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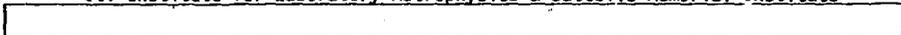
TUNABLE LASERS IN ISOTOPE SEPARATION: A COLORFUL VIEW OF A DYE CHEMIST

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TUNABLE LASERS IN ISOTOPE SEPARATION:
A COLORFUL VIEW OF A DYE CHEMIST*

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ABSTRACT

Some of the problems to be encountered in the possible large scale use of dye lasers in an isotope separation plant are discussed. Why should dye lasers be employed? How can dye photochemical decomposition and hence running costs be minimized and how serious is the effect anyway? What are toxicity problems with the dye? These and similar issues are examined.

On a technical side three topics are discussed. Firstly, the effect of laser dye deterioration on performance is examined algebraically in terms of disappearance of dye molecules and the appearance of a new, single chemical product having absorption in the fluorescence band for a single pass through a transversely pumped amplifier. Loss of output, defined as "quantum yield of laser deterioration", Q_L , is related to the true quantum yield of molecular destruction of the dye Q_M , and other known parameters. For the experimentally common, saturated gain condition, the smallest Q_L can be is Q_M , which requires a photochemically bleachable dye with high gain, preferably at high concentration, in a long cavity, operating at high injection and pumping fluxes. Reversing these conditions, the highest Q_L can be, compared with Q_M , is unrestricted.

6-Diethylamino 3-keto fluoran, an example of an oxygen tricyclic merocyanine, is described. It was first reported in the pre-1900 German literature under the name of Chromogen Red B and it is an ineffective lasing dye on account of low fluorescence quantum yield.

The techniques for measurement and the excited state absorption cross-sections are reported for the dyes rhodamine 6G fluoroborate in alcohol, rhodamine B basic solution in trifluoroethanol and kiton red S in trifluoroethanol.

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What I have to present is a very small part of our interest in laser isotope separation and laser-induced chemistry at Livermore. I am certainly interested and privileged to attend this workshop although I think my main reason for invitation to be here is that I know Steve and Mark. In some respects my interests are the very anti-thesis of the aims of the past speakers. I don't want to promote photochemistry in organic molecules, I want to prevent or circumvent it.

I am concerned with the use of dye lasers in a possible laser isotope separation process. A process my efforts would be directed toward relies on the isotope shift in the atomic uranium vapor spectrum. Thus, my interests bypass possible molecular separation processes, coincidences of known laser lines with the atomic spectrum, or other tunable lasers that could be matched to this spectrum. The first part of my talk will be concerned exclusively with the dye in such a large scale separation plant. My conclusion is that even in the present state-of-the-art, the dye is a viable option. The second part of my talk is concerned with a number of technical aspects of the dye. They are presented in the hope that they will be of interest in their own right, and they may, or may not be relevant to the problems of laser isotope separation and laser-induced chemistry. They are the algebraic analysis of the effect of laser dye deterioration on performance, the behavior of some new dye materials, and the measurement of excited state absorption.

For the wavelengths of interest, from the visible in the red, up to the ionization potential of uranium at about 200 nm, there are few coincidences of known laser lines with the atomic absorption. It is possible to employ physical "tricks", for example by mode selection of xenon laser lines we can produce coincidences and this was the basis of a separation experiment known locally as Project Morehouse which has been reported from this Laboratory. Unfortunately,

the xenon laser is an inefficient one and the separation process does not scale economically.

The dye laser on the other hand can be tuned to the wavelength of interest. At Livermore we are examining pulsed laser pumped dye lasers where the laser pumps are scalable systems such as the copper vapor laser and the doubled neodymium YAG laser.

Why do we use the dye? First, tunability. The organic molecule has a broad fluorescence band and by placing a dispersing element in the cavity we are able to select a fine line within the fluorescence band. The laser only has a high Q in the region where we force it to oscillate and because the stimulated emission process is homogeneous, we lose little in efficiency. Also, from the point of view of the dye, there is no restriction on bandwidth and band shape, thus the line can be shaped to match the atomic absorption lines, and there is no limitation in pulse length. Also, the range of wavelengths available from the dye presently extends from 340 nm to beyond a micron.

By a combination of dyes such as the rhodamines in suitable solvents we are able to cover the wavelength region from 530 nm to 700 nm using a copper vapor pump.

