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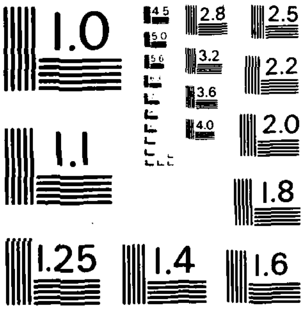

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# 1983 Annual Report on Laser Dyes

by
A. N. Fletcher
*Research Department*

**APRIL 1984**

**NAVAL WEAPONS CENTER**
**CHINA LAKE, CALIFORNIA 93555**

Naval Weapons Center
AN ACTIVITY OF THE NAVAL MATERIAL COMMAND

## FOREWORD

This report correlates the work presented in seven open literature publications on laser dyes. This work originated within the Chemistry Division and was performed and/or published in 1983. These publications covered both 6.1 and 6.2 funded work. The correlation was performed under Task Area XF62587.

This report was reviewed for technical accuracy by Rodney L. Willer and C. Denton Marrs.

Approved by
E. B. ROYCE, Head
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15 March 1984

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(U) 1983 Annual Report on Laser Dyes, by A. N. Fletcher. China Lake, Calif., Naval Weapons Center, April 1984. 76 pp. (NWC TP 6538, publication UNCLASSIFIED.)

(U) Reprints of seven published articles describing work performed at the Naval Weapons Center on laser dyes are included along with a brief discussion of the theory of dye laser degradation, dye fluorescence and quenching, improvements in dye laser lifetimes, flashlamp degradation, luminescent coolants, solvent effects, and new dyes. Techniques for obtaining over a thousand-fold improvement in dye laser lifetimes are described. The discovery of the longest-lived, moderate output, laser dye is reported.

## CONTENTS

# INTRODUCTION

As a consequence of the need for blue-green laser dyes for communications through the water (References 1-3), we began a dye synthesis program within the Chemistry Division of the Naval Weapons Center (NWC) in the early 1970s. In the mid-1970s, a test facility was constructed to evaluate long-pulse dyes lasing within the 390-400 nm region (References 4-6). The construction of this test facility and the laser-dye synthesis program was funded by the Atomic Energy Commission through Interagency Agreement SANL 284-001 with Lawrence Livermore National Laboratory, Livermore, Calif. The funding for the evaluation of the fluorescence and lasing characteristics of the new dyes and additional support for the dye synthesis program has come from NWC's Independent Research program, the Naval Ocean Systems Center (NOSC), the National Aeronautics and Space Administration (NASA), and the Electronic Materials Block of the Naval Research Laboratory (NRL), Washington, D.C.

The Laser Dye Test Facility has been improved continuously and has been expanded since its construction. A special Nd-YAG laser was installed to test the effects of dyes in coolant upon the output of the solid-state laser. This work was funded by the Naval Air Systems Command (NAVAIR) (Reference 7). A Perkin Elmer MPF 44B Fluorescence Spectrophotometer was purchased in order to be able to determine wavelength corrected fluorescence peaks and fluorescence quantum yields of dyes under various conditions (Reference 8 and 9). At present, NWC is the only laboratory within the Department of Defense (DoD) that has the capability to synthesize new dyes, determine their structure, study their fluorescence, and then to evaluate their flashlamp-pumped laser characteristics using a calibrated degradation flashlamp (or to study them by $N_2$ or excimer pumped lasers). The results of the work published in 1983 (References 7, and 9-13) are presented in Appendices A-F.

# 1983 PUBLICATIONS

## THEORETICAL

The flashlamp-pumped dye laser output can be expressed by the relationship

$$\phi = \underline{k} (\underline{I} - \underline{t}) \text{ (Joules)} \qquad (1)$$

where $\phi$ is the laser output, $k$ is the slope efficiency, $I$ is the electrical energy stored in the capacitor before delivery to the flashlamp, and $t$ is the threshold of lasing. A fundamental question arises as to how the deterioration of the dye affects the two dependent variables in Equation 1. In order to answer these two questions, Knipe first evaluated the processes that occur within the cavity of a flashlamp pumped dye laser (Appendix A) (Reference 11). These results were used to develop the 3-parameter dye degradation equations we reported in 1982 (Reference 14), and were further expanded in the study by Knipe and Fletcher presented in Appendix B (Reference 12).

Although a large variety of dyes have been fit to the dye laser degradation equations (References 13 and 15), there are some exceptions. Most of the rhodamine dyes were shown to have an overnight recovery when flashlamp pumped without an ultraviolet (UV) filter to protect them from the excitation lamp (Reference 12 and 16). The 3-parameter degradation equations would not be appropriate when the rate of pumping affects the laser output, i.e., as would be evidenced by an overnight recovery where the solution is not being pumped. It was for this reason that no major study of rhodamine dyes was published in the open literature even though lifetime measurements had been performed in this laboratory (Reference 16). Appendix B shows some possible kinetic schemes that can account for time dependent changes in laser output. One outstanding example is coumarin 480 under argon in a mixture of ethylene glycol and water (50:50 by volume). This system shows what was called a "yoyo" effect where the laser output increased as the rate of energy was increased (and decreases as the rate is decreased).

## FLUORESCENCE STUDIES

Kubin and Fletcher studied the fluorescence quantum yields of rhodamine dyes in 1982 (Reference 8). In 1983 we demonstrated that the fluorescence of a variety of coumarin dyes was measurably quenched by oxygen when the dyes were in ethanol (Appendix C) (Reference 9) but not when they were in a mixture of 50:50 by volume of ethanol:water (Appendix D). These fluorescence studies were of considerable importance as they gave a perspective as to ways that increased outputs were being found (or not being found) in the flashlamp-pumped dye laser when air was replaced by an inert gas using specific solvents (Appendices D and E).

## IMPROVEMENTS IN DYE LASER LIFETIMES

Although it has been speculated for sometime that laser dyes should degrade less if the far UV energy were excluded from their pump sources (Reference 17), the exact cost and gains of such an action had not been quantified. In Appendix E (Reference 10), we report such a study. Very marked lifetime improvements were measured but the laser output is reduced since the pump output is reduced by the filter. However, the reduction in laser output (≈2 fold) was outweighed by the gain in lifetime (≈2-1,600 fold). In addition, we showed that the removal of air could result in either small decreases in lifetime constants or as much as an 8-fold increase.

## FLASHLAMP DEGRADATION

Appendix E also presents data showing how the intensities of several flashlamps were found to decrease with time and that this decrease was a function of wavelength. We also noted that the output varied with the position along the length of a flashlamp. Very little data (if any) are available in the literature showing these effects. Such a measurement was necessary in order to be able to estimate the changes in the amount of light that was being used to degrade laser dyes in order to in turn be able to separate the effects of flashlamp degradation from those due to the degradation of the laser dye.

## LUMINESCENT COOLANTS

Although other studies had been performed on increasing the output of solid-state lasers through the use of dye in the coolant as an energy converter, the previous studies used a limited number of dyes and did not have some of our modern laser dyes available. They also did not have the knowledge of the quenching of coumarin fluorescence by air (Appendix C).

The study in Appendix F (Reference 7) was performed with the intent of using improved dyes having increased absorption. These dyes have been called bifluorophoric (Reference 18), but, more correctly, they should be called bichromophoric fluorescent dyes. In any case, these types of dyes having absorption over a wider range of wavelengths were found to be very difficult to synthesize and gave little improvement in the solid-state laser output.

It appears that dyes having a narrow emission band coupled with both a high quantum yield of fluorescence and good absorptivity would give moderate improvement in solid state laser output when used as energy converters in the coolant.

## SOLVENT EFFECTS

A valuable goal for dye laser studies is to find a usable solvent that is less flammable than the ethanol or methanol which are commonly used for the coumarin and rhodamine laser dyes. The work described in Appendix D (Reference 13) shows that the less flammable 50:50 by volume mixture of ethanol:water is a usable solvent and that it can also give longer lifetimes and higher lasing outputs depending upon the dye and the cover gas. The 50:50 mixture of ethanol:water has not been optimized nor has the oxygen percentage. Thus, further improvements should be possible through variation of these ratios. Present data suggests that ethanol yields longer lifetimes than does methanol, but in a few cases, methanol yields higher lasing outputs. These factors should be given further investigation since many dye laser users have difficulty obtaining pure ethanol because of the problems associated with its potential use as a beverage. In addition, very little is known concerning the effects of other solvents upon dye laser lifetime constants.

## NEW DYES

Three of the enclosed studies (Appendices E-G) describe the characteristics of new dyes. The importance of these depends in a large part on the wavelengths and nature of the intended usage. As the number of new laser dyes increase, increased perspective is obtained as to what functional groups yield superior laser dyes.

The study on the new oxazole dye, 4PyMPO-MePTS (Reference 19), reported in Appendix G illustrates the need for a thorough examination of the experimental parameters associated with the lasing of a dye solution. 4PyMPO-MePTS had been tested for lasing by Lee and Robb (Reference 20). They did not test it in the absence of air, however, which in turn delayed the discovery that 4PyMPO-MePTS in ethanol under argon is the longest-lived, flashlamp-pumped dye presently known. This discovery is of such importance that Appendix G was included in this report even though this paper was published in 1984. The long lifetime and improved laser output of 4PyMPO-MePTS and its related dyes, 4PyPO-MePTS and 4PyPO-$HClO_4$, caused by the removal of air, now makes this class of dyes a very serious contender for use in a practical military laser that would be of use outside the laboratory.

## CONCLUSIONS

**Because of the complexity of the photophysical and photochemical processes associated with the flashlamp-pumped dye lasers combined with the problems in the synthesis of multi-functional group dyes, progress in the development of new, improved, long-lasting laser dyes is slow. Advances are difficult to predict. Months of intensive effort may be taken to synthesize a particular dye only to find that it does not lase at all. Progress is also slow because of the variety of technical specialties that are needed for the synthesis, characterization, and evaluation of new laser dyes. Good synthetic chemistry is of little use without the instrumentation needed for dye characterization and this**

**must be close-coupled with a thorough dye laser testing capability. Add to this the low funding level used to advance the technology and it is small wonder that major advances have been made at all.**

Advances in dye laser technology, though slow in coming, are rapidly made use of by industry and universities. Most improvements do not require major changes in equipment or procedures. It has been estimated that there are 10,000 dye lasers in use (Reference 21); thus, published advances in this field no doubt also help to advance science and may some day result in useful lasers that can be used in a military operation. The dye laser still remains the simplest laser that can be tuned from 0.33 to greater than 1.8 μm (Reference 22) without the use of nonlinear optical materials.

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## Appendix A

## PHOTON CONSERVATION IN FLASHLAMP PUMPED DYE LASERS

Optical and Quantum Electronics, 15 (1983), pp. 275-278
Short Communication

*Optical and Quantum Electronics* **15** *(1983)* · *Short Communication*

# Short Communication

## *Photon conservation in flashlamp pumped dye lasers*

A general representation of the laser output per pulse of the flashlamp is deduced from an equivalence between molecules populating the upper state of the lasing transition and coherent photons populating the active cavity modes. This representation is used to derive approximate expressions relating the slope efficiency and threshold to the losses associated with the laser system.

The dominant energy transfer processes associated with a laser dye are illustrated in Fig. 1. A photon is absorbed by a dye molecule belonging to the population of the ground state, $S_0$, exciting it to the manifold of excited states, $S^*$. From $S^*$, the excited molecule is spontaneously deactivated to that part of the excited state manifold, $S_1$, associated with the lasing transition $S_1 \rightarrow S_0^*$. Let $\gamma_1$ be the probability that the deactivation to $S_1$ occurs. From $S_1$, the molecule is deactivated by the coherent radiation field to that part of the ground state manifold, $S_0^*$, associated with the lasing transition, or it is deactivated to $S_0$ or otherwise removed from the system by spontaneous processes. The induced deactivation by the coherent radiation field of the laser adds a photon to that field. Stepanov and Rubinov [1] identified $S_0^*$ with a segment of the high-energy tail of the thermal distribution of $S_0$. As a consequence of the rapidity of the thermalizing processes in the dye solution, it is usually assumed that $n_0^*$, the population density of $S_0^*$, is approximately the thermal population density associated with that segment of the high-energy tail. These processes are discussed in detail in many articles and reviews [2].

There is one characteristic of large organic molecules (usually employed as laser dyes) that has not been widely considered in the theoretical analysis of the performance of dye lasers. Over the range of wavelengths of pump radiation normally employed, the probability that a molecule from $S_0$ which absorbs a pump photon arrives at $S_1$, $\gamma_1$, is essentially independent of the wavelength associated with that photon. To a large extent this is a consequence of the rapidity of the thermalizing processes in the dye solution. One of the criteria used in the selection of laser dyes is that they have a fluorescence quantum yield, $\gamma_f$, close to 1. Since $\gamma_f \leqslant \gamma_1 \leqslant 1$, $\gamma_1$ is close to 1 for a good laser dye.

It is useful to consider each molecule that arrives at $S_1$ as a potential photon that is either added to the coherent radiation field by the induced transition, $S_1 \rightarrow S_0^*$, or is quenched by spontaneous processes. Where $n_1$ is the population density of $S_1$ at some point in the dye solution, to a close approximation the rate of quenching is $n_1/\tau_f$ where $\tau_f$ is the fluoresence lifetime of $S_1$. The rapidity of the thermalizing processes makes this a good approximation.

Consider a pulse of pump radiation which supplies absorbable photons to the cavity dye solution with a rate $q_p(t)$ where $q_p(0) = 0$ and $q_p(t^*) = 0$, $0 \leqslant t \leqslant t^*$. The rate at which potential photons are delivered to $S_1$ in that volume is $\gamma_1 f_p q_p$ where $f_p < 1$ is the fraction of absorbable pump photons that are actually absorbed by the cavity dye solution. Typically, the concentration of the laser dye is such that $f_p$ is close to 1. The rate at which potential photons are quenched can be written as $V f_d \bar{n}_1/\tau_f$ where $V$ is the resonator mode volume, $f_d \leqslant 1$ is the fraction of that volume occupied by the dye solution, and $\bar{n}_1$ is the volumetric average of the population density of $S_1$.

If the pump source is capable of initiating lasing in the cavity, at a time $t_1 > 0$ a critical distribution of potential photons will be achieved in the cavity and lasing will begin. Since the distribution of potential photons is not homogeneous, the onset of lasing may be associated with some redistribution of the potential photons. It is anticipated that this redistribution will continue during the lasing process as a consequence of the pump inhomogeneities. If the onset of lasing occurs in a time interval $\delta t < \tau_f < t_1$, the macroscopic boundary condition for the onset of lasing is $\gamma_1 f_p q_p(t_1) \simeq V f_d \bar{n}_{1_c}/\tau_f$ where $\bar{n}_{1_c}$ is that value of $\bar{n}_1$ corresponding to the initiating critical distribution of potential photons; that is, lasing occurs when the rate at which potential photons are created exceeds that necessary to maintain some critical value of their average density. The growth of the coherent laser field and the losses associated with that field will tend to inhibit further increase in the average density of the potential photons.

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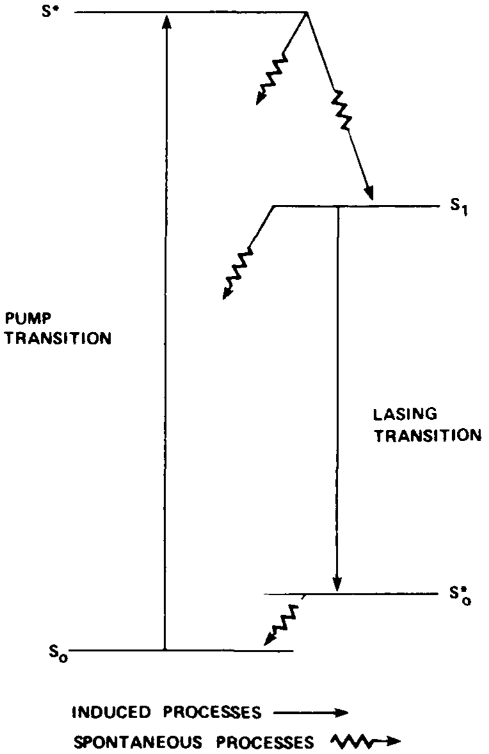

*Figure 1* Schematic representation of dominant energy transfer processes in a dye laser.

Lasing will continue until a time, $t_2$, when the rate at which potential photons are created falls below that required to maintain that critical distribution for lasing appropriate to that time. Any residual coherent field will decay with a lifetime $\tau_c^*$, the cavity lifetime at $t_2$. If $\tau_c^* \ll t_2 - t_1$, the macroscopic boundary condition appropriate for the end of lasing is $\gamma_1 f_p q_p(t_2) \simeq V f_d \bar{n}_{1_c^*}/\tau_f$ where $\bar{n}_{1_c^*}$ is the value of $\bar{n}_1$ corresponding to the final critical distribution of potential photons. Thus lasing takes place over a time interval, $t$, where $0 < t_1 < t \leqslant t_2 \leqslant t^*$. The net number of potential photons transferred to the coherent radiation field over the life of the pump pulse is

$$Q_s \simeq \int_{t_2}^{t_1} [\gamma_1 f_p q_p(t) - V f_d \bar{n}_1(t)/\tau_f]\, dt - V f_d (\bar{n}_{1_c^*} - \bar{n}_{1_c}) \qquad (1)$$

If $\tau_f \ll t_2 \quad t_1$, then $\int_{t_1}^{t_2} \bar{n}_1(t)\, dt \gg \tau_f(\bar{n}_{1_c^*} - \bar{n}_{1_c})$. Thus, for a good laser where a significant fraction of the potential photons are transferred to the coherent field, the last term in Equation 1 is insignificant. One aspect of optimizing the dye concentration is the minimization of $\int_{t_1}^{t_2} \bar{n}_1(t)\, dt$ subjected to the maintenance of a large value of $f_p$.

If $q_1(t)$ is the number of photons associated with the coherent radiation field in the cavity at time $t$, the rate at which these photons are removed from that field by processes other than that associated with redistribution of the potential photons in the dye solution can be represented as $c(\Sigma l_i) q_1(t)$ where $\tau_i = 1/cl_i$ is the lifetime associated with the $i$th process and $c$ is the velocity of light. In general, each of these lifetimes is a time dependent mean value appropriate to the spatial inhomogeneities and the mode structure of the cavity. The total loss of coherent photons due to these processes during one pulse of the flashlamp is $L = \int_{t_1}^{t_2} c(\Sigma l_i) q\, dt = c\Sigma L_i$. One part of this loss is that due to the out-coupling of radiation from the cavity, $L_0 = \int_{t_1}^{t_2} c l_0 q_1\, dt = \int_{t_1}^{t_2} q_1\, dt/\tilde{\tau}_0$ where $\tau_0$ is the output coupling lifetime of the cavity. If the cavity output is not controlled by some pulse truncating mechanism (e.g., Q-switching), $\tau_0$ is essentially constant over the lifetime of the output pulse and can readily be estimated from the optical parameters of the cavity.

It is convenient to define mean values $\tilde{l}_i = \int_{t_1}^{t_2} l_i q_1 \, dt / \int_{t_1}^{t_2} q_1 \, dt$. Then the fraction of the net number of potential photons transferred to the coherent radiation field that appear as output is $1/\tilde{\tau}_0 c \Sigma \tilde{l}_i$. Since the potential photons are the only significant source of coherent photons, the total number of photons coupled out of the laser during one pulse of the flashlamp is $Q_s/\tilde{\tau}_0 c \Sigma \tilde{l}_i$. Let $\phi(\nu)$ be the frequency distribution function for the output photons. The energy output of the laser is $E_0 = \int h\nu\phi(\nu)\, d\nu$. The number of output photons is $\int \phi(\nu)\, d\nu$. Therefore, the energy output per pulse of the flashlamp may be represented as

$$E_0 \simeq \frac{h \int_{t_1}^{t_2} (\gamma_1 f_p q_p - V f_d \bar{n}_1/\tau_f)\, dt}{\tilde{\lambda}\, \tilde{\tau}_0 \Sigma \tilde{l}_i} \tag{2}$$

where $\tilde{\lambda}$ is the appropriate mean value of the output wavelength near that for which the output of the laser is a maximum.

Assuming the pump function, $q_p$, to be proportional to $I$, the energy stored in the flashlamp driver capacitor, Equation 2 can be written as $E_0 \simeq hIF/\tilde{\lambda}\, \tilde{\tau}_0 \Sigma \tilde{l}_i$ where $F = \int_{t_1}^{t_2} (A - x)\, dt$, $A = \gamma_1 f_p q_p / I$, and $x = V f_d \bar{n}_1 / \tau_f I$.

