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DEVELOPMENT OF NEW LASER-PROTECTIVE DYES

FINAL, PHASE I REPORT

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DEVELOPMENT OF NEW LASER PROTECTIVE DYES

PHASE I PROJECT SUMMARY

The overall purpose of this Phase I research effort is to develop dyes that will be used to provide eye protection against lasers that emit light energy in the 650 nm to 1050 nm range. One of the major problems with available dyes is that they can be thermally and photochemically unstable. These drawbacks seriously limit the utility of present laser protective dyes. The objective of the Steadfast Phase I research program was to demonstrate the feasibility of stabilizing certain laser-protective dyes using Steadfast chemical and processing technology. This being accomplished, continued research in the synthesis and processing of additional dye systems that absorb throughout the desired wavelength region would be justified. Commercialization of laser-protective dye products in the form of ocular lens devices for generic and military applications should follow.

In the Phase I work, five different dyes were identified and/or synthesized and studied. Results showed that thermal stability was improved in four of the five dyes studied. This was accomplished by (a) chemical dye structure modification and (b) system additive methodology. In another set of experiments, excellent photochemical stability was found in one of the dye structures studied. Overall, background information is provided indicating the thermal stability of laser-protective dyes can be improved by applying Steadfast techniques. This Phase I work will help guide future research. Plans to incorporate dye systems into a prototype finished product (ocular lenses for field trial purposes) have been proposed in a Phase II program. Also included are plans to conduct research to uncover new laser-protective dye chromophore structures and additive systems. In this latter work, dye systems capable of broad-band absorption of laser-light energy have been proposed.

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Development of New Laser-Protective Dyes

FINAL REPORT - PHASE I PROGRAM

INTRODUCTION

The overall purpose of this research effort is to develop dyes that will provide eye protection against lasers that emit light energy in the 650 nm to 1050 nm range. One of the major problems with available dyes is that they can be thermally and photochemically unstable. These drawbacks seriously limit their utility as laser protective dyes. The objective of the Steadfast Phase I research program was to demonstrate the feasibility of using novel Steadfast chemical and processing technology to stabilize cyanine and squarylium dyes. This accomplishment will justify continued research on the synthesis and process development of additional dye systems. Laser-protective dyes meeting the rigorous in-field performance requirements of ocular products is the commercial goal of this program. This report details the results of Steadfast's Phase I studies.

The presently accepted technology for laser protection devices in both civilian and military applications is based upon dyes that absorb light at wavelengths corresponding to the emission wavelengths of the lasers. In practicing this technology, laser-light absorbing dyes have severe performance requirements such as:

- Sharp absorption bands at specific wavelengths corresponding to laser emissions.
- High extinction coefficients for efficient dye use.
- Strong resistance to saturation by impinging laser radiation.
- Robust thermal stability to enable the dye to survive processing-into-product conditions (e. g. being injection molded at 290°C in polycarbonate media to form an optical lens or shield).
- Stability to ambient conditions such as sunlight so that the optical product has a reasonable lifetime.

- Good solubility properties so the dye can be incorporated into protective lens products at sufficient concentrations to be effective.
- Low absorption in areas of the visible spectrum (other than protected wavelengths) so that the optical device will provide good visual acuity for the wearer in both daytime and nighttime situations.

No dyes have yet been developed that fulfill all these requirements. Currently known laser-protective dyes suffer from one or more of the following undesirable features:

- extraneous absorption bands in the visible region
- thermal instability
- photochemical instability
- easily saturated by laser radiation

Improved dyes are needed for laser protection in the visible to near infrared (NIR) region (690 nm to 1200 nm) and beyond. This is the subject of a proposed Phase II program.

RESULTS AND DISCUSSION

THERMAL STABILITY:

In Phase I, dyes of the cyanine and squarylium types were studied. Their general structures are presented in Figure 1 [I]. The detailed chemical structures of the dyes studied in Phase I are shown in Figure 2. The respective absorption spectra of these dyes are presented in Figures 3 and 4. Two techniques were demonstrated by Steadfast to improve the thermal stability of these dye systems:

- (1) synthetic modification of the dye structure.
- (2) stabilization chemicals used as dye additives.