What are the problems we are having with the dye right now? Typical conversion efficiencies we are able to achieve are 20% whereas the theoretical limit varies but can be as high as 70%. Improvements in this depend largely on improvements in the dye. We are placing emphasis on improvements in quantum yield, improved matching of the dye absorption band with the pump line, and reduction of the excited state absorption cross-sections in the regions of the pump and fluorescence band.

What about dye cost? During operation we slowly observe deterioration of dye laser output and this is assigned to photochemical degradation. We, therefore, look upon the dye and dye medium as consumables in the isotope separation process. Such decay is a consideration but not an important one yet. Two of the common dyes, rhodamine 6G and rhodamine B, are sold large scale (100-150 tons a year) under the names of Basic Red 1 and Basic Violet 10 at about \$8.00 per pound. The first is an ingredient of red inks. These are quite sophisticated molecules as far as organic structures are concerned. My point is, if there is a need for these or any related materials we can expect the price to come down to this level. Consider a case where we pay \$50/lb., an extraction plant the size of Oak Ridge, a quantum yield of destruction of 10^{-4} and other reasonable assumptions. If we allow the lasers to decay from 100% to 90% of output and simply throw the dye away, this will add 20¢/SWU to the cost of extraction, a price less than the cost of electricity for running the pump lasers and would consume 100 tons of dye a year. We can do this now. An improvement in quantum yield by two orders of magnitude should reduce a small problem to a negligible one. From a chemical point of view, improved stability dyes may be prepared by systematically changing molecular structure to inhibit photochemical decomposition mechanisms. This approach has been extremely successful in the blue-green region of the spectrum for the Navy SAOCS Program. Another chemical approach is to find a selective scavenger, for example, an ion exchange resin for removing dye impurities in the dye flow circuit.

Another potential problem with the dye is toxicity; for example, Red Dyes number 2 and 4 have been withdrawn as food coloring additives. I don't think this is a serious issue. The materials we are using now, under the conditions we are using them have not been reported to be toxic, although properties of the newer dyes are admittedly unknown. Rats injected with rhodamine B

intermittently over the course of two years have been found to develop tumors. The minimum quantity of dye needed to produce this effect was 3.6 g per kg. of rat, and the animals were a violet color throughout the course of the experiment. This does not represent our operational conditions; so, the dyes we use are non-toxic. Even if they were toxic, it is not a difficult matter to change the dye molecular structure to reduce toxicity yet retain lasing properties. We use some exotic solvents to maximize laser output and the discarding of these would be expensive and polluting. Simply, we would redistill and reuse them.

Now to some of the more detailed technical problems. Suppose we do nothing about the dye, how can the laser system be designed, the oscillator or amplifier, to minimize the effects of dye deterioration? I will consider the simplest system imaginable, namely a single pass through a transversely pumped amplifier, and a dye that loses gain by two processes: photochemical loss of molecules and secondly by producing a decomposition product that absorbs in the fluorescence band. We are familiar with the term quantum yield of molecular destruction Q_M , meaning the probability that an absorbed photon will cause photodecomposition. Such a term is useful for describing the economics of the dye laser, although from a systems point of view, we are interested more in the laser not molecular decay. Consider a concept "quantum yield of laser destruction" Q_L , meaning the probability that an absorbed pump photon will cause laser deterioration. It is convenient to think of this, erroneously of course, that the loss of laser output is proportional to the loss of dye molecules. The first three viewgraphs (Figures 1, 2 and 3) shows the steps leading to the general relation between Q_L and Q_M for steady state, cw conditions. The gains for passes through the dye systems are shown for the initial and deterioration conditions. From the definitions of

Q_L and Q_M , the impurity absorption loss may be related at a certain decay period, for example at $t_{1/2}$, where the output has deteriorated to half of its initial value. The second viewgraph shows propagation in the amplifier for initial and deterioration conditions. Combining these equations leads to the relation between Q_L and Q_M (Figure 3), and the cases for small signal and saturated gain with their subcases of "bleachable" dye and a strong impurity absorbing dye. For the common saturated gain condition, slowest deterioration of the amplifier occurs for a "bleachable" dye, where Q_L values as small as Q_M may be seen to be possible. General conditions favoring small Q_L are a "bleachable" dye with high gain, preferably at high concentrations in a long cavity operating at high injection and pumping fluxes. Reversing these conditions, the highest value Q_L can be, compared with Q_M , is unrestricted. Figures 4 and 5 show typical variations of Q_L/Q_M against impurity absorption cross-section and gain across the dye medium, respectively.

