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SPECTROSCOPIC STUDIES OF LUMINESCENCE
EMITTED BY DYES IRRADIATED BY LASER LIGHT

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SPECTROSCOPIC STUDIES OF LUMINESCENCE
EMITTED BY DYES IRRADIATED BY LASER LIGHT

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Introduction

To reduce the detectability of the soldier under field conditions using currently available visual and electro-optical methods, several dyes have been integrated into military equipment to blend in with the background. We have established, for the first time, that this method of approach would likely be inefficacious against multiple wavelength laser emission since materials, on the absorption of laser light, would luminesce and emit light at a wavelength differing from the laser. In order to assess the military consequences of such a phenomenon, we have rigorously pursued luminescence studies of dyed systems and found an effective method for using this characteristic of light emission to defeat the purpose for which coloring schemes are intended.

In general, luminescence is initiated by some excitation process, in our studies the absorption of laser light, that takes the ground-state molecule from the lowest vibrational level, in which it usually exists, to some excited singlet state. What happens to the molecule in the excited singlet state can be represented by the energy level diagram shown in Figure 1.

Since we are concerned only with the experimentally observable, in this case fluorescence and phosphorescence, we will not discuss processes such as vibrational redistribution, dissociation, internal conversion, etc., that are relatively fast and only in rare cases separately observable.⁽¹⁾ In fact, for the phenomenon observed we will in general restrict ourselves to fluorescence, i.e., a transition of the molecule from an excited state to the ground state, without a change in multiplicity. A typical half-life for such a

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phenomenon is about 10^{-9} to 10^{-8} sec and the emission characterizes an approximate "mirror-image" relationship between absorption and fluorescence spectra, with the fluorescence spectrum usually appearing at longer wavelengths than the absorption spectrum. Laser photolysis, extensively developed in our laboratory, (2) has provided us with a convenient technique for the measurement of emission spectra and life times of excited molecules present in dyed systems with the obvious extension to military materials.

Measuring Techniques

The emission spectra of luminescing dyes was obtained in the following way. The sample was irradiated by CW laser light, either a He-Ne or Argon-Krypton-Xenon laser, and the luminescence optically coupled to a spectrograph where the emission bandwidth was scanned and subsequently recorded on a strip chart recorder. The resulting emission curves were then spectrally corrected by use of a CDC 3300 computer. Relative intensities were determined by experimentally determining the losses inherent in our detection equipment.

Excited state life time measurements are not as straightforward as emission spectra measurements and different methods have been developed in order to extract from the experimental data the true life time. To this end we developed a well known technique, that of convolution integrals, (3,4) and applied this to our data. A brief description is relevant.

Using an Avco nitrogen laser having a pulse duration of 10 nsec FWHM at 337.1 nm and peak power output of 200 KW, we recorded both the laser pulse and the fluorescence pulse from an organic dye. We will represent this fluorescence as $P(t)$, while observing that it does not exhibit an exponential decay directly for decay times of the same order of magnitude as the excitation pulse. Instead it appears as the convolution of the excitation pulse $E(t)$ with the "true" fluorescence decay $f(t)$ as

$$(1) \quad P(t) = \int_0^t E(t-t') f(t') dt'$$

Our data will be analyzed in terms of (1) by integrating, using Simpson's rule, employing analytical forms for the integrand. The laser time profile which is highly reproducible from pulse to pulse, was fit well by the sum of two Gaussians whose parameters were determined on a curve resolver. The fluorescence function was assumed to be a simple exponential decay: $f(t) = A \exp(-t/\tau)$. A family of curves of $P(t)$ was generated and computer plotted for values of τ

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from 0.5 to 29.0 nsec (Fig. 2). The determination of τ for a particular material could then be made by visual superposition of a projected oscillograph of $P(t)$ upon a computer plot. The determination is unambiguous to within 0.5 nsec in τ .

Investigation

Since we have developed strong methods for determining emission spectra and life-times of excited molecules, we can now apply such techniques to examine the results of the interaction of laser radiation, both pulsed and CW, with materials of military concern, i.e., dyed systems, especially camouflage. If one can in effect, irradiate a dyed system with laser light and cause it to luminesce at a wavelength sufficiently removed from the exciting source, having a pulse duration related to the specific dyed system, then one has a powerful method for detection and discrimination nullifying the obvious advantage of color blend with background. In our first experiments, we induced and recorded luminescence in dyed military fabrics using a CW laser as the exciting source. In theory, the luminescent spectral bandwidth and shape should be independent of the wavelength of excitation. That this is so, is unequivocally shown in Fig. 3.