The additive treatment included singular usage or combinations of : (a) PTA (phosphotungstic acid) and (b) surface active agents (e.g. Arquad 218). Thermal stability studies were carried out by coating the experimental dye systems onto polycarbonate (PC) powder and heating to 290° C for three minutes. This time/temperature treatment was chosen to approximate the conditions needed to injection mold PC resin into ocular lens devices. The details of sample preparation and thermal stability testing are presented in Appendix 1.

Results of thermal stability tests on Dyes 1, 2, 3, 3a and 4 are presented in Tables 1 and 2. Data in Table 1 were obtained using the initial thermal treatment developed during this Phase I study (Method 1 of Thermal Stability Test in Appendix 1).

Table 1 shows that the squarylium dyes are inherently more thermally stable than the cyanines. This observation supports literature reports about the poor thermal stability of cyanine dyes [2]. Certain combinations of dye and additive(s), PTA (phosphotungstic acid) and/or Arquad 218, are found to improve both cyanine and squarylium dyes' thermal stability. The simple cyanine (Dye 1 in Table 1) showed only a small response to the additive treatment. The "pinned back" cyanine, (Dye 2 in Table 1) responded somewhat more favorably to the additive. This "pinned back" cyanine represents a synthetic approach to thermal stability improvement. By "pinning back" pendant alkyl groups of the cyanine dye molecule, it was expected that the additional ring structure in the molecule would lead to a significant thermal stability improvement. While an improvement was indeed observed, it was less than expected. In summary, "pinned back" cyanines are more thermally stable than the simple cyanines but less stable than the squaryliums (Dyes 3 and 3a in Table 1). These observations lead to the Phase II proposal to study squarylium dyes in more detail.

Table 2 compares the stability of various squarylium dyes using an alternative sample preparation method (Method 2 in Appendix 1). Here, a portion of the prepared dye/PC or dye/additive/PC mixture is used as an internal standard (unheated). The other portion of the sample is subjected to the 290°C heat treatment. The two portions of samples are then compared spectrophotometrically. The unheated sample is used as the baseline. This modified procedure was used in an attempt to improve the reproducibility of the results.

The data in Table 2 indicates that all of the squaryliums survive this thermal test very well and that there is no significant difference between them. The addition of PTA does not show any effect. Because of the high recovery level of dye alone, only deleterious effects of additives can be observed. For example, the combination of Arquad with Dyes 3 and 3a show a diminution of recovered dye.

From these data, it appears that certain additive combinations (PTA and/or Arquad 218) can improve the thermal stability of cyanine and squarylium dyes. In addition, synthetic structural modification can also improve thermal stability. The squarylium dyes are significantly more stable than the cyanines. The squaryliums and similar dyes, deserve more concentrated study. Structural modifications of these dyes should be synthesized, and combinations with the stabilization systems should be evaluated.

TABLE 1
EFFECT OF ADDITIVES ON THERMAL STABILITY OF
EXPERIMENTAL DYES
 (Values presented in terms of percent recovered)

DYE #	CONTROL	DYE:PTA (1:1)	DYE:PTA + Ar (1:1:1)	DYE+ Ar:PTA (1:1:1)
1 CYANINE	8	14	7	8
2 "PINNED BACK" CYANINE	4	2	30	17
3 SQUARYLIUM (unsubstituted)	19	18	16	32
3a "PINNED BACK" and Hydroxylated SQUARYLIUM	57	17	89	-

ABBREVIATIONS: PTA- Phosphotungstic acid, Ar- Arquad 218,

DESCRIPTION OF DYE AND ADDITIVE COMBINATIONS:

DYE:PTA Complex formed by co-evaporating (mixture of Dye and PTA) from methanol

DYE:PTA + Ar Mechanical mixture of DYE:PTA and Arquad 218

DYE+ Ar:PTA Mixture of Dye and Ar:PTA complex (made by co-evaporating Ar and PTA from methanol)

NOTE:

All Dye additive combinations prepared according to Method 1, Appendix 1. They were mixed (in a dry form) with polycarbonate powder for thermal stability testing.