Typical dyes we have been describing are of the well-known rhodamine type such as rhodamine 6G, kiton red S (Figure 6) and rhodamine B (Figure 7). They are examples of the xanthene cyanines or oxygen tricyclic cyanines. An example of an oxygen tricyclic oxonol is fluorescein. Materials that have not been reported are the xanthene merocyanines, which like the oxygen bicyclic merocyanines - the aminocoumarins, could be efficient laser dyes. 6-Diethylamino 3-keto fluoran (Figure 7) has been described in the pre-1900 chemical literature under the name Chromogen Red B, and it has recently been prepared and examined for lasing properties. Like rhodamine B, its fluorescence depends sensitively on solvent, being strongest in viscous solvents. It is much less efficient than the rhodamines as a lasing dye having a maximum response at 580 nm in ethylene glycol under nitrogen laser pumping.

Under strong laser pumping conditions a new chemical species is generated in solution, the excited S_1 state of the dye, which has its own absorption spectrum, and this can provide an energy loss mechanism. Measurements on excited singlet state absorption have been made with the apparatus of Figure 8. The dye in cell C is pumped at the absorption maximum, where the saturation flux is least. Pumping and probe beams, B_1 and B_2 , are furnished from simple 10 cm dye oscillators, made up of borosilicate optical flats, grating and dye cuvettes, pumped from the split output of an NRG nitrogen laser. The 8 ns FWHM, 2 nm bandwidth pulses are passed through spatial filters and the achromatic lenses L_1 and L_2 , focal lengths 50 and 20 cms respectively, onto an uncoated borosilicate beam splitter S. A 100 μ diameter pinhole P_1 in front of the dye-cell at the focus of L_1 permits through the most intense and homogeneous part of the pump beam (10% of total) as determined by the projection of the image from the lens L_3 . The probe beam B_2 subtends a larger diameter at the lens L_2 than B_1 at L_1 , also L_2 is a shorter focal length lens. Thus, from both diffraction and geometric optics considerations, the probe image is made smaller than the 100 μ pinhole. It is focused to 30 μ diameter, and placed at the center of the pinhole as determined by the projection from L_3 , also the probe beam is made colinear with the pump beam by removing L_3 and aligning the centers of the Airy Disk from B_1 and the projection from B_2 . Thus, the probe beam sweeps out a volume in the dye completely contained within the excitation beam volume. In order to keep the dye region as close to the pinhole as possible, the faces of regular 1 mm quartz cuvettes were ground and polished to 0.5 mm thickness. This way the exit face was no more than 2 mm from the pinhole, that is, about 10% of the d^2/λ diffraction distance. The output from L_3 was reflected onto a grating G and the first order reflexion of either B_1 or B_2 was collected on an ITT F4018 fast detector D_1 . Reference measurements of B_1 and B_2 were projected from the beam splitter S onto the same grating and hence onto a second detector D_2 . Outputs from D_1

and D_2 are compared directly on a Tektronix 7904 oscilloscope using fast 7A19 plug-ins, operating in an addition mode with a 10 ns cable delay between D_1 and D_2 . An improvement in technique would have been to employ a gated sampling integrator for comparing D_1 and D_2 .

Typical transmittances of the dye against incident intensity at the peak ground state absorption would be as shown in Figure 9. In the second saturated region, the excitation volume is assumed to consist entirely of excited state species and the measured transmittance is that of S_1 . Excited state absorptions at other wavelengths are now determined by means of the probe beam. Even the effective gain ($\sigma_e - \sigma^*$) may be probed in the fluorescence band.

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Initial response

$$\frac{dl}{dx} = \alpha l = \frac{\alpha_0 l}{\left(1 + \frac{l}{l_s}\right)}$$

By integration

$$\ln \frac{l_0}{l_1} + \frac{(l_0 - l_1)}{l_s} = \alpha_0 d$$

Response after deterioration

$$\frac{dl}{dx} = \alpha' l = (\gamma' - \beta) l = \frac{\gamma_0 l}{1 + \frac{l}{l_s}} - \beta l$$

$$\gamma_0 = \alpha_0 \frac{N'}{N} = \alpha_0 \left(1 - \frac{Q_M}{2Q_L}\right) \text{ at } t = t_{1/2}$$

By integration

$$\ln \frac{l'_0}{l_1} + \frac{l'_0 - l_1}{l_s} \left(1 + \frac{\beta}{\alpha'_0}\right) = \alpha'_0 d \quad \text{where } \alpha'_0 = \gamma_0 - \beta$$