This is the luminescence curve from an experimental camouflage fabric excited by laser wavelengths generated by a Krypton laser and a He-Ne laser. Appropriate filters were used to selectively remove the exciting wavelengths from the detector. Data, experimentally obtained on this material, indicated that the laser intensity was sufficient to induce luminescence without reaching the saturation point (i.e., the quantum yield). The laser intensity was varied from about 0.2×10^{-4} watt/mm² to 3.7×10^{-3} watt/mm² and no appreciable deviation from linearity was noted in the luminescence output. Caution must be used in selecting the level of exciting radiation since we noted thermal degradation of the sample when the laser intensity exceeded the levels used in these experiments, obscuring any meaningful data. A 5×10^{-3} W He-Ne laser was selected to do the bulk of the experiments since its power level falls within acceptable criteria and it has useful mobility and reliability.

Emission curves give us an important piece of information, i.e., determination of the wavelength bandwidth of peak intensity. From this we can develop a detection system optimized around these wavelengths with maximum sensitivity. Using τ obtained above, we used simple laboratory methods to detect luminescence, either electronically or visually. There were instances where visual detection was adequate by simply filtering out the reflected laser

light. By pulsing the laser light, we could use photo resistors and phototubes to generate either a visual display, i.e., a blinking light, or an electronic display such as the deflection on a chart recorder. Thus by optimizing the collecting optics around the wavelength of peak intensity, we could realistically detect the presence of the fabric in a completely darkened environment. With the use of lock-in amplifiers, we could detect luminescence where the background intensity was very intense, for example, in sunlight. In the laboratory, the background was made 100 times as intense as the signal of interest and we were still able to discriminate quite easily. These preliminary experiments demonstrated that only sophistication of the detection equipment was necessary to detect luminescence from a dyed material in a more realistic environment, such as natural forest background and at distances more closely associated with actual field conditions.

To test this hypothesis on a limited level, we optimized the collecting optics on a starlight scope model small, and modified it to visually display luminescence from a series of military fabrics. Photographs of the scope output were taken and are shown in Fig. 4. Each of the fabrics tested was green in color with the exception of Sample 4. This is an undyed fabric and was used as a standard for laser reflection to verify that the filter system used on the starlight scope was, in effect, only transmitting wavelengths different than the laser. As is shown in Fig. 4, the luminescence appears as a white area on the background and is indicative of the area of luminescence. The emission spectra of each fabric was similar in character so that optimization of the detector for maximum sensitivity was the same for all. Identification of the fabrics as numbered in Fig. 4 are as follows: 1) North Vietnamese uniform, 2) U.S. Tankers coveralls, 3) experimental camouflage, 4) white fabric, and 5) U.S. Army webbing. These pictures were taken from results obtained in the laboratory at a distance of about 20 feet, using the 5×10^{-3} W He-Ne laser.

To test the feasibility of detection under field conditions, this system was transported to an area where a camouflage target was positioned at least 500 feet from the observer in a clump of trees and bushes that simulated a natural forest background. The induced luminescence was easily detected and appeared as a bright spot, as in the laboratory (see Fig. 4), on the starlight scope. This test was conducted at night in order not to saturate the starlight scope, and during the test, the environs became so dark that the function of the scope to view dimly lighted terrain was completely negated.

However, this condition only enhanced the detectability of the system by increasing the signal to background ratio. Although the experimental technique used in this test was essentially simple, except that the function of the starlight scope is extremely sophisticated, we have achieved remarkable results. That is, that by laser irradiation one can readily induce luminescence in militarily relevant materials, and from a knowledge of its emission spectra, design a detecting system capable of sensing this luminescence at fairly long distances. We showed this to be easily accomplished at 500 feet, but there is no reason to believe that many multiples of this distance cannot be considered, limited mostly by sophisticated detection techniques.

The other phenomenon associated with luminescence, that is, the excited state lifetime, can be studied by measuring the intensity decay rate which is directly related to the lifetime. It is likely that lifetimes would be characteristic of the specific emitting dye system and thus would afford us a measure of identification in attempting to discriminate against interfering background. However, since decay times are, in general, in the nanosecond time frame (10^{-9} sec), it requires an exciting pulse to be shorter than the decay time in order to apply the known techniques of lifetime measurements. For practical purposes this would mean a Q-switched laser, or some other pulsed laser. Particularly suited to this task would be a tunable dye laser pumped by a nitrogen laser having a pulse width of about 10 nanoseconds. This would provide a means of selecting the exciting wavelength, in a fairly broad bandwidth, for inducing luminescence sufficient for detection and with the added feature of permitting lifetime measurements. It is exactly this system that is available in our laboratory and was used to obtain the following results.

