THE TRIARYLMETHANE PHOTOCHROMIC SYSTEM FOR
FLASHBLINDNESS PROTECTION

by

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A systematic study of three triarylmethane derivatives, synthesized for the purpose of providing improved flashblindness protection, was carried out. The use of photochromic compounds for improved protection against flashblindness was evaluated. The systematic study of three triarylmethane compounds, synthesized specifically for use in eye protection devices, was carried out. Their characteristics, which are essential to eye protection (i.e., absorption, speed of response, photostability), were measured to demonstrate the feasibility of the approach and to describe the current status of photochromic...
20. Flashblindness protection. Recommendations are given for future work.
We wish to express our thanks to Joseph F. Roach for his assistance in carrying out experiments involving very short intervals of time, and to John V. DeSalvo of AMEL, for extensive assistance in designing and constructing much of the apparatus used in this study. We wish also to thank John T. Stapler of the Organic Chemistry Group for synthesizing the compounds used in this work. Prof. Richard E. Grojean of Northeastern University was particularly helpful with his assistance in resolving experimental problems involving optics.
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THE TRIARYLMETHANE PHOTOCHROMIC SYSTEM FOR FLASHBLINDNESS PROTECTION

Introduction

The need for a system of eye protection to prevent or substantially reduce the harmful effects of high-intensity flashes of light has been a matter of concern to the military for many years. The danger to the eyes of the combat soldier from nuclear detonations usually extends well beyond the range where ionizing radiation, blast damage, and thermal damage are major threats. While permanent chorioretinal burns and temporary flashblindness may occur, the risk of incurring the former injury appears to be low, and the impairment of vision usually called flashblindness is of more concern. Over the years, programs supported by all three US Armed Services and by foreign governments as well, have explored numerous approaches to the solution of the flashblindness problem.

The electro-optical Sandia eye-protection device, whose development was initiated by the US Army in 1972, resulted in the first item offering protection in a field-useable device. Variations of the system have now been adopted by the US Air Force and US Navy. The Sandia system is based on an electro-optical ceramic element (designated PLZT) which requires a compact power supply.

An earlier, much heavier device utilizing auxiliary flash equipment was abandoned by these two branches of the Service in favor of the Sandia approach.

The British Ministry of Defense has for some time supported work on a so-called triplet-triplet method of eye protection which uses a photophysical mechanism fundamentally different from that discussed in the present work. The British system has not yet met US Army requirements.


This report summarizes the state of development of a photochromic* approach to flash protection, carried out at the Natick Research and Development Command. The compounds used are related to the class of triarylmethane dyes, a group of dyes characterized in general by their high molar absorptivity (extinction coefficient).

The major characteristics of the triarylmethane photochromics considered in this study includes the following:

a) Absorption spectrum in the uncolored state.
b) Wavelength of the activating spectrum.
c) Absorption spectrum of the colored form.
d) The difference in optical density in the visible region of the spectrum, between the uncolored and colored states.
e) Speed of response to activating electromagnetic pulse.
f) Rate of return to initial clear state.
g) The stability of the system.

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*Photochromism is defined as the reversible change of a chemical species between two states having distinguishably different absorption spectra, such change being induced in at least one direction by the action of electromagnetic radiation (light).
Objectives and Approach

The general nature of the temporal distribution of radiation from a nuclear device of given size has been reported in several places. In the atmosphere, a first pulse in the microsecond to millisecond range (the duration depending upon the size of the weapon) is followed by the major pulse, which contains most of the radiative energy of the explosion.

The first pulse is relatively rich in ultraviolet radiation; in the photochromic systems of interest here, it is this short-wavelength radiation which is used to bring about a photochromic reaction. The reaction produces highly absorbant products, which in turn block the major part of the visible light which accompanies and follows the original ultraviolet radiation.

From the point of view of the US Army, the objective of the flashblindness program is to attain an absorbance or optical density of 4.0 within 50 microseconds of the start of the activating flash. Preferably, the system should return to its clear state automatically. In the simplest and most desirable photochromic system, the color change is brought about directly by the action of the ultraviolet radiation on the photochromic material itself. It is this approach which has been followed in the work reported here.

