
1.91E-09	6.25E-08	1.00E+07	5.00E-07	10	4	0.125	0.75	1	32	0.0125	200000	1	-8.72
1.27E-09	4.17E-08	1.00E+07	5.00E-07	10	4	0.125	0.75	1	32	0.0125	300000	1	-8.89
9.56E-10	3.13E-08	1.00E+07	5.00E-07	10	4	0.125	0.75	1	32	0.0125	400000	1	-9.02
7.65E-10	2.50E-08	1.00E+07	5.00E-07	10	4	0.125	0.75	1	32	0.0125	500000	1	-9.12
ERR	1.25E-07		5.00E-07	10	4	0.125	0.75	1	32	0.0125	100000	1	ERR
ERR	6.25E-08		5.00E-07	10	4	0.125	0.75	1	32	0.0125	200000	1	ERR
ERR	4.17E-08		5.00E-07	10	4	0.125	0.75	1	32	0.0125	300000	1	ERR
ERR	3.13E-08		5.00E-07	10	4	0.125	0.75	1	32	0.0125	400000	1	ERR
ERR	2.50E-08		5.00E-07	10	4	0.125	0.75	1	32	0.0125	500000	1	ERR
ERR	ERR				4		1.00	1	ERR	0.0125		1	ERR
ERR	ERR				4		1.00	1	ERR	0.0125		1	ERR

LOG PHOTOCHROMIC SWITCHING TIME

FN (LASER POWER, ABSORPTIVITY STATE E)



PHOTOCHROMIC SWITCHING TIME

FN (LASER POWER, ABSORPTIVITY STATE E)