The upper lasing state $S_1$ is populated by the spontaneous relaxation processes from $S^*$ and by the absorption of coherent photons in the transition $S_1 \leftarrow S_0^*$. It is depopulated by spontaneous process and by the emission of coherent photons in $S_1 \rightarrow S_0^*$. It is characteristic of good laser systems that once the critical population $\bar{n}_{1_c}$ has been achieved, the growth of the coherent photon population leads to dominance by the coherent populating and depopulating processes in a time which is short compared to the spontaneous relaxation time of $S_1$. Thus, the value of $\bar{n}_1$ is maintained at a quasi-steady state value near $\bar{n}_{1_c}$. There is a body of computational evidence which supports the validity of the steady state approximation for model laser dye systems [3, 4]. On this basis $x \simeq V f_d \bar{n}_{1_c}/\tau_f I$.

With this approximation, the boundary conditions characterizing $t_1$ and $t_2$ become $A(t_1) \simeq A(t_0) \simeq x$. Hence, $t_1$, $t_2$ and thus $F$ are functions of $x$. Expanding $F$ about a point $x_0$,

$$F \simeq F_0 + F_0'(x - x_0) + \ldots \tag{3}$$

Substitution of this expression into Equation 2 yields

$$E_0 \simeq \frac{h[(F_0 - x_0 F_0')I + V f_d F_0' \bar{n}_{1_c}/\tau_f + \ldots]}{\tilde{\lambda}\, \tilde{\tau}_0 \Sigma \tilde{l}_i} \tag{4}$$

which can be written in the frequently used form $E_0 \approx k(I - I_0)$. Over the range of $I$ for which a slope efficiency, $k$, and a threshold, $I_0$, can be defined, these quantities may be approximately evaluated from Equation 4 as

$$k \approx h(F_0 - x_0 F_0')/\tilde{\lambda}\, \tilde{\tau}_0 \Sigma \tilde{l}_i \tag{5}$$

and

$$I_0 \approx -V f_d F_0' \bar{n}_{1_c}/\tau_f (F_0 - x_0 F_0') \tag{6}$$

Snavely and Peterson [5] have characterized the threshold condition by the gain over some round-trip path through the laser cavity being equal to the sum of the losses over that path. As a consequence, $\bar{n}_{1_c}$ and thus $I_0$ are linear functions of the mean values of the loss terms appropriate to the threshold condition. Therefore, over their range of validity, the slope efficiency would be expected to decrease with increases in the mean values of the loss terms $\tilde{l}_i$, and the threshold would be expected to increase with increases in the mean values of these quantities appropriate to the threshold condition at $t_1$.

As illustrated by the above example, Equation 2 can be a useful starting point for the analysis of a flashlamp pumped dye laser. It allows selective examination of individual aspects of the problem while avoiding much of the complexity of the more rigorously detailed approaches commonly used.

The derived dependence of the slope efficiency and threshold on the loss terms is consistent with the observations of Fletcher [6] for a number of dyes where the increased loss was due to the photolytic production of stable products in the dye solution. The appearance of $\tau_f$ in the denominator of Equation 6 illustrates the deleterious effect of molecules which quench $S_1$ as pointed out by Keller [3]. Since this is the only explicit dependence on $\tau_f$, Equation 6 suggests that the quenching of $S_1$ predominantly effects the threshold.

The terms $F_0$, $F_0'$ and $x_0$ appearing in Equations 5 and 6 are functions of the shape of the pump pulse. Their appearance illustrates the importance of that shape on the values of these quantities and on the range of $I$ over which they lead to a useful representation of the laser output. In particular, that range does not include the actual threshold value of $I$. At that point, both $F$ and its first derivative vanish. The value of the function in the neighborhood of the actual threshold is dominated by derivatives of order greater than one.

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## Appendix B

## EFFECTS OF SECONDARY CHEMICAL REACTIONS UPON THE PERFORMANCE OF DYE LASERS

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# EFFECTS OF SECONDARY CHEMICAL REACTIONS UPON THE PERFORMANCE OF DYE LASERS

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## Summary

The effect of absorption at the lasing wavelength due to the accumulation of reaction products from the photodegradation of a laser dye is analyzed theoretically. This analysis is used as a basis for the representation of data from dye degradation experiments in terms of absorption at the lasing wavelength. Studies of the effects of flashlamp pulse rate and time on the inferred absorption for a number of different dyes reveal the influence of secondary chemical reactions. The most significant effects are shown to be associated with spontaneous reactions where the reactants and products have markedly different molar absorptivities at the lasing wavelength.

## 1. Introduction

It is generally recognized that the degradation in performance associated with repetitious use of a dye laser is a consequence of photoinduced chemical reactions. Where the question has been addressed, it has been found that the predominant cause of degradation is the accumulation of products which absorb at the lasing wavelength [1 - 3]. It would not be unexpected for the complex organic molecules used as laser dyes to have equally complex products which undergo further reaction. This aspect of the degradation process which has largely been ignored is the focus of this paper.

Since the absorbing products are in direct competition with the population inversion, small amounts of product which would be difficult to detect by other means can have a significant effect on laser performance. To interpret this effect better, it is desirable to know the relationship between laser output and absorption at the lasing wavelength. A generally applicable approximation to this relationship results from the following analysis.

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## 2. Theory

A general expression for the output of a flashlamp-pumped dye laser has recently been derived [4]. The analysis leading to this expression will be briefly summarized. The result will be extended to identify explicitly the effects on the slope efficiency and threshold of reaction products which absorb at the lasing wavelength.

The output of a flashlamp-pumped dye laser is approximately proportional to the difference between the rate of production of molecules in the upper lasing state and their rate of spontaneous deactivation integrated over the duration of the laser pulse. If the active radiant flux from the flashlamp is assumed to be proportional to the energy $I$ supplied to the flashlamp, the rate of production of excited molecules can be written as $fI$ where $f(t)$ is the rate of production per unit input energy determined by the shape of the flashlamp pulse as a function of time $t$, the laser geometry and the dye concentration. In the quasi-steady state approximation the rate of spontaneous deactivation of the excited state under lasing conditions is proportional to an approximately constant critical average population density divided by the fluorescence lifetime of that state. The critical population density is proportional, through parameters dependent on the laser geometry, to that population corresponding to the critical inversion as defined by Snavely and Peterson [5]. It is convenient to define $x$ as the rate of spontaneous deactivation divided by $I$; thus $x = vn_{1c}/I$ where $n_{1c}$ is the excited state population density corresponding to critical inversion and $v$ is a constant determined by the laser geometry and the fluorescence lifetime. The output of the laser per flashlamp pulse can then be written as

$$\varphi = \frac{uI}{\Sigma L_i} \int_{t_1}^{t_2} (f - x)\,\mathrm{d}t \qquad (1)$$

where $u$ is a constant inversely proportional to the product of the mean output wavelength and the cavity output lifetime, the interval from $t_1$ to $t_2$ is the time interval of the laser pulse and $\Sigma L_i$ is the sum of the mean values of the losses to which coherent photons in the laser cavity are subjected during the laser pulse.

The integral

$$F(x) = \int_{t_1}^{t_2} (f - x)\,\mathrm{d}t$$

in eqn. (1) is the gross production of coherent photons per unit flashlamp energy per flashlamp pulse. The dependence of this function on the flashlamp excitation energy is through the variable $x$. The beginning and end of the laser pulse are characterized by the vanishing of the integrand: $f(t_1) = f(t_2) = x$. The derivative $F' = -\tau(x)$ where $\tau = t_2 - t_1$ is the duration of the laser pulse corresponding to a particular value of $x$. When the values of $x$ are restricted to a range about a value $x_m$ over which the change in $\tau$ is small compared with its magnitude, $F$ can be approximated by

$$F \approx F_m - \tau_m(x - x_m) \tag{2}$$

When this result is substituted into eqn. (1) the output is given by

$$\phi \approx \frac{\kappa(I - t)}{\Sigma \tilde{l}_i} \tag{3}$$

where

$$\kappa = u(F_m + \tau_m x_m)$$

$$t = \frac{\tau_m v n_{1c}}{F_m + \tau_m x_m}$$

Since the emphasis here is on product absorption at the lasing wavelength, it is convenient to measure the losses in terms of the loss due to a uniformly dispersed absorber of unit single-pass absorbance. When the laser-configuration-dependent scaling parameter is absorbed into the constant $u$,

$$\Sigma \tilde{l}_i = \tilde{A}_0 + A_p$$

where $A_0$ is the equivalent single-pass absorbance associated with the laser in the absence of products and $A_p$ is the sum of the losses due to the absorption of the products. Similarly, when the scaling factor is absorbed into $v$,

$$n_{1c} = A_d + \hat{A}_0 + A_p$$

where the absorbance $A_d$ of the dye at the lasing wavelength measures the population of the lower lasing levels under the assumption that these levels can be approximated by the high energy thermal tail of the ground state population distribution. It should be noted that the product $uv$ is independent of the choice of the loss scale. The loss terms $\tilde{A}_0$ and $\hat{A}_0$ are distinguished to allow for effects of transient processes such as triplet formation during the lasing process which, because of their inhomogeneity, may affect $\Sigma \tilde{l}_i$ and $n_{1c}$ in somewhat different ways. The slope efficiency $k = \kappa/\Sigma \tilde{l}_i$ can now be expressed as

$$k \approx \frac{k_0}{1 + A_p/\tilde{A}_0} \tag{4}$$

where $k_0 = \kappa/\tilde{A}_0$ and

$$kt \approx k\delta + \alpha \tag{5}$$

where

$$\delta = \frac{\tau_m v(A_d + \hat{A}_0 - \tilde{A}_0)}{F_m + \tau_m x_m}$$

and $\alpha = uv\tau_m$ are parameters independent of the presence of absorbing products. Equation (3) can be rewritten to display explicitly the effect of the absorbing products as

$$\phi \approx \frac{k_0(I-\delta)}{1 + A_p/A_0} - \alpha \tag{6}$$

Where the transient effects are not large, $A_0 \approx \hat{A}_0$ is primarily a function of the index of refraction and the absorbance of the solvent, the optical components of the laser, the laser geometry and the lasing wavelength and is independent of the particular dye used. This implies that the sensitivity of the laser output to product absorbance is insensitive to which dye is used. The observation of this insensitivity was reported by Fletcher and Bliss [6] relative to the change in absorbance necessary to reduce the slope efficiency to one-half of its original value.

The dependence of the threshold $t$ on product absorption is given by

$$t = t_0 + \frac{\alpha A_p}{\kappa} \tag{7}$$

where $t_0 = \delta + \alpha/k_0$. This equation together with eqn. (4) shows the opposing behavior of $k$ and $t$ first characterized by Fletcher [7].

If the product results from a straightforward global photolysis,

$$A_p = rT \tag{8}$$

where $T$ is the sum of the flashlamp energies per unit volume of dye, $T = \Sigma I/V$ and $r$ measures the overall photosensitivity of the reaction. More generally, the variation in $A_p$ with $T$ can be investigated using

$$\frac{A_p}{\kappa} = \frac{I-\delta}{\phi + \alpha} - \frac{1}{k_0} \tag{9}$$

which results from rearrangement of eqn. (6). The laser- and dye-dependent parameters $\alpha$, $\delta$ and $k_0$ can be derived empirically from the dependence of $\phi$ on $I$ at constant $T$.

It is evident from eqn. (9) that for each value of $I$ there is a corresponding maximum value of the computed $A_p/\kappa$. These limits are a consequence of the linear truncation of the function $F$ in eqn. (2). As the limit is approached for any value of $I$, that input energy ceases to be useful for characterizing product absorption. For this reason it is desirable to have output data taken over a range of flashlamp excitation energies at approximately the same value of $T$.

## 3. Experimental details

Most of the experimental conditions were the same as those previously described [8]; a Phase-R DL-10Y triaxial flashlamp was used for the test laser. In some experiments a Pyrex tube was used instead of the quartz tube separating the dye from the coolant to remove the UV portion of the flashlamp radiation (UV filtration). In addition, a Xenon Corporation N-851C water-cooled linear flashlamp pumped by their model 457 micropulser was inserted in the return flow from the test laser to the storage and mixing vessel of the dye flow system. This provided a laser-like environment without mirrors capable of rapidly subjecting the dye solution to large quantities of radiation. This linear lamp was run at 10 J per shot at pulse rates varying from 1 to 25 Hz.

The flow system was closed to the atmosphere and was provided with a port for the introduction of arbitrary gases which were bubbled through the solution in the storage vessel. This provided for controlled atmospheres of a variety of cover gases which were equilibrated with the dye solution. This system is described in greater detail elsewhere [9].

## 4. Results

### *4.1. Results for some coumarin derivatives*

For coumarin 102 dissolved in a 50:50 mixture of ethylene glycol: water, the output of the test laser proved to be a sensitive function of the rate at which energy was introduced into the solution by the micropulser lamp. Figure 1 shows results for a $1.5 \times 10^{-4}$ M solution equilibrated with argon under UV-filtered conditions. As a consequence of the ambiguity in the interpretation of the initial slope efficiency, the reciprocal $A_p/\kappa + 1/k_0$ of the slope efficiency computed from eqns. (4), (6) and (9) is plotted in this figure. The parameters $\delta = 20.7$ J and $\alpha = 8.8$ mJ were estimated graphically from the output at 40 J and 50 J in the neighborhood of the minima at $T \approx 7$ MJ dm$^{-3}$ and $T \approx 16$ MJ dm$^{-3}$. When the initial pulse rate was about 25 Hz, the output increased to a relatively stable value. Change to a pulse rate of about 1 Hz resulted in rapid degradation of the output. This degradation was followed with 50 J shots of the test laser to $1/k$ values well in excess of the 40 J limit at $2.2 \times 10^3$. After an overnight rest, the output from the solution at about 25 Hz repeated the performance of the previous day at a lower overall output and approached an apparently quasi-steady degradation rate. The results for a $2 \times 10^{-4}$ M solution under similar conditions are shown in Fig. 2.

These results imply that there is an extremely photosensitive component V in the products which absorbs at the lasing wavelength. The increase in this product in the absence of irradiation implies a photoproduced precursor X of lower molar absorptivity which reacts spontaneously to produce V. In global terms

$$\mathrm{D} \xrightarrow{h\nu} \mathrm{X} \qquad (10)$$

$$\mathrm{X} \longrightarrow \mathrm{V} \qquad (11)$$

The decrease in V associated with the high energy input rates implies that V photolyzes to a less absorbant product P:

$$\mathrm{V} \xrightarrow{h\nu} \mathrm{P} \qquad (12)$$

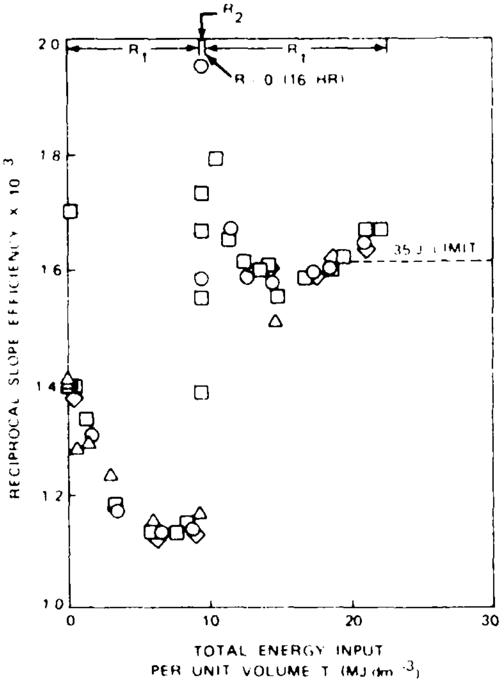

Fig. 1. Reciprocal slope efficiency as a function of total energy input for $1.5 \times 10^{-4}$ M coumarin 102 in a 50:50 mixture of ethylene glycol:water equilibrated with argon under UV-filtered conditions. Each point was computed from an average of ten closely spaced test laser output determinations at the indicated input energy *I* (, 35 J; , 40 J; , 45 J; , 50 J). The micropulser input rates and the period over which they were applied are indicated at the top of the figure ($R_1 \approx 465$ J dm$^{-3}$ s$^{-1}$; $R_2 \approx 19$ J dm$^{-3}$ s$^{-1}$).

To account for the "yo-yo" effect of the repeated changes in pulse rate shown in Fig. 2, it is necessary that X also be photolyzable to a less absorbant product P':

$$X \xrightarrow{h\nu} P' \qquad (13)$$

The rate of reaction (11) was observed in an experiment similar to that shown in Fig. 1 where a large quasi-steady state concentration of X was generated at about 20 Hz followed by no irradiation except for the occasional 50 J single-shot measurements with the test laser required to follow the degradation in output. The end point was estimated from the near-equilibrium output obtained after 2 days without irradiation. The lifetime $\tau_{11}$ of X relative to reaction (11) was estimated from the slope of the linear regression on the single-shot measurements to be about 4 h.

Under the assumption that the change in average concentration of the various components resulting from the passage of an aliquot through the

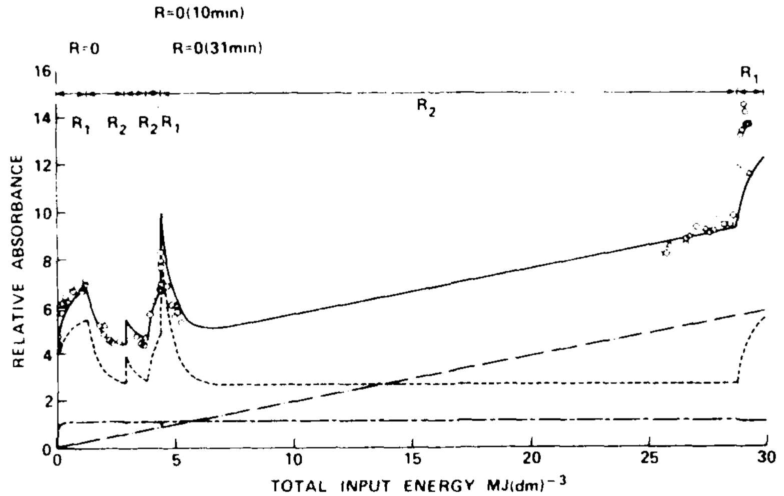

Fig. 2. Relative product absorbance as a function of total energy input for $2 \times 10^{-4}$ M coumarin 102 in a 50:50 mixture of ethylene glycol:water equilibrated with argon under UV-filtered conditions. Each point was computed from the average of ten closely spaced test laser output determinations at the indicated input energy $I$ ( , 35 J; , 40 J; , 45 J; , 50 J). The micropulser input rates are indicated at the top of the figure ($R_1 \approx 170$ J dm$^{-3}$ s$^{-1}$; $R_2 \approx 370$ J dm$^{-3}$ s$^{-1}$). Computed values based on an approximate fit to the data are plotted for the total absorbance (——) and for the individual absorbing products V (— — —), X (— · —) and P (— · —).

flow system is small, the pertinent measure of the rate $R = \mathrm{d}T/\mathrm{d}t$ of photolytic energy input is the rate of energy input divided by the volume of the system. If it is assumed that bleaching is negligible and P is P′, the kinetics associated with reactions (10) - (13) can be represented by

$$\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{d}T} = r_{10} - \frac{[\mathrm{X}]}{R\tau_{11}} - r_{13}[\mathrm{X}] \tag{14}$$

$$\frac{\mathrm{d}[\mathrm{V}]}{\mathrm{d}T} = \frac{[\mathrm{X}]}{R\tau_{11}} - r_{12}[\mathrm{V}] \tag{15}$$

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}T} = r_{13}[\mathrm{X}] + r_{12}[\mathrm{V}] \tag{16}$$

where the square brackets indicate concentration, $r$ is the photosensitivity of the photolytic reactions and $\tau_{11}$ is the lifetime of X relative to reaction (11). The observed sensitivity to $R$ when the results are viewed as a function of $T$ is a consequence of the decrease in importance of the spontaneous reaction (11) relative to the photolytic reactions as $R$ is increased.

The concentration of V corresponding to a single-pass absorbance of $\kappa$ in the test laser was used as the unit of concentration, and the value of $\tau_{11}$

(23)

estimated above and the values of $\delta$ and $\alpha$ estimated from Fig. 1 were employed to make a crude fit of the analytic solution of the kinetic equations (11) - (16) to the data plotted in Fig. 2. This fit shows the qualitative consistency between the observation and the global mechanism given above. While the fit is not precise or unique, it does exhibit the order-of-magnitude relationships required to obtain the observed "yo-yo" behavior (Table 1) and suggests that this behavior is dominated by the minor, yet highly absorbant, product species V.