A series of photochromic compounds was synthesized for study under this program. Their synthesis have been reported separately. The present report describes the pertinent photophysical characteristics of the three most promising compounds prepared thus far.


5Biological and Environmental Effects of Nuclear War, Hearings-Subcommittee on Radiation, Joint Committee on Atomic Energy, 86th Congress, 22-26 June 1959.


For photochromic compounds in general, the response obtained in a given exposure will depend both on the characteristics of the compound (molar absorptivity, speed of response, and quantum efficiency of coloration), and on those of the activating light (spectral distribution, intensity, and pulse profile). Clearly, the rise time of the activating pulse used in characterizing a compound must be very short, if a realistic response time of the photochromic system is to be measured.

The two xenon light sources described in Section III, below, were selected with this latter requirement in mind. Both have rise times in the range of the first pulse of nuclear devices of 10 to 20 kt. Although exact data on the temporal shift in ultraviolet content of the first nuclear pulse is not available for this study, information in the literature indicates that the ratio of ultraviolet to visible light of the sources used here is a reasonable approximation of the energy levels to be expected.

For precise measurement of the response times of the compound, monochromatic ultraviolet radiation (337.1 nm) from an extremely fast-pulse nitrogen superradiant source was used.

Experimental Conditions

Light Sources:

The characteristics of the light sources used for activation are given here:

<table>
<thead>
<tr>
<th>Type</th>
<th>Electrical Energy (J)</th>
<th>Peak (μ sec)</th>
<th>1/e Width (μ sec)</th>
<th>Curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xenon Corp XM-1</td>
<td>Xenon Flash</td>
<td>25.0000</td>
<td>100.000</td>
<td>300.000</td>
</tr>
<tr>
<td>Maser Optics</td>
<td>Xenon Flash</td>
<td>400.0000</td>
<td>150.000</td>
<td>300.000</td>
</tr>
<tr>
<td>AVOC Super-radiant Laser Source (337.1 nm)</td>
<td>Laser</td>
<td>0.0011</td>
<td>0.005</td>
<td>0.018</td>
</tr>
</tbody>
</table>

The optical arrangements used to measure the properties of the triarylmethane systems are given in the Appendix. The first apparatus shown (Appendix Fig. A-1), using a Xenon SPM-1 source, was designed to permit a rapid recording of the attenuation across the spectrum, which results from irradiation by a xenon flash source.

The second experimental apparatus, also shown in the Appendix, Fig. A-2, utilizes a more powerful 400 joule source. With this
arrangement, the attenuation of the single wavelength of a helium-neon laser beam by the photochromic system can be measured, and higher absorbances (optical densities) can be recorded.

The third optical train, using a nitrogen superradiant laser source, yielded accurate measurements of the very short response times of the triarylmethane photochromic compounds (Appendix Fig. A-3).

Photochromic Compounds:

Of the several classes of photochromic compounds considered in the past for use in optical shutters, the triarylmethanes have the most favorable characteristics:

1) The quantum efficiency of color formation approaches unity.

2) The molar absorptivity of the colored form is near the theoretical maximum for broad band absorption (approx. $10^5$ l/mole-cm).

3) The colored forms of the various triarylmethanes cover a wide range of absorption wavelengths.

4) The clearing rate can be controlled by the choice of solvent and by the selection of anion concentration.

In addition to these advantages, the recent elucidation of the triarylmethane coloration mechanism by this laboratory provides a useful guide for the interpretation of earlier experimental work, and led to the synthesis and subsequent evaluation of the compounds studied here.


11See Reference 7.
The structures of the three compounds selected for detailed examination of their photophysical properties are as follows:

![Chemical structures]

The unionized form of these compounds, called the leuconitrile, is colorless. Upon irradiation of the leuconitrile solution, the colored cation shown above is formed, along with the anion.

Experimental Results

Absorption in the Ultraviolet Region:

For each of the three triarylmethane leuconitriles shown above, absorption of alcohol solutions in the ultraviolet region was measured. For two of these, the absorption curves are similar (Fig. 5) showing a sharp increase in absorption below 360 nm. For the significantly different dimethyl compound III, the absorption falls somewhat lower, below 370 nm (Fig. 5).
Figure 1. Spectral Distribution of Xenon Flashtubes from 300 to 700 nm (10 nm/div).