FIGURE 1: EFFECT OF DYE DETERIORATION ON PERFORMANCE

Gain for a pass through the dye amplifier

Initial response

$$g = \alpha d - 1$$

$$= (\sigma_0 N_1 - \sigma_0 N_0) d - 1,$$

Response after deterioration

$$g' = \alpha' d - 1$$

$$= (\sigma_0 N'_1 - \sigma_0 N'_0 - \beta) d - 1 = (\gamma' - \beta) d - 1$$

Definitions of Q_M and Q_L

$$N_i = (N - N') = Q_M I_p A t / V$$

$$\frac{Q_L I_p A t}{NV} = 1/2 \text{ at } t = t_{1/2}$$

Impurity absorption loss

$$\beta = \sigma_i N_i = \frac{NQ_M}{2Q_L} \sigma_i$$

FIGURE 2: PROPAGATION WITHIN THE AMPLIFIER

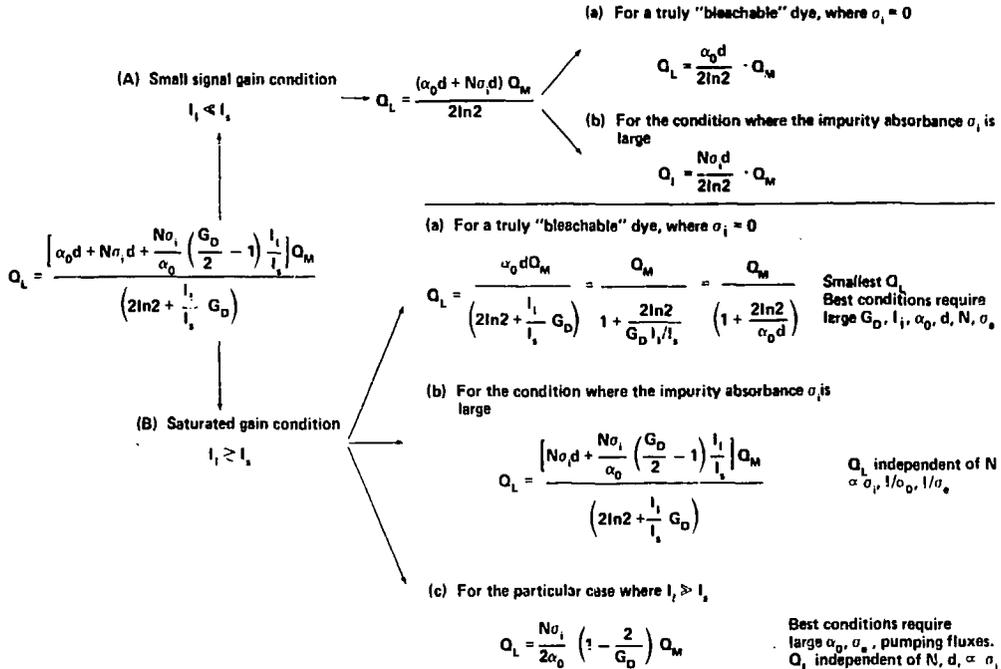
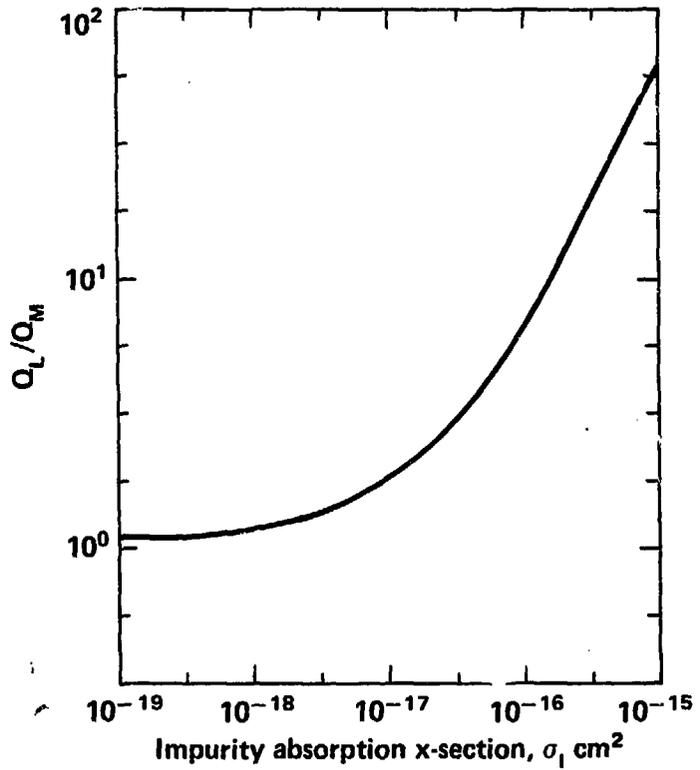
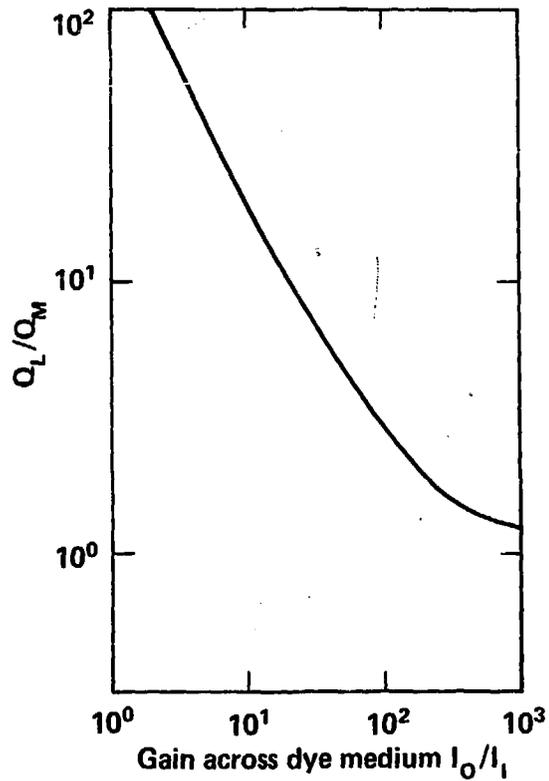