TABLE 1

Parameters used for the computed curves in Fig. 2

| | |
|---|---|
| *Lasing parameters* | |
| $k_0$ | $2.22 \times 10^{-3}$ |
| $\delta$ (J) | 20.8 |
| $\alpha$ (mJ) | 8.8 |
| *Reaction parameters*[a] | |
| $\tau_{11}$ (h) | 1 |
| $r_{10}$ (dm$^3$ J$^{-1}$) | $5.6 \times 10^{-2}$ |
| $r_{13}$ (dm$^3$ J$^{-1}$) | $2 \times 10^{-5}$ |
| $r_{12}$ (dm$^3$ J$^{-1}$) | $2 \times 10^{-6}$ |
| *Relative product absorptivities*[b] | |
| $\epsilon_V$ | 1 |
| $\epsilon_X$ | $4 \times 10^{-2}$ |
| $\epsilon_P$ | $3.4 \times 10^{-4}$ |

[a] $r_{10} \gg r_{13} \gg r_{12}$

[b] $\epsilon_V \gg \epsilon_X \gg \epsilon_P$.

The greater sensitivity to the change in pulse rate for $T \approx 29$ MJ dm$^{-3}$ relative to the initial sensitivity suggests the possibility that P (or P′) is photolyzable back to X. This would result in a quasi-steady increase in [X] and [V] as well as [P] during the long duration segment at constant $R$. This would not affect the qualitative relationships shown in Table 1. However, it does suggest that the absorbance of P at the lasing wavelength may be negligible compared with those of the other products.

The results from a test of a $2 \times 10^{-4}$ M solution of AC3F [10, 11] in ethanol equilibrated with argon are shown in Fig. 3. This test was conducted under UV-filtered conditions over a period of 7 days. In excess of 99% of the energy was introduced by the micropulser at about 23 Hz ($R \approx 385$ J dm$^{-3}$ s$^{-1}$). The times during which micropulser energy was introduced are indicated by the $T$ scale in the figure. The data were taken in closely spaced sets at 30, 35, 40 and 45 J using the test laser. The parameters $\delta \approx 18.4$ J and $\alpha \approx 13.3$ mJ were estimated from the intersection of the linear regression lines $\phi(I)$ from data in the ranges 0.7 MJ dm$^{-3}$ $< T <$ 6 MJ dm$^{-3}$ using all $I$ values and 41 MJ dm$^{-3}$ $< T <$ 46 MJ dm$^{-3}$ with $I \geq 30$ J. The initial slope efficiency $k_0 \approx 1.47 \times 10^{-3}$ was estimated from the mean values of $1/k$ computed from a data set taken before the micropulser was started.

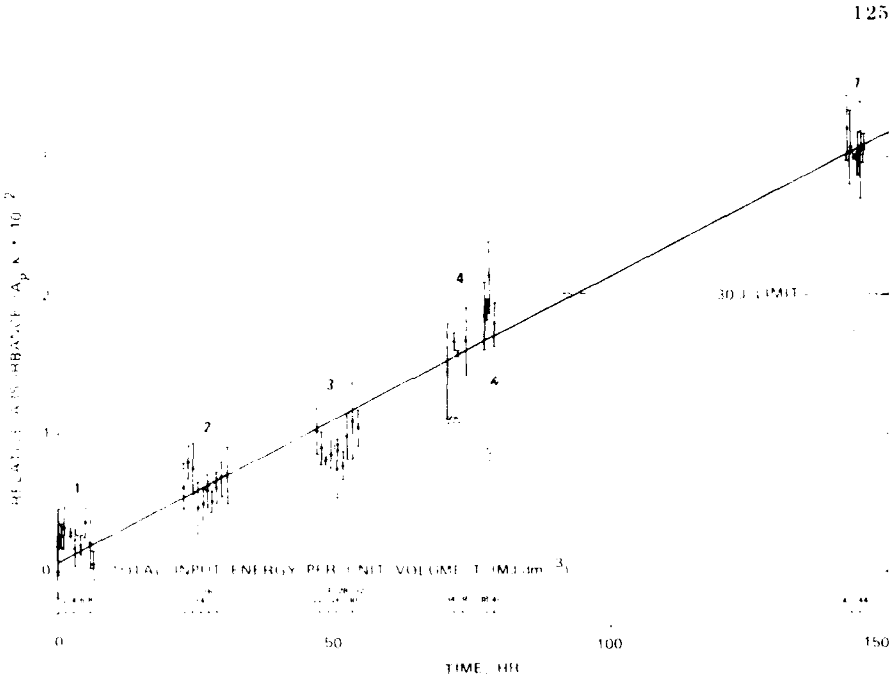

Fig. 3. Relative product absorbance as a function of time for $2 \times 10^{-4}$ M AC3F in ethanol equilibrated with argon under UV-filtered conditions. The introduction of energy by the micropulser is indicated by the secondary energy input scale at the bottom of the figure ($R \approx 385$ J dm$^{-3}$ s$^{-1}$). The points with error bars represent the centroid of the values computed from the average of ten test laser output determinations at each of the following values of input energy: 45, 40, 35 and 30 J (time, less than 60 h). Values computed from the 30 J data for time greater than 60 h are indicated by ⁝. The error bars indicate the standard deviation of the values computed from the various input energies used. The general correlation of these data with time is indicated by the linear regression line computed from the centroids · of the data taken each day when the micropulser was on. The day number is indicated by the numeral associated with each of the data groups.

The most significant change in product absorbance at the lasing wavelength is that which occurred between days 4 and 7 when the micropulser was not running. This implies the spontaneous production of a product V from a precursor X of lower molar absorptivity (*i.e.* reaction (11)). The change in relative absorbance during the 70 h period from $t$ = 5 h to $t$ = 75 h is approximately the same as that during the period from $t$ = 75 h to $t$ = 145 h even though 51% of the excitation energy was introduced during days 2 and 3 of the first period. This suggests that the average concentration of X was not very different in the two periods. Hence the steady state X relative to reactions (10) and (13) is rapidly achieved and the lifetime of X relative to reaction (11) in this case is very much longer than the 4 h estimated for the previous example. There is evidence for the establishment of the steady state in the data for the first day. Comparison of the data set obtained prior to starting the micropulser with those obtained immediately after suggests that this occurs with a total energy input of about 1 MJ dm$^{-3}$. That V is photolyzed to a somewhat lower molar absorptivity product P (reaction (12)) is suggested by the behavior of the data sets as a function of $T$ during days 2 and 3. This would imply that the depletion in X during the long dark segment from day 4 to day 7 is at least in part masked by the presence of a large concentration of the highly absorbent product V.

While differing in detail, the examples illustrated in Figs. 2 and 3 exhibit the same gross mechanistic behavior. These examples are relatively unusual in our experience. A more common observation for coumarin derivatives under UV-filtered conditions is the rapid attainment of a quasi-steady increase in relative absorbance as a function of $T$ with insignificant changes associated with changes in the rate of energy input or of overnight dark periods. Frequently the only indication of secondary reaction is that the extrapolation to $k_0$ based on the quasi-steady degradation rate is significantly smaller than that obtained just prior to the start of the degradation experiment. The preceding examples suggest that this is a consequence of the rapid establishment of a steady state X and that the quasi-steady degradation is a consequence of the accumulation of the secondary degradation products P and P′.

### *4.2. Results for some rhodamine derivatives*

Data from a $1 \times 10^{-4}$ M solution of rhodamine 116 perchlorate in ethanol (ambient atmosphere) are shown in Fig. 4. The degradation was accomplished using the test laser at a maximum value of $R = 8.9$ J dm$^{-3}$ s$^{-1}$ without UV filtration. The parameters $\delta \approx 9.3$ J and $\alpha \approx 9.5$ mJ were estimated from the intersection of the linear regression lines $\bar{\phi}(I)$ for $T <$ 25 kJ dm$^{-3}$ and 60 kJ dm$^{-3} < T <$ 86 kJ dm$^{-3}$ (25 J excluded). The data were taken over 2 days with an overnight dark period of about 17 h. The slope efficiency $k_0 \approx 1.08 \times 10^{-3}$ in the absence of product was estimated from the intercept at $T = 0$ of the linear regression line $1/k$ *versus* $T$ based on data from the first day. Based on the difference between the values $A_p/\kappa$ computed from the linear regression lines corresponding to the 2 days, about 51% of the product absorbance was lost during the 17 h when there was no irradiation as a consequence of a spontaneous reaction like (11) introduced in Section 4.1. In this case, however, V has a lower molar absorptivity than that of X. As a consequence the absence of significant deviation from the quasi-steady increase in absorbance on both days suggests that the X is the significant product of the initial global photolysis reaction (10). The use of that concentration of X corresponding to a single-pass absorbance of $\kappa$ in the test laser as unit concentration, along with the assumption of negligible bleaching, leads to $r_{10} \approx 1.3 \times 10^{-2}$ dm$^3$ J$^{-1}$. That the values derived from the slopes of the regression lines for the two days ($1.26 \times 10^{-2}$ dm$^3$ J$^{-1}$ and $1.32 \times 10^{-2}$ dm$^3$ J$^{-1}$) are not significantly different is consistent with reactions (10) and (11) being the only reactions of significance relative to the degradation of this dye. The assumption that V has negligible molar absorptivity at the lasing wavelength leads to a maximum value of $\tau_{11}$ of about 24 h.

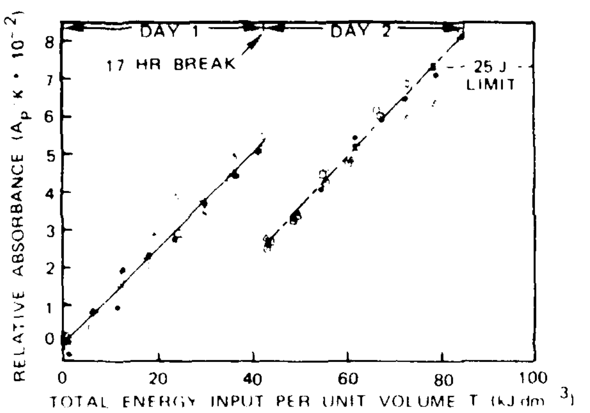

Fig. 4. Relative absorbance as a function of the total energy input for $1 \times 10^{-4}$ M rhodamine 116 perchlorate in ethanol (ambient atmosphere). The points were computed from the average of five closely spaced test laser output determinations at the indicated input energy $I$ ( , 25 J; ●, 30 J; , 35 J; , 40 J). Linear regression lines were computed from the data for each of the 2 days (25 J excluded for $T > 70$ kJ dm$^{-3}$). Degradation was accomplished using the test laser at 40 J between each of the groups of points ($R \approx 8.9$ J dm$^{-3}$ s$^{-1}$).

This, together with the estimated value of $r_{10}$, would imply a change of about 10% in the slope of $A_p/\kappa$ *versus* $T$ over the first day of reaction which would not be appreciable relative to the apparent dispersion of the data.

Data from studies of a number of rhodamine dyes in ethanol (ambient atmosphere) without UV filtration show a consistent pattern of spontaneous reaction of an initial product to a secondary product of significantly different molar absorptivity at the lasing wavelength (Table 2). From eqn. (6) the difference in laser output associated with a change in product absorbance can be written as

$$\phi - \phi' = \frac{k_0(I - \delta)(A_p{}' - A_p)/A_0}{(1 + A_p/A_0)(1 + A_p{}'/A_0)} \tag{17}$$

Since the change in output is proportional to $I - \delta$, the effect of an overnight discontinuity is seen most significantly at the largest value of $I$ used in the test laser. The change is positive if the product V has a lower molar absorptivity than that of the initial product X. The magnitude of the change is dependent on the details of the experiment as well as the kinetics. Since these details differ for the examples listed in Table 2, the magnitude of the percentage change provides a measure only of the significance of the sign of the observed change.

When some of these compounds were tested under UV-filtered conditions there was little or no evidence to suggest any effect of the spontaneous reaction (11). The most significant effect observed was for sulfarhodamine 101 where the effect was positive rather than negative as shown in Table 2 for the unfiltered conditions.

TABLE 2

Effect of overnight dark periods on the laser output from some rhodamine dyes

| *Dye (Eastman designation)* | *Molar concentration* ($\times 10^4$) | *Input energy* (J) | *Percentage change in output* | *Observed midpoint for broad band lasing* (nm) |
|---|---|---|---|---|
| Rh 110 | 1 | 40 | +23 | 572 |
| Rh 116 | 1 | 40 | +35 | 593 |
|  | 2 | 40 | +35 |  |
| Rh 19 | 1 | 35 | +78 | 593 |
|  | 2 | 35 | +55 |  |
| Rh 6G | 1 | 30 | +90 | 597 |
|  | 2 | 40 | +50 |  |
| Rh B | 1 | 35 | +14 | 625 |
|  | 2 | 40 | +11 |  |
| SRh B | 1 | 35 | +56 | 626 |
|  | 2 | 40 | +42 |  |
| Rh 3B | 1 | 40 | +25 | 630 |
|  | 2 | 40 | +20 |  |
| Rh 101 | 1 | 30 | -9 | 652 |
|  | 2 | 35 | 5 |  |
| SRh 101 | 1 | 35 | 1 | 648 |
|  | 2 | 35 | -6 |  |

## 5. Conclusions

Since the absorption of laser dye degradation products competes directly with the population inversion, the amount of absorption required to affect the output of the laser significantly is small. For lasers of the types used in these experiments, it has been estimated that about 1% absorption at the lasing wavelength is sufficient to reduce the laser output by 50% [6]. Thus laser performance is a sensitive measure of the presence of products which absorb at the lasing wavelength. As illustrated by the examples that have been discussed, eqn. (9) provides an approximate relative estimate of the total absorbance of the dye degradation products. When care is taken to exclude input energies near the threshold where the linear approximation to the function *F* is invalid, the demonstrated insensitivity of the apparent absorbance estimates to the flashlamp input energy tends to confirm that the observed effects on the laser output are dominated by product absorbance.

The estimated total product absorbance at the lasing wavelength does not discriminate among the various products present in the dye solution. By varying the experimental conditions, we have shown for a number of examples that there are several products which absorb at the lasing wavelength. The discussion of these examples illustrated that the subsequent reactions of the early products can and do profoundly affect the degradation in performance of a repetitively pumped dye laser.

We have attempted to relate our observations to the mechanism of dye degradation in a gross global framework. This is unquestionably an oversimplification of the chemical complexity of laser dye systems. In the relatively simple case of coumarin 1, five photodegradation products have been identified for a laser environment using an unfiltered flashlamp with oxygen present [3]. Only one of these, the carboxylic acid resulting from successive photo-oxidation of the methyl group, absorbs strongly at the lasing wavelength and is responsible for the degradation in laser performance under these experimental conditions. When coumarin 1 is pumped using a nitrogen laser in the absence of oxygen, the output has been shown to degrade at a rate not much less than that observed when oxygen is present [12]. This suggests other, as yet unknown, reaction paths which are not significant in the presence of oxygen.

The most commonly encountered evidence for the contribution of secondary reaction products is an initial transient associated with the establishment of quasi-steady conditions. In this case the degradation in laser performance is dominated by the final product resulting from a sequence of reaction steps. Where one of those steps is a slow spontaneous reaction, the performance of the laser can be markedly affected by the pulse rate and the number of duty cycles. As an extreme example consider the data for AC3F [11] (Fig. 3). When the number of shots or the total output energy per unit volume before the output drops below some limiting value is taken as a measure of the utility of the dye, the utility would be approximately proportional to the average pulse rate of the laser. In contrast, let us consider the data for rhodamine 116 (Fig. 4). In this case the utility would tend to decrease as the average pulse rate was increased.

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## Appendix A: nomenclature

| | |
|---|---|
| $A_0$ | mean coherent photon loss in the absence of absorbing products expressed as an equivalent single-pass absorbance |
| $A_p$ | single-pass absorbance of the absorbing products |
| $F$ | gross production of coherent photons per unit flashlamp excitation energy per flashlamp pulse |
| $h$ | Planck's constant |
| $I$ | flashlamp excitation energy per pulse |
| $k$ | slope efficiency |
| $r$ | photosensitivity factor for chemical reaction |
| $R$ | time derivative of $T$ |
| $t$ | apparent lasing threshold or time, depending on context |
| $T$ | sum of the flashlamp excitation energies per unit volume of dye solution |
| $\alpha$ | composite parameter treated as an empirical constant |
| $\delta$ | composite parameter treated as an empirical constant |
| $\epsilon$ | molar absorptivity |
| $\kappa$ | factor of proportionality relating the slope efficiency to the reciprocal of the sum of the coherent photon losses |
| $\nu$ | frequency of light |
| $\tau_{11}$ | exponential lifetime of reaction (11) |
| $\phi$ | laser output per flashlamp pulse |

## Appendix C

## THE EFFECT OF OXYGEN ON THE FLUORESCENCE QUANTUM YIELDS OF SOME COUMARIN DYES IN ETHANOL

Chemical Physics Letters, Vol. 99, No. 1
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# THE EFFECT OF OXYGEN ON THE FLUORESCENCE QUANTUM YIELDS OF SOME COUMARIN DYES IN ETHANOL

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The fluorescence quantum yields of the 7-aminocoumarin dyes coumarin 1, 102, 153, LD490, and C8F were measured using argon, air, and oxygen as cover gases. The results show that, in ethanol, oxygen does quench these dyes and that the fluorescence is significantly improved in some coumarin dyes by the removal of oxygen.

## 1. Introduction

The 7-aminocoumarin dyes are recognized as an important class of fluorescent dyes emitting in the blue-green spectral region. There is much information [1–13] on the photochemical and photophysical properties of these dyes. The cited references deal with fluorescence quantum yields and lifetimes, structure effects (butterfly forms, 3 and 4 position substitution), solvent–solute interactions, and laser lifetimes and outputs. However, with few exceptions [1,6,8] the effects of oxygen are not discussed. Schimitschek et al. [1] indicated that oxygen did not affect the laser performance or lifetime of three dyes – including coumarin 1, in ethanol. Drexhage [6] stated that there is little or no quenching of fluorescence by oxygen of coumarin 1. We found a large oxygen effect. Further, some inconsistencies are apparent in the data on fluorescence quantum yields of these dyes. For example, values for the quantum yield of coumarin 1 range from 0.5 [6] to 0.74 [5] and those of coumarin 153 range from 0.26 [11] to 0.4 [6].

We have studied the effects of argon, air, and oxygen as cover gases on the fluorescence quantum yields of a representative selection of five 7-aminocoumarin dyes (fig. 1). These results suggest that the cover gas needs to be explicitly stated and the ambient pressure should be given in order to define the dissolved gas concentration.

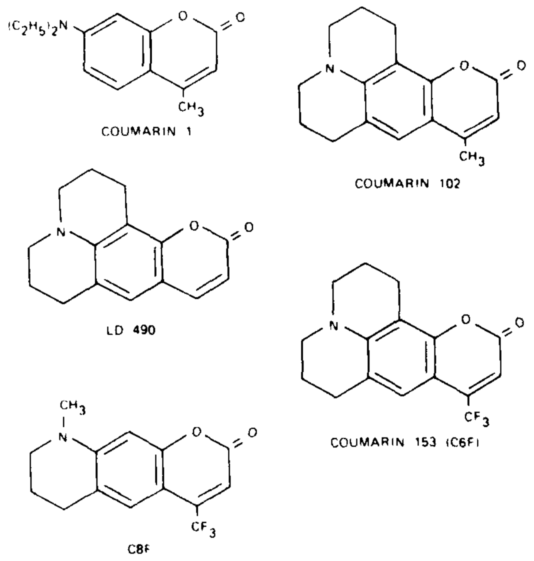

Fig. 1. *Coumarin dyes studied in this report.*

## 2. Experimental

The dyes coumarin 102, LD490, and coumarin 153 were laser grade from Eastman, Exciton, and New England Nuclear, respectively. Coumarin 1 was from Aldrich and was recrystallized from ethanol. C8F was prepared in this laboratory [7]. The ethanol solvent was 200 proof from USI and was degassed and stored under argon. The quantum yields were determined using a wavelength-corrected Perkin–Elmer MPF44B fluorescence spectrophotometer described previously [14] except that rhodamine 6G was not used as a parallel second standard along with the quinine sulfate (in 1 N $H_2SO_4$). The ambient pressure at this laboratory is generally in the range 700–705 Torr.