Figure 2. Flash Intensity Time Profile for SPM-1 (100μ sec/div).
Figure 3. Flash Intensity Time Profile for 400 J Pulse of Maser Optics (100 μsec/div).

Figure 4. Incident Intensity Time Profile for Nitrogen Superradiant Source (10 nsec/div).
Figure 5. Ultraviolet Absorption of Leuconitriles I, II (---), III (—)
In the visible region, in every case, there is no significant absorption, and solutions of these compounds appear clear and colorless, until exposed to a high level of ultraviolet radiation.

Change in Absorbance Upon Irradiation:

Upon irradiation by ultraviolet light, each compound shows a strong absorption band in the visible region; the absorption peak is at 610 nm for the first two compounds, and at 553 nm for the third. The colors of the first two solutions in alcohol are deep blue-green, and the third is deep red. (Figs. 6, 7, and 8).

In a 0.5 cm cell, the 25 joule excitation of ethanolic solution caused a change in absorbance of 1.3 for compound I, a change of 1.4 for compound II, and of 0.8 for compound III (Figs. 6, 7, and 8).

Solutions of these compounds in ethoxyethanol, incorporated in a hydrogel matrix (poroplastic, a proprietary cellulose acetate film of extremely high porosity), yield similar data.

The xenon source of higher intensity (400 joules) was used to measure the effect of a strong ultraviolet source. In Fig. 9, a change in transmittance from nearly 100% to an extremely low value is shown to occur in less than 100 microseconds. In order to evaluate more accurately the final absorbance, the experiment was repeated with the scale expanded, with the results shown in Fig. 10. The typical system shown, using compound I, attains an absorbance of more than 3 in 50 microseconds, and over 4 in less than 100 microseconds.

Precise measurement of the speed of response of these photochromic compounds was then carried out. Using a nanosecond (10^-9 sec) pulse of pure ultraviolet light (337.1 nm) of low intensity (0.01 joules), the response of the triarylmethane compound (I) is shown to fall within this very short time frame. In other words, the response of the compound is in the nanosecond range (Fig. 11).

With the less rapid 25 joules pulse (Appendix, Fig. A-1) the response of the triarylmethane solution was obviously fast enough to follow the activating pulse. The times needed to reach the absorbances which result from 25 joules irradiation are shown in Figs. 12-15.
Figure 6. Absorption Spectrum (400-800 nm) of Compound I in Ethanol.

Figure 7. Absorption Spectrum (400-800 nm) of Compound II in Ethanol.
Figure 6. Absorption Spectrum (400-800 nm) of Compound III in Ethanol.

Figure 9. Change in Transmission with Time of Compound I Solution with 400j Activation (50µ sec/div).
Figure 10. Change in Absorbance with Time of Compound I Solution with 400j Activation (50. sec/div).

Figure 11. Change in Transmission of Compound I Upon Activation with Nitrogen Superradiant Source (10 nsec/div).
Figure 12. Attenuation of SPM-1 Pulse at 633 nm by Compound II in Ethanol (100µ sec/div). Upper Curve is Unattenuated.

Figure 13. Attenuation of SPM-1 Pulse at 633 nm by Compound I in 8% Dimethylsulfoxide (100µ sec/div). Upper Curve is Unattenuated.
Figure 14. Attenuation of SPM-1 Pulse at 633 nm by Compound II in Hydrogel (100 μ sec/div). Upper Curve is Unattenuated.

Figure 15. Attenuation of SPM-1 Pulse at 633 nm by Compound I in Hydrogel (100 μ sec/div). Upper Curve is Unattenuated.
Rate of Return to Clear State:

As reported in our earlier publication,\textsuperscript{12} and by others,\textsuperscript{13a,13b} the rate of return to the clear state of these systems may be adjusted within limits, by varying various factors, including the structure of the triarylmethane itself, the pH, the solvent, the presence of excess counter ion, and the concentration of the dye itself.

In the present work, the rate of return was adjusted by the use of counter-ion to give a return to a level of absorbance equal to half the maximum in 5 to 20 seconds.