Military fabrics were irradiated by a pulsed dye laser using the exciting wavelength of 6100 Å characteristic of acridine red. The pulse shape is shown in Fig. 5. The laser pulse is the narrower of the two and measures about 13×10^{-9} sec FWHM. Superimposed on the laser pulse is the fluorescence from a dyed system and in general is typical of the types of curves we record from military materials when luminescing.

These types of measurements were accomplished in the laboratory where the luminescence could be focused into a small monochromator, the output of which was fed to a photomultiplier (RCA type 8575) and the resulting signal displayed on a Model 454 Tek-

tronix oscilloscope. The signals generated by this experimental set-up were quite large which prompted us to investigate the possibility of detecting the signal with the instrumentation previously used with a pulsed He-Ne laser, that is, the modified starlight scope. The results were surprising in that the detectability using the starlight scope was as easily accomplished as in the previous experiments. Consequently, we were able to extract both phenomena, emission spectra and decay rates using a single integrated system, i.e., starlight scope and photomultiplier system.

Conclusions

We have shown conclusively that dyed materials, especially military types, can be induced to luminesce by irradiation from laser beams. The emission spectrum can then be scanned and the wavelength of peak intensity determined. Using this information, detectors can be optimized to selectively look at the luminescence at distances commensurate with laser power, detector sensitivity and quantum yields from the dye. The spectra and pulse shape of the luminescence can yield useful information as to identification of the target, that is, as a surveillance threat. The phenomenon of induced luminescence of military fabrics, paints and other colored systems should be seriously considered in any future development of both camouflage systems and optical detection devices.

By detailed study of excited state systems, a more thorough understanding of non-radiative processes that occur can be attained. This is essential knowledge when attempting to influence the various competing processes in order to control luminescence. For instance, enhancement of intersystem crossing during collision is a very efficient process; it appears that external perturbation by quenchers are more effective at enhancing intersystem crossing than comparable internal perturbations. Studies of quenchers are currently under way at this laboratory that would allow camouflage systems to retain their physical properties, yet defeat the surveillance threat posed by possible induced luminescence.

The importance of ultra short light pulses, i.e., picosecond (10^{-12} sec) pulses becomes apparent when attempting to determine lifetime measurements from a pulsed luminescing material. If the laser pulse is in the same general time frame, then measurements are indirect and subject to interpretation. Although the convolution technique is adequate, for ease of interpretation, the exciting pulse configuration must be predetermined. To overcome this handicap, we extended our studies by using a mode-locked laser system

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and pulse extractor, capable of delivering a single laser pulse lasting less than 30 picoseconds (10^{-12} sec). With this type of pulse, simple and direct fluorescence decay measurements can be made. Fluorescence decay studies have been performed on a number of organic dyes with mode-locked ruby lasers.⁽⁵⁾ The success of this technique points the way towards illuminating the complex processes that are generated in excited state systems and directs the mode of research necessary to accomplish the task of effective camouflage.

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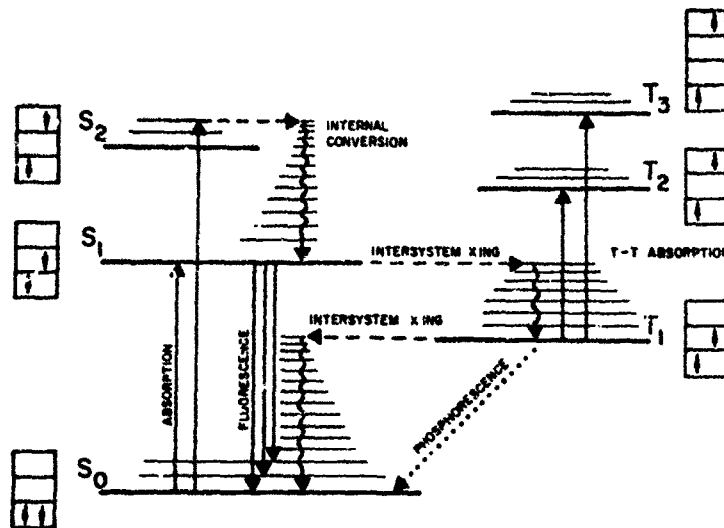


Fig. 1. Energy levels and energy transfer in a complex molecule.