FIGURE 3: DEPENDENCE OF Q_L ON Q_M



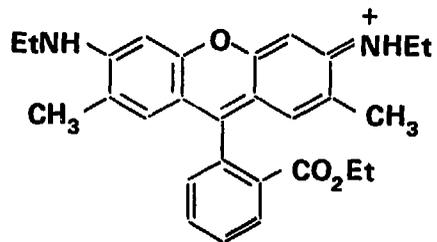
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FIGURE 4: DETERIORATION OF OUTPUT VS. IMPURITY ABSORPTION CROSS-SECTION

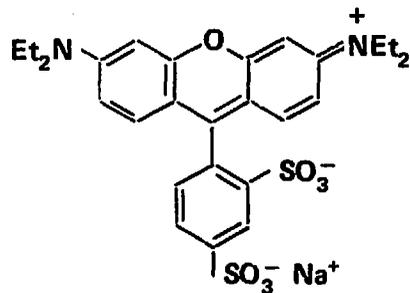


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FIGURE 5: DETERIORATION OF OUTPUT VS. GAIN ACROSS DYE MEDIUM

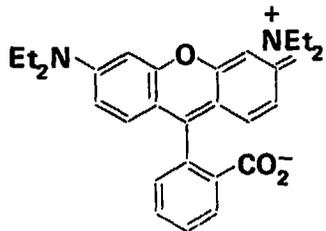


Rhodamine 6G

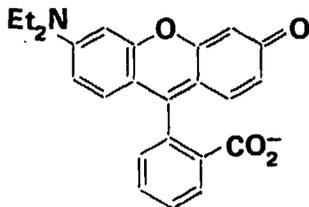


Kiton red S

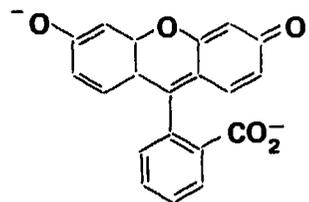
FIGURE 6: XANTHENE DYE MOLECULAR STRUCTURES