Measurements of the fluorescence quantum yields under argon were made using the argon-saturated ethanol as solvent and additionally saturating the sample in the cuvette for 60 s intervals with argon flowing at 0.5 $cm^3/s$. The fluorescence was measured after each saturation and the process repeated until a constant area was obtained on the recorder. Solution volume in the cuvettes ranged from 2.85 to 2.95 $cm^3$ at 25°C as determined by weight. The 1 cm quartz cuvettes were weighed before and after each saturation. The loss in weight ($\approx$0.002 g) was assumed to be due to ethanol evaporation. Ethanol was added to the cuvette and the weight kept constant to within 5 parts per 1000 for the dye solution. This amounted to adding one drop of solvent from a small pipette for each minute of saturation. Between two and five saturations were generally required to obtain an apparently constant area for a given cover gas. Each cover gas was passed through ethanol before entering the cuvette in order to minimize evaporation. The argon was stock 99.9% minimum oil free, and the oxygen was aviator grade used without further treatment. The air was purified laboratory compressed air. In some cases, the same solution was used for all three cover gases. However, it was found that using a fresh solution for each cover gas cut the number of saturations necessary to reach a constant area. Solutions that were run with oxygen were resaturated with argon to check return to the argon value.

Results were calculated as described by Demas and Crosby [15].

## 3. Results

Table 1 gives the results of this work. The fluorescence quantum yields are the averages of two or more determinations. Excitation and emission wavelengths are the peak maxima. The expected spectral shifts between H, $CH_3$, and $CF_3$ are seen for substitution in the 4 position for the butterfly coumarins. The relative quantum yields in most cases show a strong effect due to increasing amounts of oxygen. Coumarin 102 shows little change between air and argon and similarly for coumarin 153. All show a significant drop in the presence of pure oxygen. The quinine sulfate standard (in 1 N $H_2SO_4$) was similarly checked. The recorded differences are well within the experimental error and are in accord with the observations that quinine sulfate is not subject to oxygen quenching.

Table 2 gives the results for a few determinations to show the effects of standing and resaturation from one cover gas to another. These samples were stoppered to prevent evaporation of the ethanol; however, the cuvettes were not completely gas tight. The most significant data are for coumarin 1 where the quantum yield under oxygen was determined and then left to stand over a weekend. The quantum yield rose to 0.72 or almost the air result. Either equilibrium with the atmosphere was essentially complete or oxygen reacted with the ethanol and the reduced concentration of oxygen

Table 1
Quantum yields of coumarin dyes for different cover gases

| Dye | [C] (mole/ℓ) | $\lambda_E$ (nm) | $\lambda_F$ (nm) | $\phi_f(O_2)$ | $\phi_f$(air) | $\phi_f$(Ar) |
|---|---|---|---|---|---|---|
| coumarin 1 | $6.4 \times 10^{-7}$ | 373 | 448 | 0.57 | 0.79 | 0.85 |
| coumarin 102 | $6.4 \times 10^{-7}$ | 389 | 466 | 0.58 | 0.99 | 1.04 |
| coumarin 153 | $7.1 \times 10^{-7}$ | 423 | 531 | 0.45 | 0.58 | 0.61 |
| C8F | $7.2 \times 10^{-7}$ | 410 | 515 | 0.63 | 0.76 | 0.90 |
| LD 490 | $6.2 \times 10^{-7}$ | 394 | 474 | 0.63 | 0.82 | 1.00 |
| QSH | $1.3 \times 10^{-6}$ | 350 | 454 | 0.54 | 0.55 std | 0.56 |

Table 2
Standing time and resaturation effects on quantum yields

| Compound | $\phi_f$(Ar) | $\phi_f$(Ar) overnight | $\phi_f$(Ar) resaturation | $\phi_f$(air) | $\phi_f$($O_2$) | $\phi$($O_2$) stand over weekend | $\phi_f$($O_2$) resaturation |
|---|---|---|---|---|---|---|---|
| coumarin 1 | 0.85 | 0.84 | 0.87 | | | | |
| coumarin 1 | | | | 0.79 | 0.57 | 0.72 | 0.56 |
| coumarin 102 | 1.04 | – | 1.03 | | 0.58 | – | 0.59 |
| coumarin 153 | 0.61 | | 0.61 | 0.58 | | | |
| LD 490 | 1.00 | | 0.98 | | 0.59 | | |

let the quantum yield rise. Resaturation with oxygen restored the oxygen cover gas quantum yield.

## 4. Discussion

No previous parametric studies of cover gas effects on 7-aminocoumarin dyes have been reported. Our results are contrary to those of Drexhage [6]. Oxygen and argon can have a significant effect on the fluorescence quantum yields of 7-aminocoumarin dyes in general. However, the effects do vary from dye to dye. With some dyes in ethanol (e.g. coumarins 102 and 153) there is little difference between air and argon. Oxygen always led to quenching in ethanol for the dyes in this study. For the dyes reported here, oxygen replacement by argon either had little effect or increased the quantum yield. However, we have evidence [16] that oxygen does not always decrease the quantum yield of coumarin dyes in other solvents such as ethanol–water.

Table 3 compares many of the values of the fluorescence quantum yields reported using ethanol as the solvent for the dyes in this study. The wide range of values is suggestive of several sources of error and is not likely to be due to cover gas effects alone.

All of these dyes lase well [18]. Although not exactly comparable because the laser output depends upon both the slope efficiency and the threshold of lasing, the slope efficiency of dyes coumarin 102, 153, C8F, and LD490 in ethanol were reduced to ≈70% of the argon value by oxygen cover gas [19]. The same approximate reduction is found here for the effect of oxygen on the fluorescence quantum yields of the coumarin dyes in this work. The laser results were suggestive of quenching by oxygen, though they are certainly not quantitative and do not have a one to one theoretical basis with respect to fluorescence.

The coumarin 102 results here are interesting. Apparently, there is little difference in the quantum yields observed in air and argon. However, a large oxygen effect is noted. With these limited data, a crude Stern

Table 3
Comparison of quantum yields in ethanol with air as a cover gas

| Compound | $\phi_f$, $T = 25.0°C$ this laboratory | $\phi_f$, other laboratories |
|---|---|---|
| coumarin 1 | 0.79, 0.67 [8] | 0.59 [11], 0.64 [9], 0.5 [6] [a], 0.74 [5] |
| coumarin 102 | 0.99, 0.93 [8] | 0.74 [11], 0.6 [6] [a] |
| coumarin 153 | 0.58, 0.55 [8] | 0.26 [11], 0.4 [6] |
| C8F | 0.76, 0.78 [8] | 0.65 [11] |
| LD 490 | 0.82, 0.72 [8] | |

[a] In ref. [17] Drexhage reports these dyes to have fluorescence quantum yields of above 0.7 as opposed to those he gives in ref. [6].

Volmer plot was made in order to check the consistency of the data. The behavior of coumarins 1 and 153 appears quite normal for such a plot. LD490, while having a slope comparable to coumarins 1 and 153, is displaced vertically somewhat and its extrapolation to the origin is not as good. Thus, the effect of oxygen appears proportionately larger for LD490 compared to coumarins 1 and 153. The behaviour of C8F is intermediate and is similar to LD490 in that its extrapolation to zero is not too good. However, inclusion of error bars on the Stern–Volmer plot of these limited data, would lead one to ascribe little significance to these deviations. In the case of coumarin 102 the Stern–Volmer slope is approximately twice as great as the other dyes and does not extrapolate to the origin. We would add that it was not our intent to determine Stern–Volmer constants so we did not obtain data over the wide pressure range needed to make accurate Stern–Volmer plots.

The main thrust of this paper is to show that oxygen does indeed quench some coumarin dyes in ethanol and that significant improvements in the luminosity of some coumarin dyes can be obtained by its removal.

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# Appendix D

# LASING AND FLUORESCENT CHARACTERISTICS OF NINE, NEW FLASHLAMP-PUMPABLE COUMARIN DYES IN ETHANOL AND ETHANOL:WATER

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# LASING AND FLUORESCENT CHARACTERISTICS OF NINE, NEW, FLASHLAMP-PUMPABLE, COUMARIN DYES IN ETHANOL AND ETHANOL:WATER

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Received 14 March 1983

In[illegible] lasing [illegible] outputs and/or lifetimes [illegible] and water and the proper [illegible] coumarin dyes. The new dyes [illegible] 3-position

## 1. Introduction

*Increased laser* outputs [illegible] solvents of low flammability and toxicity are continuing goals for dye laser technology. Changing functional groups within classes of dyes having good lasing characteristics has proven to be a useful way of finding new laser dyes [1,2]. These changes provide not only the possibility of an improved dye but also helps to provide some insight as to whether or not to use that functional group with other classes of dyes.

We report here the lasing characteristics of nine coumarin dyes where different functional groups have been substituted at the 3-position of the parent, rigidized, "butterfly", 7-amino coumarin dye known as C6H and sold by the Exciton Chemical Corporation as dye LD-490 [3]. The structure of the parent dye is shown in fig. 1. These dyes were found to respond favorably [illegible] same ethanol water mixture [illegible]. The mixture not only shifts the useful lasing [illegible] and lowers the flammability of the solvent somewhat but it can yield higher laser outputs and lifetimes for some of the dyes.

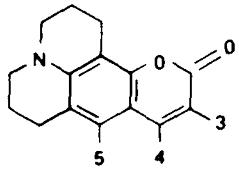

Fig. 1. Parent Dye, C6H

## 2. Experimental

The fluorescence measurements were made by right angle illumination in a 1-cm long cell with a wavelength corrected Perkin-Elmer Model 44B Fluorescence Spectrophotometer. The model 44B was calibrated with a Perkin-Elmer tungsten lamp using wavelength corrections stored in the 44B's computer. Absorption measurements were made in a 10-cm long cell using a Beckman DU-7 spectrophotometer or a Cary 14. Quinine sulfate in 1N $H_2SO_4$ was used as the quantum yield standard. Absorbance at the excitation wavelength was held to less than 0.02 cm$^{-1}$. Flowing dye solutions having an absorbance normally in the range of 4–5 cm$^{-1}$ were used in a Phase-R DL-10Y triaxial flashlamp using a 55% reflectivity output mirror. An exception was Dye (6) whose solubility limited the absorbance cm$^{-1}$ to about 2.2.

Dye degradation was performed with a Xenon Corp. linear N-851C xenon-filled flashlamp operating at 10 J of electrical energy input. Light from both the degradation flashlamp and the dye laser were separated from the dye solution by Pyrex glass in order to minimize exposure to light below 300 nm. Corrections were made for changes in the flashlamp output with time. Lasing wavelengths were measured with a Spex 3/4-meter spectrograph. Mercury emission lines were used for calibration. Details of this dye laser system and the flashlamp corrections are reported elsewhere [4].

Data from the dye laser output, $\phi$, were fit using a computer to the three constants $a$, $b$, and $c$,

$$\phi = a + bI/(1 + cT) , \tag{1}$$

where $I$ is the input energy per flash and the total input energy per unit volume of the dye solution is represented by $T$. It has been shown that $b$ can be equated to the initial slope efficiency, $k_0$, and that $a$ can be equated to the product of $-k_0$ and the initial threshold, $t_0$ [5]. The value of $1/c$ is the lifetime constant of the dye solution under the conditions of the experiment.

Table 1 presents the absorption and fluorescence characteristics of the nine new coumarin dyes along with those of the parent dye (0), C6H (Exciton LD-490). The dyes were prepared by conventional synthetic techniques [6]. Table 2 presents the lasing and lifetime parameters. Dye (2) should not be used with material made of polyethylene as it either is adsorbed on the surface or diffuses into it. Polypropylene or Teflon appears to be satisfactory for use with Dye (2).

Table 1
Fluorescence and absorbance characteristics of the nine new dyes a).

| Dye number | 3-substituent (molecular weight of dye) | Solvent b) | $S_1$ – $S_0$ bands (nm) | | Fluorescence quantum yield | |
|---|---|---|---|---|---|---|
| | | | Absorbance | fluorescence | under air | under argon |
| 0 | Hydrogen | EtOH | 393 | 476 | 0.82 | 0.92 |
| 0 | (241) | EtOH: water | 404 | 488 | 0.96 | 0.98 |
| 1 | 2-benzimidazolyl | EtOH | 465 | 506 | 0.94 | 0.97 |
| 1 | (358) | EtOH: water | 473 | 512 | 1.00 | 1.00 |
| 2 | 2-benzothiazolyl | EtOH | 480 | 519 | 0.90 | 0.95 |
| 2 | (374) | EtOH: water | 490 | 526 | [illegible] | 0.99 |
| 3 | 2-benzoxazolyl | EtOH | 462 | 504 | 0.94 | 0.97 |
| 3 | (358) | EtOH: water | 474 | 512 | 0.89 | 0.91 |
| 4 | Methylsulfonyl | EtOH | 430 | 480 | 0.82 | 0.77 |
| 4 | (319) | EtOH: water | 442 | 488 | 0.87 | 0.87 |
| 5 | Phenyl | EtOH | 415 | 492 | 0.83 | 0.94 |
| 5 | (31[illegible]) | EtOH: water | 424 | 502 | 0.95 | 0.95 |
| 6 | Phenylsulfonyl | EtOH | 440 | 484 | 0.89 | 0.94 |
| 6 | (381) | EtOH: water | 450 | 492 | 1.00 | 1.00 |
| 7 | 2-pyridyl | EtOH | 435 | 494 | 0.74 | 0.86 |
| 7 | (318) | EtOH: water | 442 | 502 | 0.88 | 0.85 |
| 8 | 3-pyridyl | EtOH | 425 | 496 | 0.85 | 0.94 |
| 8 | (318) | EtOH: water | 433 | 506 | 0.98 | 0.98 |
| 9 | 4-pyridyl | EtOH | 437 | 500 | 0.80 | 0.94 |
| 9 | (318) | EtOH: water | 445 | 508 | 0.88 | 0.87 |

a) Dyes (1) and (2) were previously prepared for energy-transfer [7] but had not been tested for lasing.
b) EtOH = ethanol. EtOH: water = one part EtOH added to one part water by volume.

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Table 2
Lasing characteristics of the nine new dyes.

| Dye no. | Cover gas | $k_0 \times 10^3$ | $E_0$ (Joule) | $1/c$ (MJ dm$^{-3}$) | Lasing wavelength (nm) | |
|---|---|---|---|---|---|---|
| | | | | | Range | Midpoint |
| Ethanol as solvent | | | | | | |
| 0 | air | 1.8 | 22.7 | 4.3 | 477 489 | 483 |
| 0 | argon | 2.1 | 22.0 | 19.0 | 478 489 | 483 |
| 1 | air | 1.3 | 20.7 | 25.0 | 526 541 | 534 |
| 1 | argon | 1.4 | 17.6 | 19.0 | 531 544 | 537 |
| 2 | air | 1.0 | 19.5 | 48.0 | 541 554 | 547 |
| 2 | argon | 1.1 | 12.6 | 9.0 | 540 555 | 547 |
| 3 | air | 1.3 | 19.1 | 22.0 | 525 541 | 533 |
| 3 | argon | 1.5 | 12.9 | 6.9 | 525 543 | 534 |
| 4 | air | 1.7 | 21.6 | 7.5 | 492 508 | 500 |
| 4 | argon | 1.6 | 21.8 | 36.0 | 492 507 | 499 |
| 5 | air | 1.3 | 24.2 | 5.0 | 498 511 | 504 |
| 5 | argon | 1.4 | 19.6 | 20.0 | 498 512 | 505 |
| 6 | air | 1.5 | 20.2 | 5.3 | 493 508 | 501 |
| 6 | argon | 1.6 | 16.1 | 4.8 | 494 510 | 502 |
| 7 | air | 1.1 | 19.6 | 6.1 | 505 518 | 512 |
| 7 | argon | 1.2 | 18.5 | 6.4 | 507 517 | 512 |
| 8 | air | 1.7 | 18.3 | 6.7 | 504 518 | 511 |
| 8 | argon | 1.9 | 16.6 | 17.0 | 504 519 | 512 |
| 9 | air | 1.8 | 16.2 | 6.8 | 511 522 | 516 |
| 9 | argon | 2.0 | 17.2 | 9.2 | 512 521 | 517 |
| Ethanol water as solvent | | | | | | |
| 0 | air | 2.4 | 21.7 | 2.4 | 485 508 | 497 |
| 0 | argon | 2.2 | 21.7 | 8.5 | 484 508 | 496 |
| 1 | air | 1.5 | 19.4 | 35.0 | 542 554 | 548 |
| 1 | argon | 1.3 | 17.4 | 170.0 | 530 548 | 539 |
| 2 | air | 1.3 | 16.7 | 50.0 | 547 564 | 555 |
| 2 | argon | 1.2 | 15.1 | 35.0 | 543 562 | 552 |
| 3 | air | 2.0 | 18.6 | 170.0 | 537 553 | 545 |
| 3 | argon | 2.0 | 17.6 | 110.0 | 537 553 | 545 |
| 4 | air | 1.8 | 21.3 | 84.0 | 505 524 | 514 |
| 4 | argon | 1.6 | 20.7 | 32.0 | 504 523 | 513 |
| 5 | air | 2.0 | 19.7 | 3.8 | 505 520 | 513 |
| 5 | argon | 1.7 | 18.6 | 15.0 | 505 523 | 514 |
| 6 | air | 2.0 | 21.1 | 49.0 | 505 524 | 514 |
| 6 | argon | 1.9 | 20.6 | 71.0 | 505 524 | 514 |
| 7 | air | 1.4 | 19.9 | 7.2 | 520 536 | 528 |
| 7 | argon | 1.3 | 18.9 | 5.0 | 518 525 | 522 |
| 8 | air | 2.2 | 18.8 | 4.9 | 513 527 | 520 |
| 8 | argon | 2.7 | 16.6 | 11.0 | 513 528 | 520 |
| 9 | air | 1.3 | 22.7 | 7.1 | 532 549 | 541 |
| 9 | argon | 2.5 | 16.4 | 8.1 | 520 533 | 526 |

## 3. Discussion

There are three experimental parameters that have been varied in this study: (a) the substituent at the 3-position; (b) the presence or absence of oxygen; and (c) the use of 50:50 by volume of water in addition to measurements in ethanol. Changing the functional group from hydrogen to those of Dyes (1–9) causes a red shift in the wavelengths of fluorescence and lasing. Table 3 shows the pattern of changes that occur through the effects of the solvent and cover gas changes upon lasing. It is seen, for example, that for most of the dyes, at least a 20% improvement in output is found in changing from ethanol to ethanol:water. Some of this improvement can be attributed to the improved thermal properties of water as a lasing media [8]. Except for the pyridyl substituted Dyes (7), (8), and (9), an improvement is seen for the laser output when ethanol is the solvent and air is replaced by argon. Both the ethanol:water and the argon changes appear to affect lifetime about 50% of the time. Some of the lifetime changes are quite significant however.

Although there is a somewhat consistent picture of improvements through changes in the experimental parameters, the greatest improvements are seen in the changes of the 3-substituent. Up to a tenfold improvement in lifetime over the parent dye, LD-490, is seen for Dye (2) in ethanol:water for example. Dyes (7) and (8) have very high outputs, even though their lifetimes are low. Their outputs are comparable to those that we have measured for rhodamine 6G [4,9].

Table 3
Dyes showing an improvement [a] with an indicated parameter change.

| Static parameter | Dye number improvement in | |
|---|---|---|
| | Lifetime constant, Lc | Laser output |
| Solvent | Change from air to argon | |
| ethanol | 0,4,5,8 | 0,1,2,3,5,6 |
| ethanol:water | 0,1,5,8 | 8,9 |
| | Change from argon to air | |
| ethanol | 2,3 | |
| ethanol:water | 4 | |
| Cover gas | Change from ethanol to ethanol:water | |
| air | 3,4,6 | 0,1,2,3,5,6,7,8 |
| argon | 1,2,3,6 | 3,5,7,8,9 |
| | Change from ethanol:water to ethanol | |
| air | 0 | 9 |
| argon | 0 | |

[a] 50% increase or more in dye solution lifetime constant, 20% increase or more in test dye laser output for 50 J input.

For the most part, the changes seen in the lasing characteristics of table 2 are reflected by the fluorescence seen in table 1. Jones et al. reported that the 4-substituted, rigidized, 7-amino coumarin dyes maintain their level of fluorescence emission in more polar solvents in contrast to the decrease observed for the non-rigidized coumarins [10]. We find that most of the rigidized, "butterfly", unsubstituted as well as most of the nine new 3-substituted, coumarins actually have an increase in their fluorescence quantum yields in going from ethanol to the more polar ethanol:water solvent. The laser outputs also show a corresponding increase in many cases.