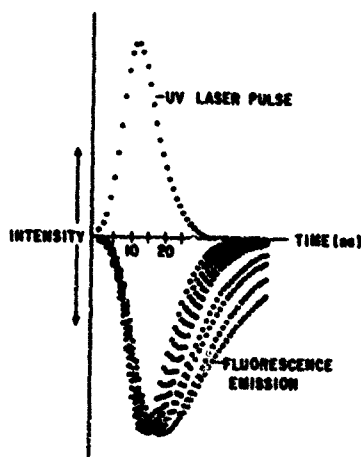


Fig. 2. Computer-plotted time profiles of the laser pulse and a family of fluorescence emission pulses. (The fluorescence curves calculated from the convolution integral (1) are for decay times $\tau = 3, 4, 5, 6, 7, 10, 12, 15,$ and 20 nanoseconds.)

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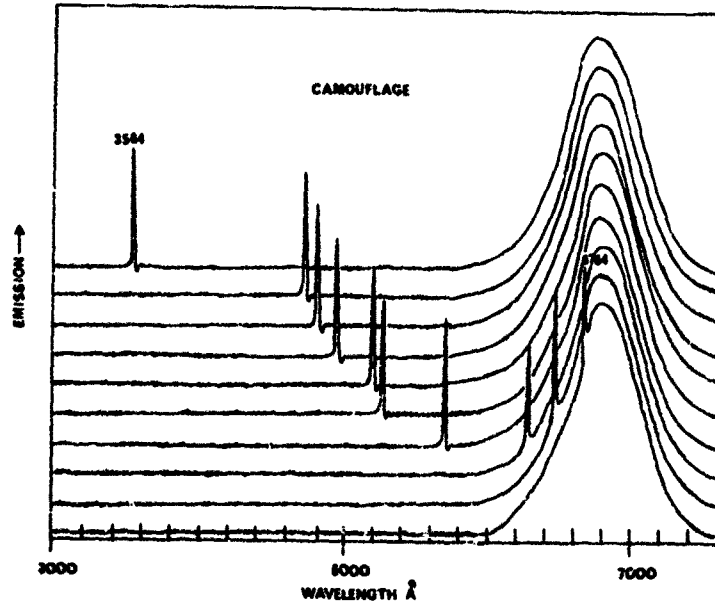


Fig. 3. Characteristic fabric luminescence as the laser wavelength of excitation was varied.

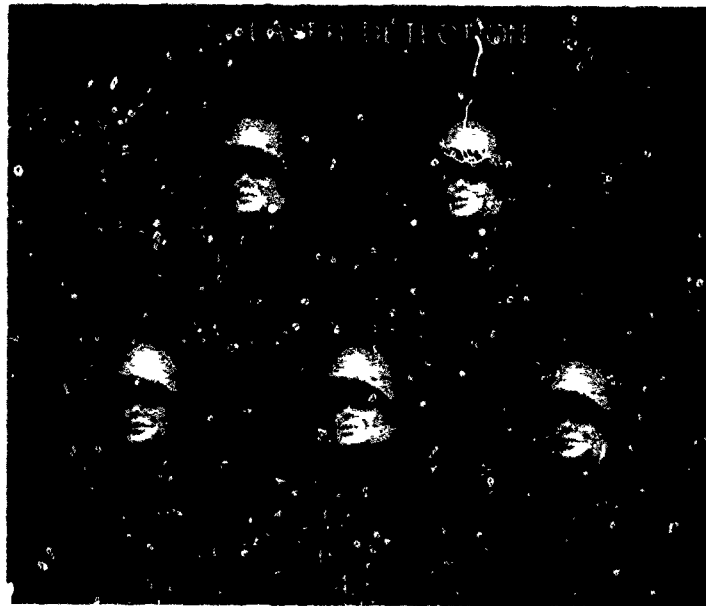
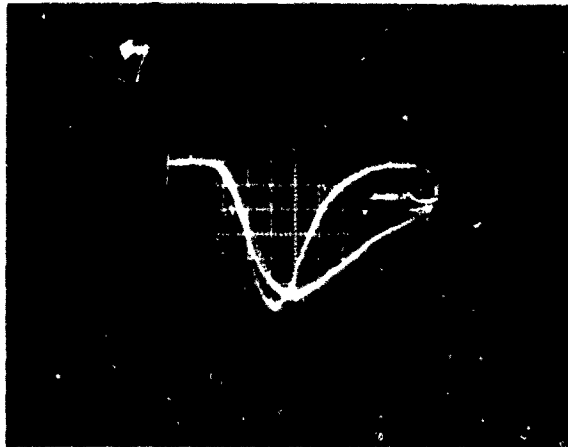


Fig. 4. Starlight scope display of fabric luminescence. The white region on the helmet is the luminescence from the fabric. Note the absence of such on sample 4.

PULSED DETECTION



5×10^{-9} SEC.

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Fig. 5. Oscilloscope display of dye laser pulse, the narrow one, and fluorescence. The sweep speed is 5×10^{-9} sec. per div.

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