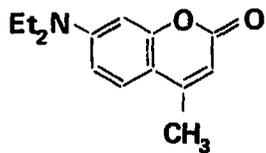
Rhodamine B



Chromogen red B



Fluorescein



**7-Diethylamino 4-Methyl
Coumarin**

FIGURE 7; DYE MOLECULAR STRUCTURES

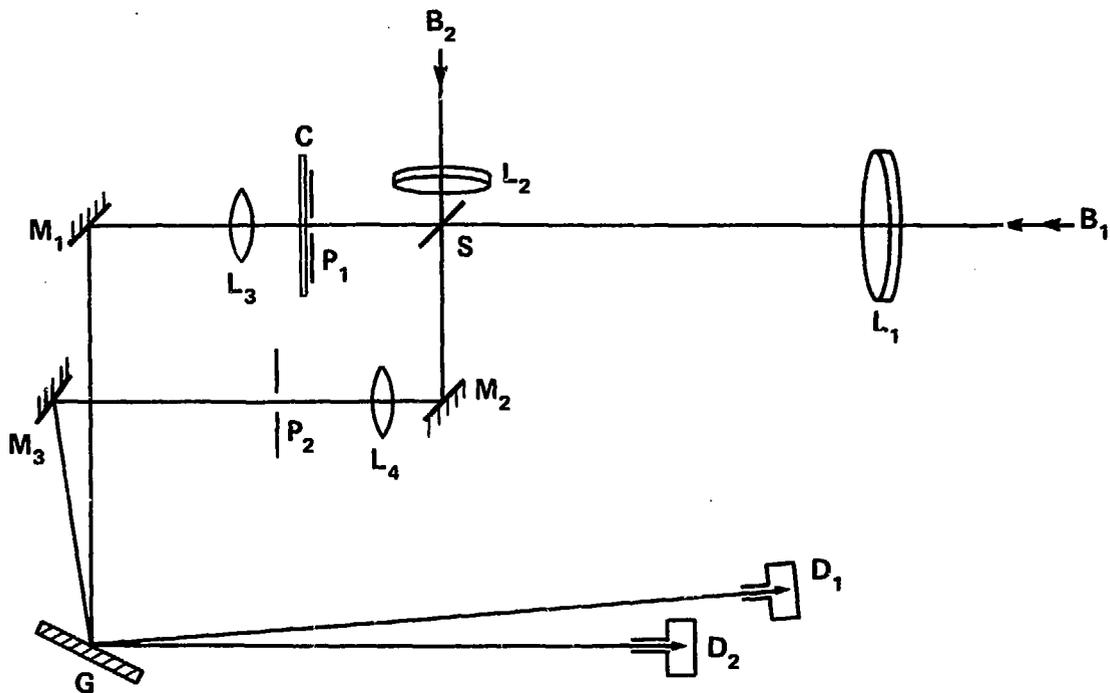


FIGURE 8: MEASUREMENT OF DYE EXCITED SINGLET ABSORPTION

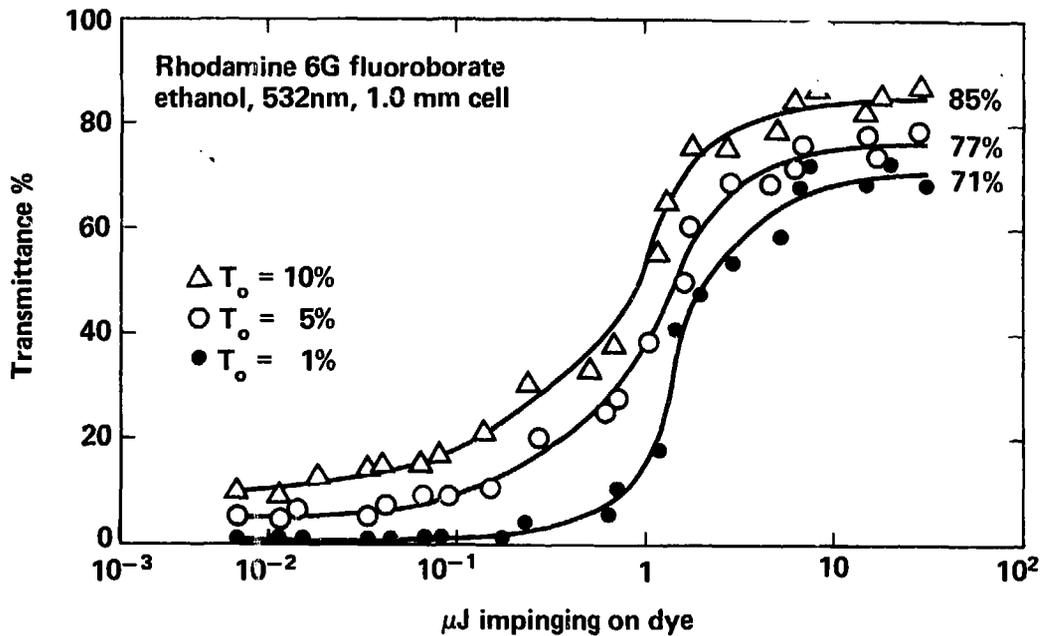


FIGURE 9: SATURATION CURVES FOR A LASING DYE