TABLE 2

THERMAL STABILITY COMPARISON OF SQUARYLIUM-DYES
AND ADDITIVE COMBINATIONS^{(a) (b)}
(values presented in terms of Percent recovered)

DYE #	CONTROL	DYE:PTA	DYE:PTA + Ar
3 SQUARYLIUM (unsubstituted)	96	77	31
3a "PINNED BACK" and Hydroxylated SQUARYLIUM	77	77	58
4 HYDROXYLATED SQUARYLIUM	78	87	71

(a) For abbreviations and descriptions see Table 1

(b) All dye/additive combinations prepared according to Method 2, Appendix 1. They were mixed (in a dry form) with polycarbonate powder for thermal stability testing.

The optical properties of the thermal decomposition products of laser-protective dyes are critical. If such by-products strongly absorb visible light, then photopic and scotopic transmission will be seriously impaired by any thermal lens manufacturing process such as injection molding. Figure 5 shows the negligible effect on visible absorption resulting from the thermal decomposition of Dye 3, a squarylium dye, with and without additives. This was generally observed for the squarylium chromophores. In the course of thermal testing none showed a significant absorption increase in the visible spectrum, even when, as shown in Figure 5 with Arquad only, most of the dye was thermally degraded by the experiment. Thus, we can conclude that thermal degradation by-products from squarylium chromophores, with or without these additives, are of minor concern in the development of suitable laser-protective lenses. The procedure used for these experiments was Method 2, described in Appendix 1. Samples of dye alone, dye with PTA, dye with PTA:Arquad, and dye with Arquad were prepared, thermally treated, and spectrophotometrically analyzed, as shown in Figure 5.

PHOTOCHEMICAL STABILITY:

Photochemical stability studies were conducted on **Dyes 1, 2 and 3** (see Figure 2). A solvent casting procedure was developed for preparation of clear, dyed, polycarbonate films as a model system for dyed lenses. This procedure does not require heating and yields clear samples of polycarbonate film containing the experimental dyes. The films were irradiated in a Rayonet Model RPR-208 photochemical reactor[3] to induce degradation of the chromophore by light absorption. The irradiated films were then analyzed spectrophotometrically for remaining dye concentration. The photochemical stability test procedure is detailed in Appendix 1. Results of these photochemical exposure experiments are presented in Table 3.

TABLE 3
PHOTOCHEMICAL STABILITY STUDIES

<u>DYE</u>	<u>APPROXIMATE HALF-LIFE</u>
1	35 min
2	20 min
3	3000 min
3a	1400 min
4	>20,000 min

The data in Table 3 shows that the squarylium chromophores (**Dyes 3, 3a and 4**), are markedly more stable to intense irradiation by near-infrared, visible and UV light than are the cyanines (**Dyes 1 and 2**). One of the squaryliums (**Dye 4**) exhibits exceptional photochemical stability compared with squarylium **Dyes 3 and 3a**. Coupled with their superior thermal stability and visually transparent thermal degradation by-products, squarylium chromophores represent the best candidate dyes, of those evaluated, for injection molding into laser-protective polycarbonate lens devices.