Marling et al. found that the removal of oxygen made a dramatic reduction in the lasing output of all of the nine coumarin dyes in ethanol that they tested [11]. Similarly, a wide variety of coumarin and quinolone dyes tested in this laboratory were reported to have reduced outputs when oxygen was removed [2]. Since the opposite effect, an increase in laser output upon removal of oxygen, is found in the present study, it is suggested that intersystem crossing from electronically excited, upper singlet states to the triplet manifold plays a significant role in coumarin laser dyes. Oxygen is presumably needed to quench triplet-state coumarin molecules whose TT absorption would otherwise restrict lasing action [11]. In this study, in contrast to those cited above, a Pyrex light filter prevents the transitions to the upper-excited singlet states.

An unusual result shown in table 2 is the difference observed in the wavelengths of lasing caused by the cover gas for Dyes (1), (7), and (9) in ethanol:water. Dye (1) under argon shows a blue shift, Dyes (7), and (9) under air show a red shift. Although there are many factors that make measurements of the range of lasing wavelengths inexact, such as the energy per laser pulse striking the photographic film, these shifts appear to be quite real. Transient photophysical effects, such as TT absorption, that are either accelerated or quenched by oxygen, are suggested causes of these anomalies. For Dye (9) this transient also appears to markedly reduce the laser output.

Although this discussion has placed emphasis upon the improvements that can occur by changing a substituent, solvent or cover gas, it should be noted that such changes are of little value if the corresponding lasing wavelength does not match the need of a specific application. For this reason, a series of dyes are needed and the corresponding experimental factors evaluated, in order to obtain the optimum laser dye for a given application. The results shown here indicate that operational conditions as well as substituent changes are of importance in efforts to evaluate and hence obtain improved laser dyes.

## Acknowledgement

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# Appendix E

# LASER DYE STABILITY. PART 9. EFFECTS OF A PYREX UV FILTER AND COVER GASES

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# Laser Dye Stability

## Part 9. Effects of a Pyrex UV Filter and Cover Gases

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**Abstract.** A figure-of-merit (FOM) consisting of the initial laser slope efficiency times the dye lifetime constant is used to compare the effect of a Pyrex light filter and the cover gas upon the output characteristics of six laser dye solutions. The FOM is found to improve using the Pyrex filter from 2-fold (coumarin 102 under air) up to 3800-fold (rhodamine 6G under argon). In most cases, the use of argon in place of air for a coumarin dye not only improves the laser output, but also increases the lifetime constant. However, two of the coumarin dyes had an increase in lifetime under air as compared to under argon. This difference is explained in terms of the relative energy levels of the singlet and triplet states of these dyes.

In order to measure long-lived dye solutions, a separate output-monitored linear flashlamp was used to degrade the solutions. The dye lifetime constants were corrected for changes in the output of this linear flashlamp. The relative output of this dye degradation flashlamp was found to depend upon the wavelength of the measurement and the position of the sensor along the length of the lamp. The variation in the output of several flashlamps is shown for lamps operating up to a total of 30 million flashes. The lifetime constants of the dye LD-490 measured by using the coaxial laser flashlamp was found to be comparable with, but lower than, the constants obtained from using the linear dye-degradation flashlamp.

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Studies on the photo-bleaching of dyes are of limited usefulness in predicting flashlamp-pumped dye laser lifetime characteristics. Although there are exceptions such as the tricarbocyanine dyes [1], bleaching is usually not significant prior to the initiation of major changes in the laser output. On the other hand, changes in the absorption of the dye solution at the lasing wavelength do occur for coumarin [2–4] and rhodamine dyes [5] concurrently with output degradation, i.e., increased absorption at the lasing wavelength plays a major role in the degradation of the output of the dye laser [6].

Since radiation at wavelengths below 300 nm is of sufficient energy to break many of the bonds in laser dyes [7], exclusion of these wavelengths should improve the stability of the dye laser output. Although there have been examples where some degree of uv filtration has been used or the effects suggested as the cause of improved lifetime [4, 8–10], there have been only a few studies [11–13] that showed the actual changes in the operational characteristics that resulted from the introduction of uv filtration to a dye laser solution. The data and scope in [11–13] were limited, which suggested the need of a more thorough examination of the changes that could be expected through the introduction of a uv filter. Because of its stability and availability, laboratory-grade Pyrex was chosen as the uv filter.

When the goal of improving dye laser lifetime is considered, the type of cover gas must not be neglected. The removal of oxygen has been indicated both as having no effect on dye laser lifetime of coumarin dyes (with some uv filtration) [14], as well as reducing the lifetime (with no uv filtration) [15]. Oxygen removal has been reported to extend the lifetime of tricarbocyanine dyes (with some uv filtration) [1]. Since oxygen has both positive and negative effects upon the photolysis of dyes [16] and because of the above possible conflicts [14, 15], its effects were included along with those of the Pyrex uv filter in this study.

It shall be shown that removal of oxygen not only extends the lifetime but can also increase the output of some laser dye solutions. In general, the laser output (and the fluorescence quantum yield [17]) of coumarin dyes in ethanol was found to be quenched by oxygen. The lifetime improvement through the removal of oxygen is not general, however, as some of the dyes showed higher lifetime constants under air.

Two different lifetime constants have been used in this series, $\tau$, and $1/c$. For reasons cited in [18], $1/c$ will be used as the laser determined lifetime constant.

## 1. Calculations

### *1.1. Laser Degradation and Lifetime Equations*

The output, $\phi$, of a flashlamp pumped dye laser can be described by

$$\phi = k(I - t), \tag{1}$$

where $k$ is called the slope efficiency, $I$ is the electrical input energy stored in a capacitor prior to discharge through the flashlamp, and $t$ is the threshold of lasing. A term that will be used in the measurement of the degradation of the laser output is

$$T = \sum^{n} I/V, \tag{2}$$

where $V$ is the total volume of the dye solution being circulated through the laser cavity and $n$ is the number of flashlamp pulses. The degradation of the laser output can be expressed by

$$\phi = a + bI/(1 + cT) \tag{3}$$

from [18] based upon the results of [6]. Combining with equivalent terms of (1),

$$\phi = -k_0 t_0 + k_0 I/(1 + cT), \tag{4}$$

where the sub-zeros indicate initial values. When the value $k$ of (1) degrades to $k_0/2$, the value of $T$ will be taken as the degradation constant, $1/c$, for the specific experiment.

The actual lifetime of a dye solution depends upon the fraction of degradation, $D$, that is allowed from the initial output,

$$\phi = (1 - D)\phi_0. \tag{5}$$

In [18] it was shown that the value of $T$ for a specific degree of degradation, $D$, in a given laser can be expressed by

$$T = \frac{D}{c} \frac{(I - t_0)}{[I(1 - D) + Dt_0]}. \tag{6}$$

### *1.2. Determination of 1/c from τ Values*

In order to make use of earlier lifetime constants calculated as $\tau$, it is necessary to be able to calculate $1/c$ values. A quick approximation can be made for small values of $\tau$ and $1/c$

$$1/c \cong 2\tau. \tag{7}$$

A more exact expression can be made by noting that the earlier 4-parameter equation loosely overlaps (6) up to $I = 2t_0$ [18]. Thus, taking $D = 0.5$, $I = 2t_0$ and using the constants $\tau$ and $\mu_4$ from the 4-parameter expression

$$1/c = 3[x + 2\tau - (x^2 + (2\tau)^2)^{1/2}]/2, \tag{7}$$

where

$$x = (I - t_0)/\mu_4 = t_0/\mu_4. \tag{8}$$

### *1.3. Figure-of-Merit (FOM)*

A very useful term that allows comparison of different dyes is the lifetime constant multiplied by the initial slope efficiency

$$\mathrm{FOM} = k_0/c. \tag{9}$$

This FOM can be related to the total output energy that the laser can produce [19]. The FOM is a particularly convenient term to compare the relative merits of dyes having different slope efficiencies and lifetime constants.

## 2. Experimental

### *2.1. Equipment and Materials*

A Phase-R DL-10Y triaxial flashtube was used in place of the coaxial DL-5 that was used for earlier work in this series. Emission from 400–700 nm of this flashlamp in our system had a 10–90% risetime of about 200 ns and a FWHM of 750 ns. Pyrex glass was used in place of the usual quartz tube used to separate the dye solution from the coolant. The internal diameter of the dye solution tube was 6 mm as opposed to the 5 mm of the DL-5. Separate stainless steel heat exchangers were used to temper the dye solution and the water used as the coolant. The temperatures of these liquids were controlled to 0.01 °C measured at their exit from the flashtube. A Laser Precision Rj-7000 series microprocessor based pyroelectric energy meter was used to measure the output energy of the laser.

A Xenon Corporation (Wilmington, Massachusetts) N-851C water-cooled linear flashlamp was used at rates up to 25 Hz to degrade the dye solution. This flashtube has a 7 mm inner diameter bore and 101 mm between its electrodes. The 15 mm outer diameter water-cooled version of this flashlamp was placed into the center of a 0.125 dm$^3$ Pyrex jacket through which the dye solution flowed. Water was held between the outside wall of the flashlamp and the inside wall of the jacket in order to reduce reflection losses. The annular thickness of the jacket was 8 mm. Aluminum foil surrounded the jacket except in those places that were monitored by light pipes. Four 3.2 mm diameter fiber-optic glass light pipes were fixed in position 25 mm apart along the length of the Pyrex jacket to monitor the output of the degradation flashlamp. Position 1 was close to the anode of the flashlamp. The positions of the light pipes were symmetrical with respect to the center of the flashlamp. Each light pipe led to a different narrow bandpass multi-dielectric light filter and on to a second light pipe. The second light pipe associated with each filter could be reproducibly fixed *in front* of a Laser Precision RjP-765 Silicon type detector. The degradation lamp was driven by the Xenon Corporation Model 457 Micropulser using a 0.2 μF capacitor. The system yields a 1.4 μs FWHM pulse for a 10-J input for light falling in the wavelength range of 400–700 nm. The risetime 10–90% was 0.9 μs.

The degradation lamp is located so that it receives dye solution from the laser head before it enters the dye reservoir. Part of the dye solution being pumped to the 90 mm millipore fluid filter is diverted back to the reservoir. This bypass continuously removes any bubbles from the filter and produces a vigorous mixing action in the dye reservoir. Other features were primarily the same as reported earlier except for the use of a separate degradation lamp, the triaxial configuration, and our present use of insulated Teflon tubing in place of polyethylene.

Reagent grade ethanol from United States Industrial or Spectroquality methanol from Burdick and Jackson were the solvents used in this report. The laser dyes AC3F [20] and C8F [21] were supplied by Dr. R.A. Henry of this laboratory. Argon was purified by a Matheson 8301 Hydrox purifier gettering furnace just prior to use. The cover gas was pre-saturated with the solvent prior to going to a fritted glass bubbler under the surface of the solution in the dye solution reservoir. Minimum flow rates of a 0.1 dm$^3$ min were used continuously while the dye solution was being tested for lasing characteristics.

## 2.2. *Procedures*

A problem associated with testing different dyes arises from contamination from a previously tested dye. This problem is particularly acute if the contaminant absorbs at the lasing wavelength. The problem is further compounded for week-long tests where slow diffusion of dye from tubing connections could very well provide a significant amount of contamination.

Our procedure to solve the above problems is to test dyes in a sequence where the absorbance and lasing wavelengths are increasing. Thus, previously tested dyes would absorb at shorter wavelengths than that of lasing. Our laser system is designed so that most of the equipment is located on a vertical axis with a low drain point. After each change of dye, hot ethanol is continuously refluxed through the system for several hours. Where possible, the system is filled with ethanol so as to encourage diffusion from the tubing connectors. Examination of this ethanol for fluorescence by means of ultraviolet light after having stood over a weekend gives a convenient measure of the effectiveness of the cleaning procedure (and may indicate the need for an additional reflux).

The test apparatus is operated with a minimum of 0.55 dm$^3$ of dye solution. We find that a preliminary hour of flowing of argon or oxygen does not appear to be sufficient. We, consequently, flow argon or oxygen overnight through a slowly circulating dye solution prior to laser testing.

The dye solution leaving the laser head is maintained at 27.3 °C, the average temperature of the laser container [11]. The temperature difference between the coolant and the dye at a pre-flash is held to 0.10 ± 0.01 °C with the coolant being warmer than the dye. In contrast to the notion that the dye and coolant must be ±0.05 °C of each other [22], we find improved output with a warmer coolant [23] and that reproducibility of laser output is sensitive to 0.01 °C changes in the relative temperature of coolant and dye. Some sensitivity is also evident for the absolute temperature of the solutions even when the temperature differential is maintained. Since the temperatures of these fluids are monitored as they just exit the laser cavity, an increase in temperature of the coolant is observed when the laser is operating. At flash inputs of the order of 30–40 J, the temperature of the coolant is usually only 0.01 °C warmer than its initial value when there is a time of 10 s between each pulse as is used in our usual operating procedure. Using the microprocessor averaging capability of the Laser Precision 7000 series energy meter, an average of 10 laser pulses is obtained for each output measurement recorded.

The output of the degradation lamp must be calibrated with dye-free solvent since light from the degradation flashlamp passes through the dye laser fluid before reaching the four light pipes. Calibration is made regularly for each position and a few times also for each of the four different filters at each position. The voltage of the Model 457 Micropulser is set to produce 10 J as measured on its analog readout. Using the lamp output at slow pulse rates measured by the 706 nm filter as a reference, the voltage of the Micropulser must be increased in order to have the same level of emission from the flashlamp when its pulse rate is increased (this increase is necessary because of the limited capabilities of the power supply). It is, consequently, necessary to increase the control potentiometer of the Micropulser from 10,000 V at low pulse rates up to around 11,000 V at 25 Hz. At these fast rates the microprocessor is used to average 100 flashes for an individual lamp output reading. The ratio of the output of the degradation lamp at a given position divided by its value for a new lamp is determined as the lamp optical factor at that position. An average of all but the 706 mm filter is used as the optical factor of the lamp. The optical factor is multiplied by the measured lifetime term in order to obtain an optical-factor-corrected lifetime constant that should be obtainable through the use of a new nondegrading flashlamp.

Table 1 Absolute output wavelength readings for N-851C lamp No 3 when new

| | Midpoint of filter bandpass (nm) | | | |
|---|---|---|---|---|
| Position | 406 | 436 | 546 | 706 |
| | 0.430 × 10 [illegible] | 0.733 × 10 [illegible] | 0.361 × 10 [illegible] | 0.640 × 10 [illegible][a] |
| 2 | 0.473 | 0.802 | 0.394[a] | 0.664 |
| 3 | 0.485 | 0.817[a] | 0.403 | 0.682 |
| 4 | 0.326[a] | 0.572 | 0.273 | 0.367 |

[a] Normal location for light filter measurements

Table 2 Relative output for N-851C lamp No 3 at 46,000 kJ total input

| | Wavelength of midpoint of filter bandpass (nm) | | | |
|---|---|---|---|---|
| Position | 406 | 436 | 546 | 706 |
| 1 | 0.709 | 0.718 | 0.720 | 0.857[a] |
| 2 | 0.651 | 0.667 | 0.718[a] | 0.866 |
| 3 | 0.627 | 0.667[a] | 0.687 | 0.853 |
| 4 | 0.587[a] | 0.594 | 0.619 | 0.774 |
| Average | 0.644 ± 0.051 | 0.662 ± 0.051 | 0.686 ± 0.047 | 0.837 ± 0.043 |

[a] Normal location for light filter measurements

## 2.3. *Optical Factor Determination*

Table 1 illustrates the initial output readings of the third linear flashlamp that was used in this study. Outputs using four different light filters are examined at four different positions along the axis of the lamp. Since the silicon detector is wavelength sensitive and because of the different bandpaths of the filters, direct comparisons of values can be made only for light transmitted through an individual filter. Table 1 illustrates that positions 1–3 have almost equivalent illumination but that position 4, close to the cathode of the lamp, has a measurably reduced output independent of wavelength. Position 4 thus appears to have a lower temperature xenon plasma than the remainder of the arc between the electrodes. Table 2 shows the relative values of outputs compared to the new values shown in Table 1 after the lamp had been used. The effect of the cooler plasma at position 4 is now reflected in a more rapid degradation in lamp output in this position. Position 1, in contrast, shows a much higher output for those filters that are sensitive to the absorption of light by the deposit formed on the inner walls of the flashtube. Table 2 shows that at a given position, light is absorbed at 406 nm slightly more than at 436 or 546 nm, and that these three wavelengths absorb significantly more than at 706 nm. Since we are only interested in light that is used to pump the dye that falls at wavelengths higher than the 300 nm of our Pyrex filter but less than 560 nm, the light transmission of the 706 filter is of no use for our optical factor for the dyes of this study (the 706 nm light is used to establish a constant output of the flashlamp as the pulse rate is increased since none of the dyes tested in this report have electronic transitions at 706 nm). The average of the remaining relative outputs of the other filter measurements when they are in their normal locations is 0.66 from the values of Table 2. Since this is quite close to the 4-position average of filter 406 and identical to that of filter 436, the average making use of the 546 filter gives a good measure of the light emission at all four positions where the $S_1 \leftarrow S_0$ bands of the dye fall below 550 nm. The value 0.66 falls fairly close to the output of the 436 nm filter when mounted close to the center of the lamp. Our first lamp calibration used just this single filter system.

At 179 million joules input, the 4-position average of the relative outputs of flashlamp No. 3 was 0.594, 0.606, 0.632, and 0.807 as measured by the 406, 436, 546, and 706 nm filters, respectively. The average measured using the three 406–546 nm filters when tested in their normal positions was 0.599. We see again that the wavelength averaged in their "normal" positions is equivalent to the position average of the 406 or 436 nm filters even though there has been 133 million joules additional input to the flashlamp compared to when the data of Table 2 were obtained.

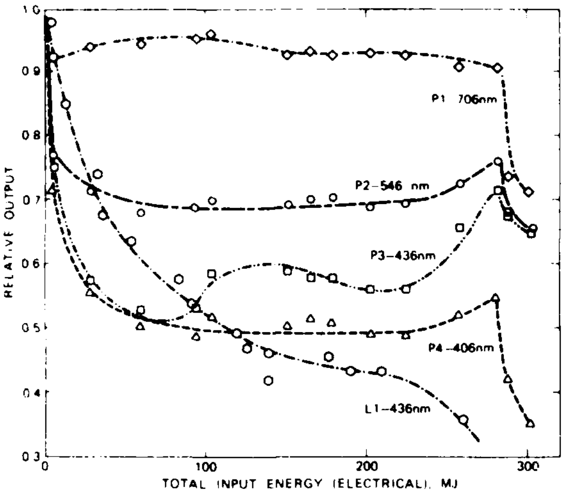

Fig. 1. Variation of degradation lamp No. 2 output as a function of wavelength and total input energy. Curves P4-406 nm, P3-436 nm, P2-546 nm, and P1-706 nm are values relative to measurements on the new lamp measured at positions 1-4 at the indicated wavelengths, respectively. Curve L1-436 nm results from similar measurements *obtained using flashlamp No. 1 with the light pipe* 436 nm filter sensor system placed near the center of the lamp.

Table 3. Lifetime constants for LD-490 with and without the use of a separate degradation lamp

| Test no. | Cover gas | Optical factor | Corrected lifetime constant [MJdm$^{-3}$] |
|---|---|---|---|
| Methanol as solvent | | | |
| 5722 | Air | None$^{a}$ | 0.89 |
| 5726 | Air | 1.0$^{b}$ | 0.70 |
| 5743 | Air | 1.0$^{b}$ | 1.10 |
| 6001 | Air | 1.0$^{b}$ | 1.90 |
| 6316 | Air | 0.55 | 1.30 |
| 6335 | Air | 0.45 | 2.10 |
| 6342 | Air | 0.60 | 2.90 |
| 6544 | Air | 0.60 | 1.30 |
| | | Average | 1.50 ± 0.5 |
| 6551 | Oxygen | None$^{a}$ | 1.30 |
| 6318 | Oxygen | 0.50 | 0.89 |
| Ethanol as solvent | | | |
| 6339 | Oxygen | None$^{a}$ | 0.88 |
| 6341 | Oxygen | None$^{a}$ | 0.73 |
| | | Average | 0.81 ± 0.11 |
| 6320 | Oxygen | 0.50 | 1.04 |
| 6337 | Oxygen | 0.46 | 1.25 |
| 6601 | Oxygen | 0.63 | 1.65 |
| | | Average | 1.30 ± 0.3 |

[a] Using only DL-10Y lamp for degradation.
[b] Using nonmonitored Xenon Corporation N-725C flashlamp for degradation.