Evaluation of Photo-Depletion:

In the work described here, the various triarylmethane solutions were repeatedly exposed to intense flashes. No fatigue or photo-depletion was observed, after a hundred cycles.

Although the triarylmethanes in their colorless (leuco) form are photo-stable for extended periods, the transient colored form may be subject to deterioration if exposed to a source for extended period of time.\textsuperscript{14} In the uses contemplated here for these compounds, no serious problem would be expected.

The triarylmethanes are active only in liquid solution or in matrices which have a high liquid content, such as hydrogel. A functioning system might use a solvent of low volatility completely sealed between lenses completely sealed between face plates. A program in this area has shown the feasibility of achieving such a sealed system. Although the photochemical coloration of a triarylmethane system is unaffected by atmospheric oxygen, the introduction of acidic impurities could reduce the observed clearing rate. An increase in the viscosity of the medium would have a similar effect.

\textsuperscript{14}See Reference 7.
Conclusions

These results demonstrate that it is feasible for a device which uses a system based upon the triarylmethane dye derivatives to function as active agents in an optical shutter that will give an optical density change greater than 3 in less than 100μ sec. In addition, it is shown that this system can be incorporated into a thin (50-mil) hydrophilic plastic film without loss of any of its photochromic properties.*

These results are encouraging. However, before complete protection can be provided by this type of device, improvements are needed in three areas.

First, the overall sensitivity of the active compounds must be improved to utilize more of the available radiation to provide more energy for the coloration reaction; new compounds with bathochromic substituents are needed. Thus far, however, new compounds with higher absorption in near-UV region have shown a lower efficiency in the coloration reaction. As a result only small increases in the actual absorption were observed. As a result of the recent elucidation of the photochemistry of this class of materials, new triarylmethanes with polycyclic aromatic ring substituents can be expected to give improved performance - to optimize the tradeoff between reduced quantum efficiencies of coloration and increased light absorption in the spectral region around 400 nm.

Secondly, since the triarylmethane photochromic system is active only in solution or in a highly hydrophilic film, sealed cells containing the solution or specific plastic layers are needed. These cells should be tightly sealed to prevent the loss of solvent over a period of time. It is necessary therefore, to develop a method to seal the active elements to the shutter into an optical lens for military use. Ideally the filter system should consist of a sealed, lightweight plastic cell, with good optical properties for undistorted vision when the device is open. One face plate of the cell should allow unattenuated UV transmission for activation of the sealed photochromic system. As noted above, results obtained in this area have been encouraging.

*Photochromism is defined as the reversible change of a chemical species between two states having distinguishably different absorption spectra, such change being induced in at least one direction by the action of electromagnetic radiation (light).

Finally, the dye cations produced by the singlet photochemical reaction should absorb strongly in the region of maximum eye sensitivity (i.e., photopic eye response is at a maximum at 556 nm and scotopic at 505 nm). Until recently, most of the triarylmethane compounds upon activation produced cations absorbing approximately 60 nm higher than the desired wavelength. However, compound III described in this study shows a striking improvement in this respect; its absorption band is very close to the photopic response of the eye. In addition, if the entire region for protection cannot be covered by one compound, mixtures of two or more photochromics may be practical. With resolution of the problems outlined above, it should be possible to provide a lightweight inexpensive optical shutter to provide high open transmission and a closed density greater than 3 in the visual region following activation by intense light similar to the initial pulse from a nuclear explosion.

1. Fiber Optics (Optical Train)
2. Xenon SFM-1 Flash and Sample Holder
3. Sample
4. Tektronix 7J20-RSS Rapid-Scan Spectrometer
5. Tungsten Iodine Source
6. Oscilloscope, Tektronix 7904

Figure A-1
1. He-Ne Laser (632.8 nm)
2. 400j Flash Head (Maser Optics)
3. Sample
4. Polarizer
5. Pin Photodiode Detector
6. Pin Photodiode Trigger
7. Tektronix 535A Oscilloscope

Figure A-2
1. Nitrogen Superradiant Source  
2. Partial Reflector  
3. Sample Cell  
4. He-Ne Laser Monitor (632.8 nm)  
5. Pin or Photomultiplier Detector  
6. Pin Trigger for Scope  
7. Tektronix 454 Oscilloscope

Figure A-3