PHASE I PROGRAM CONCLUSIONS

1. Cyanine type dye chromophores exhibit the poorest thermal and photochemical stability among the dyes studied.
2. Squarylium dyes showed the best overall thermal and photochemical stability among the dyes studied. Their thermal degradation by-products do not absorb in the visible range. Squarylium dyes, therefore, represent the best candidates, evaluated thus far, for injection molding into laser-protective polycarbonate lens products. The commercialization of laser-protective dyes based on this Steadfast technology appears feasible.
3. The usefulness of phosphotungstic acid (PTA) as a thermal stabilizer is demonstrated. The appropriate quantities or ratios for maximizing the stabilization effect of the PTA additive has yet to be determined.
4. Mixtures of PTA and Arquad 218 (surface active agent) were found to enhance the thermal stability of some dyes. Optimum additive ratios and mixing sequences must be determined.
5. Synthetic modification of the squarylium chromophores led to dramatic (10X) differences in photochemical stability. Variations in thermal stability were not as dramatic because of the already excellent thermal properties of this class of dyes.
6. Photochemical stability studies by irradiating dye-containing polycarbonate films with near-infrared, visible and UV radiation show that squarylium dyes are more photochemically stable than the cyanines.
7. Laboratory techniques for approximating the thermal conditions of a dye/polycarbonate injection molding process have been developed. The technique involves coating the dye or dye/additive system onto polycarbonate powder and heating this coated powder (under a nitrogen atmosphere) for three minutes at 290°C. The dye concentration after treatment is measured by dissolving the dye/polymer sample in methylene chloride and determining the surviving dye concentration spectrophotometrically. These data are compared with untreated samples.

8. A photochemical stability test has been developed by casting a film of dye/polycarbonate system, irradiating the film in a near-infrared, visible and UV light source, determining the degradation characteristics of the dye spectrophotometrically, and comparing the data to non-irradiated films.

FUTURE PLANS

A follow-on research and development program has been prepared and submitted. In this Phase II work, a two year program of synthesizing and stabilizing new laser-protective dyes, especially for the near-infrared region is proposed. Two families of dyes will be investigated and methods of thermal and photochemical stabilization will be developed. During the first year, sets of lenses for field trials from at least five sets of dyes will be produced. In addition, technical reports will be generated describing the technology developed. It is expected that several dyes will be available for commercialization at the end of this Phase II program. Specific tasks to be carried out in Phase II are:

- Task 1. Review with technical monitor the major objectives of the laser-protective dye program.
- Task 2. Synthesize new squarylium, croconium and other candidate dye configurations that meet the listed performance requirements. Apply Steadfast's stabilization technologies as needed. Also, determine the effect of combining several dye systems in an effort to develop a broad band NIR absorber.
- Task 3. Extend Phase I test procedures. Develop and implement a technique for fabricating small, molded, laboratory test coupons of experimental dye/PC material.
- Task 4. Evaluate experimental laser-protective dyes and dye systems according to the test procedures developed in Task 3.
- Task 5. Review Steadfast Phase II results with technical monitor at appropriate times during the strategic parts of the program. Decide which laser-protective dye(s) are to be field tested. Proceed to injection mold the successful candidate dyes according to Tasks 6, 7 and 8. The synthesis effort will

cycle back to Task 2 and design-synthesize-prepare new compounds that will meet requirements. It is anticipated that at least five (5) different dye systems will be carried to field trial status during the course of this Phase II work.

Task 6. Discuss/decide/coordinate with outside injection molder (sub-contractor) the configuration and quantity of lens material/product to be field tested.

Task 7. Synthesize enough candidate laser-protective dye(s) and prepare enough dye/PC material for injection molding into prototype lens devices.

Task 8. Work with outside injection molder on fabricating final laser-protective lens products in the quantity and configuration specified by the contractor.

Task 9. Deliver final prototype lenses to contractor for field evaluation.

Task 10. Prepare final report on Phase II effort.

Deliverables during the first twelve (12) months of the Phase II effort are:

1. Preparation of at least five (5) candidate squarylium, croconium and other suitable laser-protection dye systems that appear to meet the requirements for such a product.
2. Issue monthly reports presenting the results of laboratory tests on the experimental dye systems as outlined in Tasks 2 and 5. Candidate laser protection dye(s) will be identified.
3. Deliver to the contractor twenty (20) prototype lenses for each candidate dye system selected for field testing.
4. Final report on Phase II effort.