## 2.4. *Change in Optical Factor*

The relative output measured by the 436 nm filter for lamp No. 1 along with relative values of all four wavelengths for lamp No. 2 are shown in Fig. 1. The average relative output of the three lower wavelength filters was close to 0.60 for a major portion of its useful lifetime. When lamp No. 2 made a rise in output followed by a rapid drop, we felt it was time to remove it from service. Similarly, when the output of lamp No. 1 began to drop rapidly, we removed it from service. Lamp No. 1 showed a *uniform brown colored* deposit while lamp No. 2 showed a distinctly heavier brown coloration near the cathode end of the lamp.

## 2.5. *Comparison of Degradation Constants of the* DL-10Y *and the* N-851C

Since the N-851C has a sufficiently short pulse to be used as a dye laser pump source, it is not necessary that its dye degradation characteristics be identical to those of the DL-10Y. However, since the total input energies of the two lamps are added, it is desirable that the degradation be similar for short-lived dyes. For long-lived dyes, the majority of the input energy is provided by the N-851C so that the energy input of the DL-10Y is negligible. Since one of the objectives in the use of a separate degradation flashlamp is not to degrade the output-testing system, a comparison between the two flashlamp is limited consequently to short-lived dyes.

Table 3 compares lifetime constants for LD-490 under a variety of conditions. Except for methanol under oxygen, the average lifetime constants are somewhat higher when the degradation lamp is used. One of the problems that is encountered in obtaining reproducible results, besides the varying optical factor, is that the degradation equations do not fit the initial portion of any coumarin dye. This problem can be seen in Fig. 2 where a rapid drop is seen at the very start of the run. This rapid drop can be explained in terms of the reaction kinetics where one of the initial photodegradation products has a small absorbance at the lasing wavelength [19]. A better fit to the degradation equations is consequently obtained where this initial drop is excluded from the calculations.

## 2.6. *Effect of Cover Gas Upon Laser Constants*

Table 4 presents representative data showing the effects of oxygen, air and argon upon the lasing constants of (4) for a number of dyes. The slowly degrading output of a dye laser measured with different input

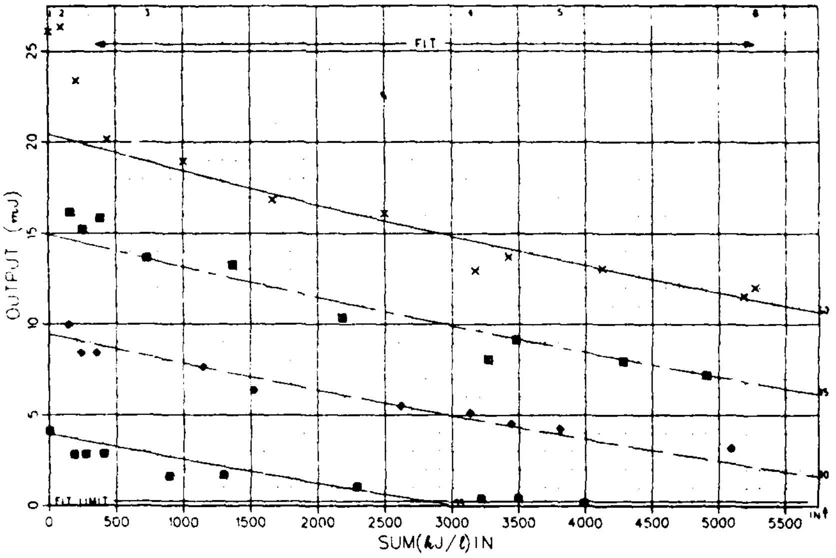

Fig. 2. Computer generated laser degradation curves showing rapid initial drop in output of experimental data. Individual laser output curves are for inputs of × 50 J, ■ 45 J, ◆ 40 J and ● 35 J. Dye is C8F in ethanol under oxygen. Initial output values were made only for 35 and 50 J input. Numbers at top of chart indicate changes in rate of photolysis. Each experimental point is the average of 10 determinations

Table 4. Dye laser characterization constants for different cover gases for a series of 2.0 × 10⁻³ M dyes in ethanol

| Trivial name of dye | Dye no.ᵃ | Cover gas | $k_r \times 10^5$ | $t_0$ [J] | Lamp optical factor | Corrected FC [MJdm⁻³] | FOM [kJdm⁻³] |
|---|---|---|---|---|---|---|---|
| Coum 102 | 17 | Oxygen | 1.10 | 29.8 | 0.70 | 0.24 | 0.26 |
| | | Air | 1.53 | 23.9 | 0.65 | 0.66 | 1.0 |
| | | Argon | 1.58 | 22.3 | 0.66 | 5.16 | 8.1 |
| LD 490 | 18 | Oxygen | 1.58 | 29.1 | 0.63 | 1.66 | 2.6 |
| | | Air | 1.79 | 22.7 | 0.63 | 4.28 | 7.6 |
| | | Argon | 2.07 | 22.0 | 0.63 | 19.4 | 40.0 |
| AC 3F | 22 | Oxygen | 1.43 | 27.8 | 0.47 | 18.5 | 26.0 |
| | | Air | 1.45 | 28.0 | 0.42 | 40.7 | 59.0 |
| | | Argon | 1.40 | 27.3 | 0.49 | 229.0 | 320.0 |
| C8F | 30 | Oxygen | 1.10 | 31.4 | 0.62 | 16.4 | 18.0 |
| | | Air | 1.19 | 27.3 | 0.62 | 84.5 | 100.0 |
| | | Argon | 0.87 | 22.6 | 0.62 | 34.3 | 54.0 |
| Coum 153 | 33 | Oxygen | 1.00 | 36.1 | 0.63 | 8.5 | 8.5 |
| | | Air | 1.09 | 30.4 | 0.63 | 26.2 | 29.0 |
| | | Argon | 1.40 | 24.8 | 0.63 | 10.6 | 15.0 |
| Rhod 6G Tetrafluoro borateᵇ | | Oxygen | 3.14 | 16.0 | 0.54 | 43.2 | 140.0 |
| | | Air | 3.03 | 16.1 | 0.64 | 168.0 | 510.0 |
| | | Argon | 3.35 | 15.9 | 0.58 | 345.0 | 1200.0 |

ᵃ Found in [24]
ᵇ 1.0 × 10⁻³ M

energies has limited precision in the determination of the constants of (4). This is particularly true since the determination of both $k_r$ and $t_0$ are interrelated. The overall picture of the data in Table 4, however, shows a distinct trend towards oxygen quenching of the laser output of the coumarin dyes. This observation is reinforced since the more accurate measurement of the fluorescence quantum yields of coumarin dyes show a distinct quenching by oxygen [17].

## 3. Discussion

### 3.1. *Degradation Lamp Characteristics*

The variation in the output of degradation flashlamp N-851-WC with wavelength, position on the lamp, and total input energy shows the necessity of the use of an optical correction factor in the measurement of dye lifetime. Comparison of the 436 nm filter outputs in Fig. 1 as well as the visual observation of the lamps after usage indicates that each lamp changes somewhat differently for the same value of the total input energy. Since the energy absorbed by the dye occurs over a range of wavelengths, a single optical factor is only an approximation. The error introduced by this approximation is small, however, compared to the $10^5$ range of lifetime constants that can be measured with our system.

The results of Tables 1 and 2 along with Fig. 1 certainly raise questions concerning the actual change in light output that occurs in a flashlamp where an optical filter is not employed. Statements made concerning the relative changes in the output of a flashlamp should both indicate the wavelengths and examine the past history of the lamp. Both lamps, Nos. 1 and 2, show very stable outputs after they have been used a short period of time. Tests performed on a lamp that had been previously "burned-in" by a small amount of preliminary operation would consequently present a markedly smaller degradation rate than would an unused lamp. Similarly, a detector that was more sensitive to the near-infrared could show a negligible change in lamp output compared to the real changes occurring at the wavelengths where the dye is being pumped.

### 3.2. *Effect of Pyrex Filter*

The ratios of the FOM's of the dyes under air to values calculated from the data from [11] and [24], $R_1$(uv), are shown in Table 5. Even though the operational comparison between coaxial laser outputs with triaxial is dependent upon the relative temperatures of the dye and the coolant of the triaxial, there is no doubt that the use of a Pyrex filter makes a significant improvement in the FOM. This value is only 2-fold for coumarin 102, but is as high as 1600-fold for rhodamine 6G.

### 3.3. *Effect of Oxygen*

In contrast to the statement by Schmitschek et al. [14], it is obvious that the presence of air makes a distinct effect upon both the output and the lifetime of coumarin dyes. For those coumarin dyes tested here that lase below 500 nm, the removal of oxygen not only improves the laser output by increasing the value of $k_0$ and/or lowering $t_0$, but markedly increases the value of the lifetime constants i.e. The dyes, C8F and coumarin 153, however, show an increase in lifetime under air. Since these dyes have been red-shifted compared to the dyes lasing below 500 nm, their $S_1 \leftarrow S_0$ electronic transitions have obviously been reduced. If their triplet energy level, $T_1$, has remained fixed or lowered to a reduced degree, the red-shifting can be considered to bring the $S_1$ and $T_1$ levels closer to each other which in turn will facilitate intersystem crossing. It is possible to conclude that the chemically reactive triplet state [16], which is readily quenched by oxygen, is produced easier by the red-shifted coumarin dyes, and that the presence of some oxygen will in turn yield a longer laser lifetime for these dyes. Since, as is shown in Tables 4 and 5, the presence of pure oxygen produces a *smaller lifetime constant* than in air, there is no doubt that a specific concentration of oxygen is needed to optimize the lifetime of each of these red-shifted coumarin dyes.

Table 5. Ratios of FOM's

| Dye | $R_1$<br>(uv) | $R_2$<br>(oxygen) | $R_3$<br>(argon) | $R_1R_3$<br>(uv, argon) |
|---|---|---|---|---|
| Coum 102 | 1.9 | 0.26 | 8.1 | 15 |
| FD-490 | 10.0 | 0.34 | 5.3 | 53 |
| AC3F | 45.0 | 0.44 | 5.4 | 240 |
| C8F | 290.0 | 0.18 | 0.54 | 160 |
| Coum 153 | 83.0 | 0.29 | 0.52 | 43 |
| Rhod 6G | 1600.0 | 0.27 | 2.40 | 3800 |
|  | Average | 0.30 ± 0.09 |  |  |

$R_1$ FOM with a Pyrex filter and under air FOM without Pyrex filter under air

$R_2$ FOM with Pyrex filter under oxygen FOM with Pyrex filter under air

$R_3$ FOM with Pyrex filter under argon FOM with Pyrex filter under air

As can be seen in Table 4 and the ratio of FOM under argon ratio FOM(air) values of Table 5, except for the red-shifted dyes, C8F and coumarin 153, the removal of air makes a 5-to-8 fold improvement in FOM's of the coumarin dyes and doubles that of rhodamine 6G.

We had previously reported that both 100% oxygen and the complete removal of oxygen was deleterious to the lifetime of coumarin dyes [15]. In the presence of a Pyrex uv filter, upper singlet states are protected from single photon excitation and as shown in Table 5, *in many cases*, the lifetime of coumarin dyes is improved by the removal of oxygen. It is assumed that intersystem crossing to the reactive triplet state is reduced by the limitation of singlet states to the lower levels by means of the Pyrex uv filter.

### 3.4. *Conflicts in Rhodamine 6G Lifetime Improvements*

Knyazev et al. [10], reported no change in the lifetime of rhodamine 6G in ethanol under air when a uv filter was used. *Since these workers* used the number of flashes as a measure of lifetime, which has been shown to be a poor measurement [18], it is not possible to directly compare their results with those of our present study. It should be noted, however, that they were using a very long pulse width of 70 µs FWHM as opposed to the 1.4 used in this study. It is quite possible that bleaching of the dye may have been the major degrading factor in their study. They proposed a major improvement in the lifetime of rhodamine 6G through the use of 2-propanol in place of ethanol. In this laboratory, the lifetime constants obtained in the two solvents under argon are comparable, with a lower $k_{\text{[illegible]}}$ found when 2-propanol was used as the solvent.

## 4. Conclusions

The use of a selected-wavelength-monitored degradation flashlamp allows the determination of a lifetime constant of a dye solution. The use of Pyrex to filter light below 300 nm is found to make from slight (coumarin 102 under air) to dramatic (rhodamine 6G under argon) improvements in the operating characteristics of the dye laser. The use of such a filter is recommended wherever stable output is needed from a flashlamp pumped dye laser. The coumarin dyes showed an improved output by the removal of oxygen when a Pyrex filter is present, but the red-shifted coumarin dyes had a larger lifetime constant under air. Pure oxygen, on the other hand, gave only 30% of the FOM's compared to air as the cover gas.

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# Appendix F

# LUMINESCENT COOLANTS FOR SOLID-STATE LASERS

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Applied Physics B Photophysics and Laser Chemistry

# Luminescent Coolants for Solid-State Lasers

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**Abstract.** Solutions of 13 fluorescent dyes have been used as energy transfer agents in place of the normal coolant of a Nd-YAG laser. Dye mixtures were used in a few cases where incomplete absorption of flashlamp pump energy was observed. Improvements of over 100% in laser output were observed for some dyes having a long Stokes shift when tested at both a low-input energy and a low-pulse rate. However, the absolute improvement in laser output for these dye solutions was small, and the improvement could be obtained almost as well by merely increasing the pulse rate. Various factors associated with the effectiveness of transfer-dye solutions are discussed.

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The presence of a fluorescent dye in the liquid coolant of a solid-state laser can both serve to protect the laser rod from harmful short wavelength radiation as well as re-emit unused energy from the flashlamp at the pump bands of the rod. Improvements in laser output as high as 130% have been reported through the use of such luminescent energy-transfer dye solutions [1].

There are a number of parameters that determine whether an improvement in laser output will be obtained through the use of a luminescent liquid filter. The transfer of light from the flashlamp to the dye solution is dependent upon the concentration and molar absorptivity of the dye, as well as the path length, when the dye solution is in direct contact with the flashlamp. If the dye solution is used only as a filter around the rod, then the reflectivity, as well as the design of the walls of the laser cavity become of importance. In general, one would like to be able to raise the concentration of the dye to the extent needed so that at least 90% of the light from the flashlamp is absorbed at all wavelengths below a major pump band of the rod. In practice, solubility and low molar absorptivity limit the ability to absorb all of the desired lamp emission.

A major consideration of the effectiveness of an energy-transfer dye solution to improve the output of a solid-state laser are the factors affecting the loss of direct lamp-to-rod emission. Since the fluorescing dye solution emits in all directions, at least half of the light absorbed by the dye that would have otherwise pumped the rod is lost through re-absorption by the flashlamp. In addition, there are internal energy losses within the dye due to fluorescent quantum yields being less than 100%. Since the fluorescent emission bands from most dyes are quite broad, the re-emitted light will seldom have an exact 1:1 correspondence to the pump bands of the rod. In addition, the absorption of the rod at the wavelengths of emission of the dye must be 90–99% if effective use is to be made of the fluorescence of the dye. Thus, significant reductions of laser output can occur where absorption of an energy-transfer dye solution occurs at wavelengths of direct lamp-to-rod energy transfer.

The purpose of the present study was to determine whether broad-absorption-band dyes having minimal absorption at pump bands would be superior to dyes previously tested by others when used as a coolant for Nd-YAG lasers [1–4]. In order to increase the width of the absorption bands of good fluorescing dyes, we had planned to link one fluorescent dye (donor) to a good fluorescing dye (acceptor) with an insulating link. Schäfer and coworkers [5, 6] have reported that such combinations of dyes (where the fluorescence of the donor matches the absorbance of the acceptor) yield dyes having additive absorptivity with essentially the same fluorescing (and lasing) characteristics of the ac-

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Table 1. Spectrometric characteristics of dyes used in this study

| Dye | | | Solvent | Wavelength λ (nm) | λ Peak (nm) | Fluorescence Quantum Yield |
|---|---|---|---|---|---|---|
| No. | Trivial Name | Source | | Absorption | Fluorescence | |
| 1 | Brilliant sulphaflavine | ALD 12,183-2 | Ethanol | 425 | 522 | [illegible] |
| 2 | Coumarin 6 | EXC | Ethanol | 458 | 504 | 0.88 |
| 3 | Coumarin 6 BF | " | Ethanol | 477 | 519 | 0.88 |
| 4 | Coumarin 7 BF | " | Ethanol | 455 | 507 | .7[illegible] |
| 5 | CSF | | Ethanol | 409 | 516 | 0.[illegible]2 |
| 6 | Na Fluorescein | Recrystallized | Ethanol (basic) | 502 | 5[illegible] | 0.90 |
| | | | Water (basic) | 491 | 513 | 0.95 |
| | Na FP | | Ethanol (basic) | 504 | 531 | .8[illegible] |
| | | | Water (basic) | 492 | 522 | [illegible] |
| 7 | Pyrazoline [illegible] | NEN | Ethanol | 423 | 531 | 0.58 |
| 8 | Pyrazoline [illegible] | " | Ethanol | 380 | 493 | 0.66 |
| 9 | Pyrazoline 2 | " | Ethanol | 396 | 5[illegible]3 | 0.65 |
| 10 | [illegible] | EK 2[illegible] | Water | 454 | 5[illegible]4 | 1.00 |
| 11 | Rhodamine 110 | EXC | Ethanol (basic) | 501 | 524 | 0.92 |
| 12 | Rhodamine 6G | EXC | Ethanol | 528 | 558 | 0.95 |

NEN New England Nuclear
EK Eastman Kodak Company
EXC Exciton Chemical Company
ALD Aldrich Chemical Company

[a] See Fig. 1 for materials prepared in this laboratory

ceptor dye alone. Since such bifluorophoric dyes sometimes yield two distinct emission bands *when the energy* transfer is not effective, we tried to obtain bifluorophoric dyes with a single emission band, i.e., a bichromophoric dye with emission centered at a selected wavelength. In practice, we found (for the purposes of this study) that pyrazoline dyes with their high molar absorptivity and high solubility were easier to synthesize and use than were the bichromophoric dyes. Similarly, mixed dyes (where both had emission in the target region of 510-590 nm) were found to yield slightly higher output than one dye alone. Since both dyes would be emitting at the target wavelength, the usual problem of one dye robbing pump energy from the other was not a significant factor (so long as both dyes had comparable fluorescence quantum yields). In the course of the study, we discovered that the pulse rate made a marked effect upon the improvement that was observed through the use of energy transfer dyes at low average-power input. Previous studies concerned with the use of energy-transfer dyes made no reference to the pulse rate at which their measurements were made [1-4].

## 1. Experimental

### 1.1. *Laser Characteristics*

A WEC* Corporation model W-770 A Nd:YAG laser was used to evaluate the dyes of this report. Two flashlamp pulsewidths were used. A short pulse of 40 µs and a 150-µs-long pulse at full-width half-maximum. The baseline widths of these two pulses were 60 *and 275 µs, respectively.* Flashlamp inputs below 10 J were made with the short pulse; flashlamp inputs 10 J and higher were made with the long pulse. The 57 mm (2.25 inch) long, 6.35 mm (0.25 inch) diameter Nd-YAG laser rod was jacketed by an 11 mm outside-diameter pyrex tube leaving a 1.3 mm-annular space for the flow of coolant. The EG and G FX-33C-2 xenon-filled flashlamp was 6 mm in outside diameter and was jacketed with a 13 mm outside-diameter pyrex tube leaving 2.5 mm-annular space for the flow of coolant. The separation of the center line of the lamp to the center line of the rod was 19.1 mm (0.75 inch). The ends of the laser rod were flat-flat plano-parallel with anti-reflection coatings. The output mirror was flat-flat with one side having an anti-reflection coating and the other 55% reflectivity coating. It was separated 30 cm from a 10-meter radius 99.9% rear mirror. The rod, lamp, and dry silver-plated metal-reflector cavity all had their own individual cooling supplies. The coolants were held to 27 ± 5 °C. Typically, 1.5 l flowing at 1.9 l per minute was used for the solution cooling the lamp or the lamp rod combination. The dye solution was flowed through a 10 µm pore-size polypropylene filter to remove bubbles.

A Perkin-Elmer Model 44-B fluorescence spectrophotometer with output corrected for lamp output and detector response was used to measure excitation and fluorescence spectra. Relative fluorescence quantum yields were determined using quinine sulfate in 1.0 N $H_2SO_4$ as standard.

### *1.2 Measurements*

A Laser Precision model Rj-7200 radiometer was used with their 1 cm² pyroelectric detector to obtain digital measurements of the laser output. For measurements at 10 Hz and higher, the microprocessor of the Rj-7200 was used to average 100 measurements. At slower rates, the microprocessor was used to average groups of 10 measurements. For short pulses, a minimum of three sets of 10 measurements each were made at the rates below 10 Hz in the sequence of increasing input energy. This set of three was then repeated a second time. Since it was possible to exceed the recommended rating of the pyroelectric detector, an attenuation filter was usually placed between the laser and the detector. The factor for the filter was determined by the ratio of the with- and without-filter using the Rj-7200 digital readout.

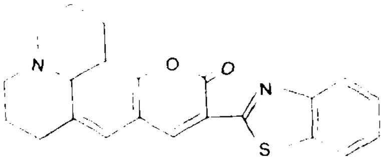
The percent change caused by the use of a dye in a solvent was calculated with respect to average values of the solvent only using data obtained before and after the specific dye test. The dye test consisted of the various rate effects, if tested, as well as the effect of the different input energies at the two different pulse widths. When two dyes were being tested, the solvent was tested first. After testing of the first dye was completed, the second dye was then added and the testing resumed. After completion of testing of the second dye, the solvent alone was evaluated.

## 2. Results and Discussion

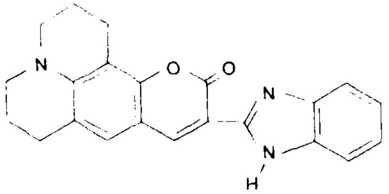
### *2.1 Dye Characteristics*

Table 1 lists the 13 dyes that were used in this study along with some of their spectral characteristics. Many of these dyes have been used previously as laser dyes [7, 8]. We make use of trivial names for the purpose of rapid, positive identification in preference to the more exact (but lengthy) chemical names of the dyes. Of course, we insure that these names can be traced either to the structure of the dye or the source of commercially available dyes. Figure 1 shows the structure of those dyes that were specifically synthesized for this study. Dye No. 7 of Fig. 1 was the only bichromophoric dye that was prepared in sufficient quantity to allow testing. It is formed using fluorescein (Dye No. 6 of Table 1) as the acceptor and a pyrazoline as the donor. Unfortunately, Dye No. 7 did not show just the fluorescence quantum yield found for the acceptor alone in water. In water where pyrazolines are known to have reduced fluorescence quantum yields [9], the fluorescence quantum yield of Dye No. 7 was found to be less than that in ethanol, i.e., the donor and acceptor are still interacting with each other electronically.

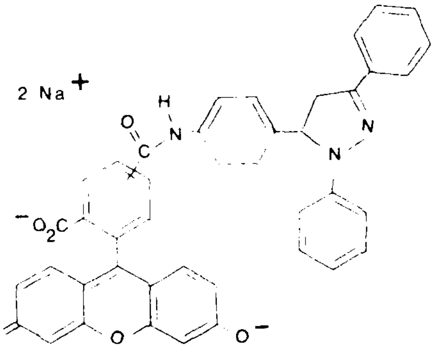
Dye 3 Coumarin 6BF



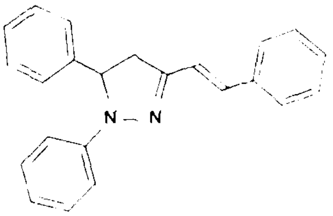
Dye 4 Coumarin 7BF



Dye 7 $Na_2FP$



Dye 9 Pyrazoline 1



Dye 10 Pyrazoline 2

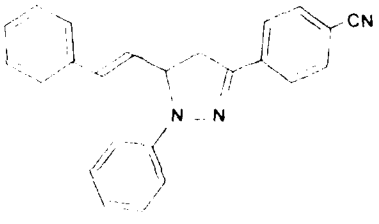


Fig. 1. Structure of dyes synthesized for this program.

### *2.2 Effect of Pulse Rate and Flashlamp Loading*

The effects of heating of the rod through an increase in the average power are quite evident in Table 2. The output per pulse is seen to increase as the pulse rate increases for a "fixed" input energy. This effect

Table 2. Effect of pulse rate and input energy upon measured laser output in mJ using ethanol coolant. Measured ×6.5 = actual output energy in mJ

| Pulse rate (Hz) | Input energy (J) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 3 | 4 | 5 | 6 | 7 | 10 | 25 | 40 |
| 0.064 | [illegible] | 2.18 | 4.23 | 6.64 | 9.71 | 20.8 | 73.7 | 125.8 |
| 0.36 | 0.867 | | 4.99 | | 10.16 | | | |
| [illegible] | 0.968 | | 5.54 | | [illegible] | | | |
| [illegible] | 1.60 | 3.42 | 5.58 | 8.58 | 11.22 | 21.4 | [illegible] | 108.8 |
| [illegible] | 1.217 | | 6.21 | | 12.30 | | | |
| [illegible] | 1.189 | | 5.93 | | 11.60 | | | |

Table 3. Effect of pulse rate and input energy upon measured laser output increase using dye in coolant. Measured increase in mJ in output energy using 10 [illegible] molar pyrazoline 2 in ethanol surrounding lamp and [illegible] rod. Argon was used as the cover gas. Measured ×6.5 = actual output energy increase

| Pulse rate (Hz) | Input energy (J) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 3 | 4 | 5 | 6 | 7 | 10 | 25 | 40 |
| 0.064 | 0.308 | 0.882 | 0.892 | 1.40 | 1.61 | 1.96 | [illegible] | 14.1 |
| [illegible] | [illegible] | | 1.039 | | 1.37 | | | |
| [illegible] | [illegible] | | 1.002 | | 1.44 | | | |
| [illegible] | [illegible] | 0.840 | 1.073 | [illegible] | 1.96 | 2.28 | [illegible] | 12.7 |
| 6 | [illegible] | | 1.020 | | 1.53 | | | |
| 8 | [illegible] | | 1.073 | | 1.56 | | | |

is most significant at low input energies. At 7 J and higher input energies, only a slight increase is observed by increasing the pulse rate. Since we set our voltage for the energy required for just one pulse, the output per pulse drops at the higher average input energies. This is no doubt due to the limitations of the power supply since the average voltage measured is lowered at the higher pulse rates, i.e., the actual input energy no doubt decreases somewhat as the repetition rate increases. Since our primary interest was to measure the effect of the dye, we did not correct for the limitations of the power supply.

The measured increase in the output of the laser due to the introduction of dye are shown in Table 3 for the dye pyrazoline-2. The increase is much less dependent upon the pulse rate for a given input energy than found for the solvent alone. Very large percentage increases are found in Table 4 for the low average power input; the improvement due to the dye is highly magnified because of the much reduced output of the cool laser rod with no dye present. One must consequently compare at least 7 J input results (for two systems) in order to determine the effects of different concentrations and dyes. Because of these complicating rate and input energy effects, the usual slope efficiencies and lasing threshold were not calculated in this study.

Vodop'yanov and coworkers have reported that a 30% improvement in output should be expected for Nd-YAG using rhodamine 6G as an energy converter if the discharge power of the flashlamp was in the range of 1–1.5 MW cm$^3$ [1]. They also indicate that a short pulse on the order of 100 µs is superior to conversion found for a long 250 µs pulse. Our maximum power density was 0.25 MW cm$^3$, and we observed a maximum percent improvement for rhodamine 6G in the range of 8–10% (Table 4). This improvement agrees quite closely with that predicted by Vodop'yanov and coworkers. We also observed improved outputs for the shorter pulses as compared to the longer for all of the dyes that we tested.

### 2.3. *Effect of Dye Concentration*

As the concentration of the dye solution increases, a number of effects occur. The first involves the increased amount of pumplight that is absorbed by the dye due to the Beer-Lambert relationship

$$a = \varepsilon bc, \tag{1}$$

where $a$ is the absorbance of the dye, $\varepsilon$ is the molar absorbance coefficient at a specific wavelength, and $c$ is the molar concentration. When the absorbance of the dye reaches the value of 2, then 99% of the input light is absorbed. For dyes having higher molar absorbance, the thickness $b$ of the dye can be proportionately reduced. The second factor that is of importance is where the light is absorbed. For the case of

Table 4. Percent improvement in laser output using pyrazoline-2 ethanol coolant as a function of pulse rate and input energy. Argon cover gas with dye solution flowing past lamp and rod

| Pulse rate [Hz] | Input energy [J] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 3 | 4 | 5 | 6 | 7 | 10 | 25 | 40 |
| | $1 \times 10^{-4}$ M Pyrazoline-2 | | | | | | | |
| 0.64 | 34 | 18 | 8 | 8 | 10 | 9 | 7 | 6 |
| 1.36 | 19 | | 10 | | 10 | | | |
| 2 | 17 | | 9 | | 9 | | | |
| 5 | 14 | 11 | 13 | | 10 | 6 | 8 | 7 |
| 10 | 16 | | 12 | | 9 | | | |
| 15 | 14 | | 13 | | 10 | | | |
| Average | | | 10.8 | 5 | 9.7 | 7.8 | 7.8 | 6.8 |
| | $3 \times 10^{-4}$ M Pyrazoline-2 | | | | | | | |
| 0.64 | 8 | 22 | 13 | 12 | 11 | 11 | 9 | 11 |
| 1.36 | 38 | | 14 | | 12 | | | |
| 2 | 33 | | 11 | | 11 | | | |
| 5 | 28 | 16 | 13 | 10 | 12 | 8 | 8 | 10 |
| 10 | 26 | | 15 | | 10 | | | |
| 15 | 28 | | 14 | | 12 | | | |
| Average | | | 13.0 | 11.0 | 11.3 | 9.8 | 8.8 | 10.8 |
| | $1 \times 10^{-3}$ M Pyrazoline-2 | | | | | | | |
| 0.64 | 81 | 27 | 21 | 21 | 17 | 9 | 11 | 13 |
| 1.36 | 39 | | 21 | | 16 | | | |
| 2 | 39 | | 19 | | 16 | | | |
| 5 | 37 | 16 | 19 | 15 | 17 | 11 | 11 | 12 |
| 10 | 33 | | 16 | | 12 | | | |
| 15 | 35 | | 18 | | 14 | | | |
| Average | | | 19.0 | 18.0 | 15.3 | 10.0 | 11.0 | 12.8 |

the dye surrounding the lamp, it is necessary for the image of the fluorescing dye solution to be transferred to the rod. If the image of the dye solution is much larger than the size of the rod, the transfer will be inefficient. Thus, even though 99% of the light at a given wavelength is being absorbed, increasing the concentration can still cause an improvement in the location of the fluorescing portion of the dye. The concentration of the dye cannot be increased without impunity, however. Not only is there a solubility limitation, but dye self-association and concentration quenching of excited states [10] will limit the efficiency of fluorescence. As seen in Table 3, pyrazoline-2 can be increased up to $10^{-3}$ molar with increasing improvements in energy transfer.

### 2.4 *Effect of Band Robbing*

The effects of the dye robbing energy from the rod through absorption of energy at a major rod pumping band can be seen in Table 5. The absorption of rhodamine 6G in ethanol peaks at 530 nm, a major Nd-YAG absorption band. Low concentrations of

Table 5. Percent change in laser output using rhodamine 6G in ethanol

| Dye concentration $\times 10^{-4}$ M | Input energy [J] | | | | | |
|---|---|---|---|---|---|---|
| | 3 | 5 | 7 | 10 | 25 | 40 |
| | Dye solution around lamp only [0.6 Hz] | | | | | |
| 0.5 | 15 | 4 | 3 | | | |
| 1 | 10 | 2 | 0 | | | |
| 3 | 1 | 4 | 5 | | | |
| 10 | 12 | 14 | 13 | 7 | 6 | |
| | Dye solution around rod only [0.6 Hz] | | | | | |
| 1 | 15 | 1 | 3 | | | |
| 3 | 19 | 2 | 5 | | | |
| 10 | 21 | 6 | 2 | | | |
| | Dye solution around lamp and rod [5 Hz] | | | | | |
| 1 | 50 | 5 | 2 | 6 | 2 | 1 |
| 3 | 33 | 11 | 7 | 5 | 5 | 8 |
| 10 | 38 | 9 | 10 | 7 | 7 | 8 |

rhodamine 6G make a major decrease in the energy transfer since there is insufficient light being absorbed by the dye to pump effectively the 580 nm band. Yet, the direct lamp-to-530 band is being robbed of energy by the dye. When the effective thickness of the dye is increased by flowing past both the rod and the lamp, the greatest percentage of losses occur. Because of poor reflectivity of the cavity in the uv (and because of the smaller thickness of the dye solution around the rod), only losses were found for rhodamine 6G around the rod. The greatest overall improvements are seen for rhodamine 6G flowing just around the lamp. With increasing concentration, the increased overall light absorption is countered by the effects of the band robbing. For the dye that is just around the lamp, the overall light absorption less the band robbing is improved compared to dye solution around both the lamp and the rod. For dyes having negligible absorption at wavelengths greater than 500 nm, the type of loss seen in Table 5 at low input energies is greatly reduced. An example of this is seen in pyrazoline-2 in Table 4.

### 2.5 *Effects of Different Dyes*

Table 6 shows the percent improvements observed for a variety of dyes, many of which have not been previously tested for energy transfer. Dyes such as pyrene-1 and brilliant sulphaflavine suffer by having both limited solubility and molar absorptivity. Forming the butterfly configuration on coumarin 6 (and 7), coumarin 6 BF, shown in Fig. 1, shifts the fluorescence emission towards the red and yields a better match with the Nd-YAG pump bands. Unfortunately, the solubility of coumarin 6 BF in ethanol is lower than that of

Table 6. Change in laser output using high concentrations of dye solution

| First dye |  | Second dye or base |  | Cover gas | Solvent | Pulse rate [Hz] | Dye soln location* | % change | Input energy [J] |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Name | Conc M × 10³ | Name | Conc M × 10³ |  |  |  |  | 3 | 5 | 7 | 10 | 25 | 40 |
| B. Sulphaflavine | 3 |  |  | Air | Ethanol | 0.64 | I | 7 | 5 | 5 | 6 | 4 |  |
|  | 3 |  |  | Argon | Ethanol | 0.64 | I | 9 | 6 | 6 | 7 | 5 |  |
|  | 3 | Rh6G | 10 | Air | Ethanol | 0.64 | I | n.l. | 5 | 4 | n.l. | 3 |  |
|  | 3 | Rh6G | 10 | Argon | Ethanol | 0.64 | I | 7 | 5 | 2 | 1 | 2 |  |
| Coumarin 6 | 10 |  |  | Air | Ethanol | 0.64 | I | 100 | 26 | 17 | 10 | 5 | 3 |
|  | 10 |  |  | Air | Ethanol | 18.0 | I | 50 | 20 | 16 |  |  |  |
|  | 10 | Pyrazoline-1 | 10 | Air | Ethanol | 0.64 | I | 78 | 25 | 20 | 9 | 9 | 11 |
|  | 10 | Pyrazoline-1 | 10 | Air | Ethanol | 18.0 | I | 49 | 21 | 16 |  |  |  |
| Coumarin 6 BF | 1 |  |  | Argon | Ethanol | 5.0 | I and R | 19 | 6 | 4 | 9 | 8 | 10 |
|  | 1 | Pyrazoline-2 | 3 | Argon | Ethanol | 5.0 | I and R | 6 | 13 | 12 | 3 | 11 | 13 |
|  | 1 | Pyrazoline-2 | 10 | Argon | Ethanol | 5.0 | I and R | 0 | 38 | 13 | 8 | 11 | 14 |
| Coumarin 7 BF | 1 |  |  | Argon | Ethanol | 5.0 | I and R | 67 | 33 | 11 | 12 | 10 | 9 |
| CSI | 10 |  |  | Argon | Ethanol | 5.0 | I and R | 38 | 38 | 11 | 10 | 9 | 9 |
|  | 10 | Pyrazoline-1 | 3 | Argon | Ethanol | 5.0 | I and R | 39 | 39 | 13 | 12 | 10 | 9 |
| Na fluorescein | 3 | NaOH | 10 | Air | Ethanol | 0.64 | I | 1 | 1 | 4 |  |  |  |
|  | 3 |  |  | Air | Water | 0.64 | I | 32 | 5 | 3 |  |  |  |
|  | 3 | LiOH | 0.3 | Air | Water | 0.64 | I | 22 | 5 | 2 |  |  |  |
|  | 3 | LiOH | 2 | Air | Water | 0.64 | I | n.l. | 17 | -8 | n.l. | 14 |  |
| Na FP | 1 |  |  | Air | Water | 0.64 | I | 3 | 12 | 9 | n.l. | 4 |  |
| Pilot 495 | 10 |  |  | Air | Ethanol | 0.64 | I | 16 | 7 | 7 | 3 | 10 |  |
|  | 10 |  |  | Argon | Ethanol | 0.64 | I | 17 | 5 | 5 | 4 | 10 |  |
|  | 10 | Rh6G | 10 | Argon | Ethanol | 0.64 | I | 2 | 6 | 7 | 2 | 1 |  |
| Pyrazoline-1 | 10 |  |  | Air | Ethanol | 0.64 | I | 35 | 18 | 14 | 8 | 6 |  |
|  | 30 |  |  | Argon | Ethanol | 0.64 | I | 54 | 19 | 14 |  |  |  |
|  | 17 |  |  | Argon | Ethanol | 0.64 | I | 88 | 21 | 16 | 12 | 12 |  |
|  | 17 | Pilot 495 | 3 | Air | Ethanol | 0.64 | I | 11 | 5 | 7 |  |  |  |
|  | 17 | Pilot 495 | 3 | Argon | Ethanol | 0.64 | I | 35 | 13 | 12 | 7 | 8 |  |
| Pyrazoline-1 | 10 |  |  | Argon | Ethanol | 0.64 | R | 16 | 8 | 6 | 1 | 2 | 3 |
|  | 10 |  |  | Argon | Ethanol | 18.0 | R | 22 | 10 | 7 | 1 | 2 |  |
| Pyrazoline-2 | 10 |  |  | Air | Ethanol | 0.64 | I | 25 | 19 | 12 | 9 | 8 |  |
|  | 10 |  |  | Argon | Ethanol | 0.64 | I | 25 | 18 | 14 |  |  |  |
|  | 10 | Rh6G | 3 | Argon | Ethanol | 0.64 | I | -6 | 6 | 3 |  |  |  |
| Pyrazoline-2 | 30 |  |  | Argon | Ethanol | 0.64 | I | 101 | 23 | 16 | 15 | 10 | 11 |
|  | 10 |  |  | Argon | Ethanol | 18.0 | I | 41 | 15 | 15 |  |  |  |
|  | 10 | Coumarin 6 | 2 | Argon | Ethanol | 0.64 | I | 116 | 25 | 23 | 9 | 5 | 9 |
|  | 10 | Coumarin 6 | 2 | Argon | Ethanol | 18.0 | I | 50 | 18 | 18 |  |  |  |
| Pyranine | 1 |  |  | Air | Water | 0.6 | I | n.l. | 7 | 5 |  |  |  |
|  | 1 | Na fluorescein | 1 | Air | Water | 0.64 | I | n.l. | 12 | 10 |  |  |  |
|  | 1 | + LiOH | + 0.3 | Air | Water | 0.64 | I | n.l. | 4 | 0.3 |  |  |  |
| Rhodamine 110 | 10 |  |  | Air | Ethanol | 0.64 | I | 14 | 1 | 1 | -4 | 0 |  |

I   Around lamp
R   Around laser rod

n.l.   No lasing observed

coumarin 6 so that the improved wavelength characteristics cannot be used. Coumarin 6 is one of the better dyes for short pulses, but it is found to be of only moderate value for the long pulses. This can be seen not only for the coumarin 6 results but also when coumarin 6 is added to pyrazoline-2. The mixed solution has an increase in output for short pulses and a decrease for long pulses. This suggests that photophysical processes are occurring on the longer pulses (triplet-triplet absorption?) that are reducing the fluorescence emission. In addition to photophysical changes, chemical changes may occur that increase the absorption of the pump light. Rhodamine 6 G, for example, is known to disproportionate through collision of excited state molecules resulting in the formation of a radical cation and a radical anion [11]. These radical species have their own distinct absorption which may last as long as milliseconds.

The one bichromophoric dye tested that was made from linking fluorescein with a pyrazoline, Na₂FP, was tested *in* water *in* the absence of base since our tests on fluorescein showed these conditions to be optimum for energy *transfer*. Unfortunately, the linkage gives a *red shift resulting in band robbing and* a drop in the quantum yield in water (Table 1).

The dye yielding the best energy transfer in our system was pyrazoline-2 in ethanol. Figure 2 shows that the fluorescence quantum yield is not only moderate at 0.7 but that it drops markedly at increased temperatures. Figure 3 shows the excitation spectrum and emission for pyrazoline-2. Its very broad emission causes a major portion of its fluorescence to miss the pump-bands of Nd-YAG.

Rhodamine 6 G has a small Stokes shift and consequently has a considerable overlap between its fluorescence and its $S_1 \leftarrow S_n$ absorption band. When used at moderately high concentrations, the effective bandwidth of rhodamine 6 G fluorescence is much narrower than for most organic dyes resulting in a good dye-to-light-to-rod energy transfer. This effective narrow bandwidth effect is useful only for those dyes having a fluorescence quantum yield near one. The multiple absorption re-emission of a dye with quantum yields much less than one causes an effective reduction in their fluorescence quantum yields [10].

### 2.6. *Effect of Mixed Dyes*

In this study we used more than one dye for the purpose of filling in areas of poor absorbance. As can be seen in Table 1, many of the dyes have such large Stokes shifts that they will loose a considerable amount of the available pump energy if they are concentration limited. Our purpose was consequently not to try to transfer energy from one dye to another as we chose only those dyes that had significant fluorescence in the target region of 500–600 nm. In practice, the mixed dyes yield only slight improvements over the single dyes at high concentration.

## 3. *Conclusions*

The improvement of solid-state laser rod output through the use of dye solution energy converters is dependent upon a variety of factors. Besides the need for high fluorescence quantum yields, solubility, and molar absorptivity, there is a need to have the absorption bands of the dye not overlap the major pump bands of the rod. In particular, the fluorescence emission bands of most dyes are too broad and consequently miss a major portion of Nd-YAG pump bands. Our best energy transfer results were found to be with dyes such as pyrazoline-2 *or coumarin 6* whose quantum yields were less *than that of rhodamine 6 G* but whose long Stokes shift resulted in less pump-band robbing. In addition, self-absorption of *rhodamine 6 G* yields a narrower apparent emission band that matches the Nd-YAG pump bands better than do the long Stokes shift dyes. Mixed dye solutions were found to yield only slight improvements even though they helped to "fill in" blank absorption areas.

Over 100% improvement in efficiency was observed using energy transfer dyes at low pulse rates and operating near the lasing threshold. This major improvement was observed only under conditions involving a low average power and was lost at higher power loadings.

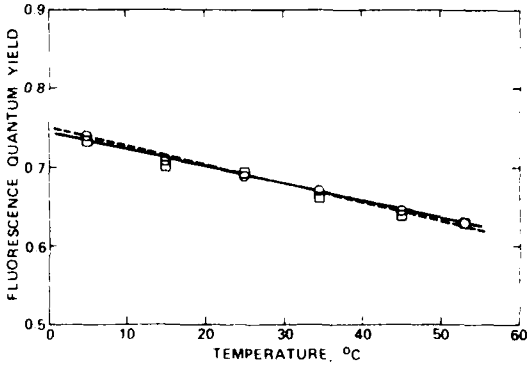


Fig. 2. Effect of temperature upon the fluorescence quantum yields of pyrazoline-1 and -2 (□ pyrazoline-1, ○ pyrazoline-2).

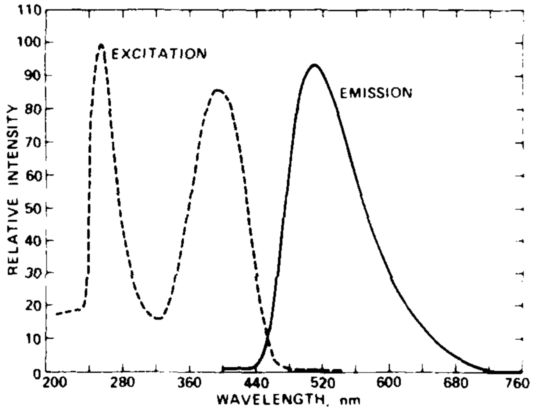


Fig. 3. Excitation and emission spectrum of pyrazoline-2.

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# Appendix G

# FLUORESCENCE AND LASING CHARACTERISTICS OF SOME LONG-LIVED FLASHLAMP-PUMPABLE, OXAZOLE DYES

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# FLUORESCENCE AND LASING CHARACTERISTICS OF SOME LONG-LIVED FLASHLAMP-PUMPABLE, OXAZOLE DYES

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The effects of dye structure, cover gas, and solvent are all shown to be critical to laser output and lifetime. The N-methyl tosylate salt of 2-(4-pyridyl)-5-(4-methoxyphenyl) oxazole in ethanol under argon is found to be the longest-lived, moderate output, laser dye solution of any that have been reported.

## 1. Introduction

Until the study by Lee and Robb [1], oxazoles had shown little success as flashlamp-pumpable laser dyes. Molecular engineering had been performed on oxazoles to make them more absorptive [2] and to attach triplet-state quenchers to them [3,4]. Although considerable improvements were observed, the lasing outputs of the modified oxazoles were still low compared to other classes of dyes. Even with the use of the very high mirror reflectivities ($R_1R_2 = 0.97$) and the extremely rapid rise-time (50 ns) of the flashlamp used by Furumoto and Ceccon [5], the oxazoles showed high lasing thresholds compared to those of other laser dyes [6]. (Of course, the high mirror reflectivities limit the useful output of a laser and the short rise-time is difficult to obtain in large flashlamps.)

Lee and Robb showed that salts of a pyridyl substituted phenyloxazole in water had relatively low laser outputs and moderate durations of lasing with flashlamp pumping. Since they had protected their dye solutions from uv radiation only below 220 nm and used crude lifetime measuring techniques [7], we decided to test these compounds more thoroughly using our dye laser test facility. Our test setup uses a triaxial flashlamp having a 300-nm cutoff Pyrex uv filter to contain the lasing solution, and a wavelength and intensity corrected linear flashlamp for dye degradation [8].

We made a more thorough evaluation of the effects of solvent and cover gas upon the lasing as well as determined some of the fluorescence characteristics of the dyes examined by Lee and Robb. We also examined another pyridinium oxazole as well as a few of the dyes recommended, but not tested, by Lee and Robb. Under very specific experimental conditions, one of the dye modifications yields the highest lifetime with moderate laser output of any solution that we have ever tested.

## 2. Experimental

The flashlamp-pumped laser made use of a Phase-R DL-10Y with a Pyrex jacket separating the dye and the water coolant. The rise-time of this flashlamp was 200 ns. The output mirror had a nominal 55% reflectivity at the lasing wavelength. The dye solution degradation was performed primarily with a Xenon Corp. N-851C water-cooled linear flashlamp at 10 J (electrical) input. This system is described in greater detail elsewhere [8]. An Avco-Everett C400 $N_2$ laser Dial-a-Line dye laser combination was used to test some of the solutions for lasing [9]. This laser pumps at 337.1 nm with 10 ns pulses. Fluorescence quantum yields were determined using a Perkin-Elmer MPF-44B with corrected spectra. The equipment and techniques have been previously described [10]. Reagent grade ethanol from United States Industrial,

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(North-Holland Publishing Division)

"Distilled-in-Glass" quality organic solvents from Burdick and Jackson, and deionized, filtered water were used as solvents. The 2-(4-pyridyl)-5-phenyloxazole and its salts were purchased from Aldrich Chemical Co. and were used as received. The remaining oxazole-type dyes were synthesized in this laboratory using conventional techniques. The concentrations of the solutions used for flashlamp testing were selected so as to have an absorbance of 4–5 cm$^{-1}$ in the $S_1 \leftarrow S_0$ absorption band. For nitrogen laser pumping, solutions were $10^{-3}$ *M* up to saturation as required to have a short depth of penetration by the $N_2$ pump beam.

Fig. 1 shows the structure of the pyridyl substituted dyes tested along with two comparison dyes, AC3F and Coumarin 314. A third comparison dye, Coumarin 487, was obtained from the Phase-R Corporation. Laser outputs, $\phi$, for a specific electrical input energy to the flashlamp, $I$, were computer fitted to the relationship derived by Fletcher and Knipe [7],

$$\phi = a + bI/(1 + cT) , \qquad (1)$$

where $T$ is the total input energy, $\Sigma I$, per unit volume. The initial lasing slope efficiency, $k_0$, is taken as equivalent to $b$ while the initial lasing threshold, $t_0$, is taken as equivalent to $a/k_0$. The lifetime constant is $1/c$ in J dm$^{-3}$. The lifetime constants should be taken as relative measurements since there has as yet not been any demonstrated capability to transfer such constants between different laser configurations [6,7]. These lifetime constants are at least an improvement however, over the number of flashes to 50% of laser output which has been shown to be dependent upon the input energy and the threshold of lasing [6,7].

Table 1 shows the fluorescence characteristics of most of the dyes examined. Table 2 shows conditions where pumping by a short, 10 ns, 20 kW pulse from a nitrogen laser did not cause lasing. Table 3 shows the flashlamp-pumped lasing data.

## 3. Discussion

In table 3, we find that the lasing outputs of the pyridinium salts reported by Lee and Robb have low lasing outputs under air compared to coumarin compounds. We also find, however, that the laser output can be markedly improved when air is replaced by ar-

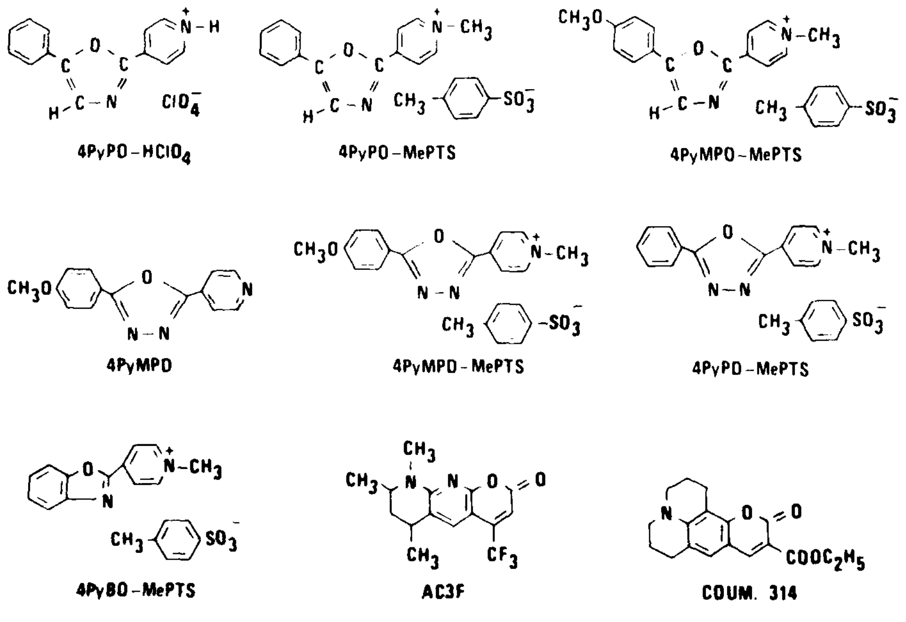

Fig. 1. Dye structures.

Table 1
Fluorescence measurements of some pyridyl substituted dyes

| Dye | Solvent | Emission peak, nm | Fluorescence quantum yield under | | |
|---|---|---|---|---|---|
| | | | argon | air | oxygen |
| 4PyPO-HClO$_4$ | ethanol [a] | 474 | 1.00 | 1.00 | 0.96 |
| 4PyPO-HClO$_4$ | water [a] | 476 | 0.83 | 0.83 | 0.82 |
| 4PyPO-MePTS | ethanol | 482 | 0.74 | 0.74 | 0.75 |
| 4PyPO-MePTS | ethanol:water [b] | 480 | 0.97 | 0.97 | 0.97 |
| 4PyPO-MePTS | water | 480 | 0.89 | 0.90 | 0.86 |
| 4PyMPO-MePTS | ethanol | 567 | 0.76 | 0.73 | 0.65 |
| 4PyMPO-MePTS | water | 578 | 0.35 | 0.38 | 0.37 |
| 4PyMPD | ethanol | 422 | | 0.79 | |
| 4PyMPD-HClO$_4$ | ethanol [c] | 596 | | 0.057 | |
| 4PyMPD-MePTS | ethanol | 604 | | 0.097 | |
| 4PyPD-MePTS | ethanol | 444 | | 0.042 | |
| 4PyBO-MePTS | ethanol | 456 | | 0.040 | |
| 3PyBO-MePTS | ethanol | 466 | | | |

[a] $10^{-3}$ *M* in HClO$_4$. [b] 50:50 by volume. [c] $5 \times 10^{-3}$ *M* in HClO$_4$.

gon as the cover gas. This improvement is not reflected in the fluorescence quantum yields of table 1. In contrast to the coumarin laser dyes [8,11,12], the oxazole dyes tested here show only slight quenching of their fluorescence by oxygen.

The salts of pyridyl substituted oxadiazole and benzoxazole dyes recommended by Lee and Robb did not show lasing action even when nitrogen laser pumped in a variety of solvents (table 2). Krasovitskii et al., note that oxadiazole derivatives have lower fluorescence quantum yields than do the oxazoles [13]. Low fluorescence quantum yields (in ethanol, table 1) of both the pyridyl substituted oxadiazoles and benzoxazoles salts are a likely reason for their not lasing. However, since 4PyMPO has a fluorescence quantum yield of 0.79 (table 1) in ethanol, a low yield cannot be the cause of its failure to lase.

Table 2
Dye solutions that did not lase (20 kW peak, N$_2$ laser pumped).

| Dye | Solvent |
|---|---|
| 4PyPD-HX | water [a],[b] |
| 4PyMPD | ethanol, benzene |
| 4PyMPD-HClO$_4$ | ethanol [a], water [a] |
| 4PyMPD-MePTS | water |
| 4PyPD-MePTS | ethanol [c], water [c], DMF, acetonitrile |
| 4PyBO-MePTS | ethanol [c], water [c], DMF, acetonitrile |
| 3PyBO-MePTS | ethanol, water |

[a] $10^{-2}$ *M* HClO$_4$. [b] $10^{-2}$ *M* HCl.
[c] Also did not lase when flashlamp pumped with the DL-10Y triaxial system.

The use of ethanol:water, 50:50 by volume, can cause a marked improvement over the results of ethanol as reported by Fletcher et al. [12]. A marked improvement in output and lifetime was found for 4PyPO-MePTS in ethanol:water under argon. In contrast, AC3F showed an improvement under air but a marked decrease under argon by this change to a mixed solvent. Using methanol gave even different results from that of ethanol:water. Although these more polar solvents red-shift the output of coumarin dyes from results found in ethanol, little change in wavelengths was noted for the pyridinium oxazole dyes because of changing solvents.

The dye modification showing the greatest improvement in this study was the attachment of a methoxy to the phenyl group of 4PyPO to form 4PyMPO (fig. 1). This group causes a very marked red-shift in fluorescence and lasing wavelengths. This modification was made by Lee and Robb but their results were not reported in [1]. Lee and Robb were looking for good water soluble dyes. It is surprising that 4PyMPO-MePTS can be made to lase at all in water since it has a fluorescence quantum yield of only 0.38. However, even though its fluorescence

Table 3
Lasing characteristics of pyridyl substituted oxazole salts and comparison dyes at 2 × 10$^{-4}$ molar.

| Dye designation | Solvent | Cover gas | Lasing | | | |
|---|---|---|---|---|---|---|
| | | | Slope efficiency, $k_0 \times 10^3$ | Threshold, $t_0$, J | Lifetime constant 1/c, MJdm$^{-3}$ | Wavelength, nm |
| 4PyPO-HClO$_4$ | ethanol[a)] | air, argon | did not lase | | | |
| 4PyPO-HClO$_4$ | water[a)] | air | 0.38 | 43.0 | n.d.[b)] | 494–511 |
| 4PyPO-HClO$_4$ | water[a)] | argon | 0.57 | 40.7 | 320.0 | 494–512 |
| 4PyPO-MePTS | ethanol | air | 0.47 | 41.0 | n.d.[b)] | 492–507 |
| 4PyPO-MePTS | ethanol | argon | 0.56 | 31.4 | 35.0 | 493–508 |
| 4PyPO-MePTS | water | air | 0.51 | 35.8 | 107.0 | 494–512 |
| 4PyPO-MePTS | water | argon | 0.67 | 34.2 | 157.0 | 494–512 |
| 4PyPO-MePTS | ethanol:water | air | 0.59 | 35.5 | 112.0 | 496–507 |
| 4PyPO-MePTS | ethanol:water | argon | 0.74 | 34.8 | 690.0 | 495–511 |
| 4PyMPO-MePTS | ethanol | air | n.d.[b)] | ~50.0 | n.d.[b)] | n.d.[b)] |
| 4PyMPO-MePTS | ethanol[c)] | argon | 1.6 | 21.0 | 2000.0 | 560–583 |
| 4PyMPO-MePTS | ethanol | argon | 1.5 | 22.0 | >10000.0 | 567–587 |
| 4PyMPO-MePTS | 2-propanol[c)] | air | n.d.[b)] | ~45.0 | n.d.[b)] | n.d.[b)] |
| 4PyMPO-MePTS | 2-propanol[c)] | argon | 1.4 | 16.9 | 16.0 | 559–582 |
| 4PyMPO-MePTS | methanol | argon | 1.0 | 25.6 | >10000.0 | 571–588 |
| 4PyMPO-MePTS | water | argon | 0.45 | 41.0 | n.d.[b)] | 571–591 |
| Coum 314 | ethanol | air | 1.9 | 19.8 | 2.8 | 492–504 |
| Coum 314 | ethanol | argon | 2.1 | 17.3 | 1.6 | 492–507 |
| Coum 314 | methanol | air | 1.9 | 19.3 | 4.0 | 496–508 |
| Coum 487 | ethanol | air | 2.5 | 25.3 | 3.3 | 474–498 |
| Coum 487 | ethanol | argon | 2.0 | 23.8 | 6.3 | 474–498 |
| Coum 487 | ethanol:water | air | 2.4 | 24.8 | 6.3 | 487–507 |
| Coum 487 | ethanol:water | argon | 2.2 | 24.1 | 10.0 | 487–507 |
| Coum 487 | methanol | air | 4.1 | 21.1 | 2.4 | 481–503 |
| Coum 487 | methanol | argon | 3.8 | 20.4 | 7.1 | 481–503 |
| AC3F | ethanol | air | 1.5 | 28.0 | 41.0 | 480–497 |
| AC3F | ethanol | argon | 1.4 | 27.3 | 229.0 | 480–497 |
| AC3F | ethanol:water | air | 1.7 | 27.1 | 313.0 | 490–514 |
| AC3F | ethanol:water | argon | 2.0 | 22.7 | 0.6 | 490–514 |
| AC3F | methanol | air | 1.2 | 30.1 | 80.0 | 482–509 |
| AC3F | methanol | argon | 1.2 | 28.3 | 113.0 | 484–512 |

[a)] 10$^{-2}$ molar in HClO$_4$. [b)] Not determined. [c)] Dye at 1 × 10$^{-4}$ molar.

quantum yield in ethanol is less than that observed for 4PyPO-HClO$_4$ and is of the same magnitude as 4PyPO-MePTS, its lasing output is much better than these dyes in ethanol under argon (particularly better than 4PyPO-HClO$_4$ as we could not get this material to lase flashlamp-pumped starting with either 4PyPO or 4PyPO CHI from Aldrich). (We used HClO$_4$ rather than HCl because of the corrosive nature of the latter acid).

The results of attempts to lase 4PyMPO MePTS under air in ethanol show a very high threshold even though oxygen shows little effect upon the fluorescence (table 1). Thus, attempts to lase this dye in water or ethanol under air using flashlamp pumping would suggest a very poor dye. However, when dissolved in ethanol under argon, 4PyMPO–MePTS, is the longest-lived, moderate-output dye that we have tested. Only at 10$^{-4}$ molar did we measure a lifetime for it in ethanol. Going to 2 × 10$^{-4}$ *M* and using 600 ml of solution, the lasing output was slightly increasing after 50 hours of testing a continuous electrical input of 250 W. A similar high lifetime was observed using methanol under argon but with reduced laser output. In 2-propanol, however, the lifetime of 4PyMPO MePTS was only moderatly good. Again, oxygen caused a marked quenching of the lasing output in both of these last two solvents.

## 4. Blue-green dye solution comparison

For the optimum safety from fires, 4PyPO MePTS in water under argon would be the best dye solution of those examined here. For optimum output where lifetime was not critical, Coumarin 487 in methanol would be preferred at wavelengths to the blue side of 500 nm and Coumarin 314 would be preferred to the red side. However, if both output and long lifetime are of importance, AC3F would be the preferred dye.

## 5. Conclusions

The ability to predict the lasing characteristics resulting from molecular engineering of dye molecules is quite limited. Experimental parameters such as the choice of the solvent and its cover gas can markedly affect the results. The oxazoles, in particular, appear to be quite sensitive to such changes.

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