APPENDIX 1: EXPERIMENTAL PROCEDURES USED IN THIS PHASE I STUDY

A. MATERIALS AND SAMPLE PREPARATION

The dyes used in this study were: Dye 1: pinacyanol chloride, Eastman Kodak 622, Eastman Kodak Co., Rochester, NY. Dyes 2, 3a and 4: Steadfast synthesized. Dye 3: Squarylium III, Aldrich Chemical Co., Milwaukee, WI. The phosphotungstic acid (PTA) was obtained from Aldrich Chemical Co, Milwaukee, WI. The Arquad 218 was obtained from AKZO -Chemical Division, McCook, IL. The polycarbonate (PC) was obtained from General Electric Company, Pittsfield, MA as a special, low additive polymer powder.

The stabilized dye complexes were prepared by combining equal weights of dye and PTA in a methanol slurry and evaporating the solvent after mixing for about 30 minutes. The residue is filtered, washed with ether and air dried. The Arquad:PTA complex was prepared in the same manner.

B. THERMAL STABILITY TESTING

Method 1: Initially, thermal stability was evaluated by mechanically dispersing dye and additives with pure polycarbonate powder (ca. 2mg dye/1gm powder) and then immersing a test tube containing the mixture in an oil bath at 290° C, under a nitrogen atmosphere, for three minutes. After cooling, the sample was dissolved in methylene chloride. The solution was then analyzed spectrophotometrically for remaining dye. The data shown in Table 1 were taken from samples treated this way.

Method 2: A methylene chloride solution of the dye is evaporated to dryness in a test tube. A weighed sample of polycarbonate powder is added, followed by a small volume of methanol which contains additives, as appropriate. The damp powder is dried in a vacuum oven several hours at about 45° C and then divided into two parts. One part is heated and analyzed as described above; the second is analyzed without heating, serving as a control for the first portion. Data presented in Table 2 were obtained using Method 2 prepared samples. Experience with this technique has shown somewhat better agreement among replications, but still without the +/-5%

precision the method should attain. Further improvement could come from better control of the nitrogen blanket during the heating stage, eg., minimization of cooling by the gas stream and rigid exclusion of oxygen. Improvements in thermal test methodology will continue during the course of this work.

C. PHOTOCHEMICAL STABILITY TESTING

Dyes were photochemically tested in films of polycarbonate, prepared by coating 15% solutions of polycarbonate in methylene chloride containing an amount of dye estimated to yield an absorbance of 1.5 absorbance units at their wavelength of maximum absorbance, in film 70 microns thick. Samples were coated on glass using a fixed gap and doctor blade, dried, and placed in a vacuum oven for several hours at 45° C. They were then removed from the glass slide, mounted, measured on a spectrophotometer, and exposed to broad band radiation in a Rayonet photochemical reactor [3]. The spectrum was remeasured periodically and the decay profile of the dye established from the loss in absorbance at the wavelength of maximum absorption. More accurate comparison of the decay rates of the dyes requires additional instrumentation and more precise measurements.

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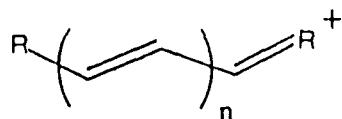
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d.) T. H. James, Ed., Theory of Photographic Processes, MacMillan, New York (1977).

- [3] Southern New England Ultraviolet Company, 55 Connally Pky., Hamden, CT, 1987 Catalog, Rayonet Special Preparative Photochemical Reactor.

Figure 1

General Chemical Structure of Cyanine and Squarylium dyes

CYANINES :



SQUARYLIUMS :

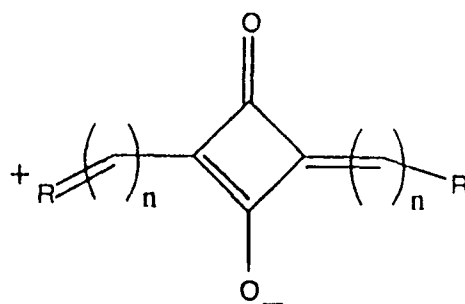


Figure 2
Chemical Structure of Dyes Studied in Phase I

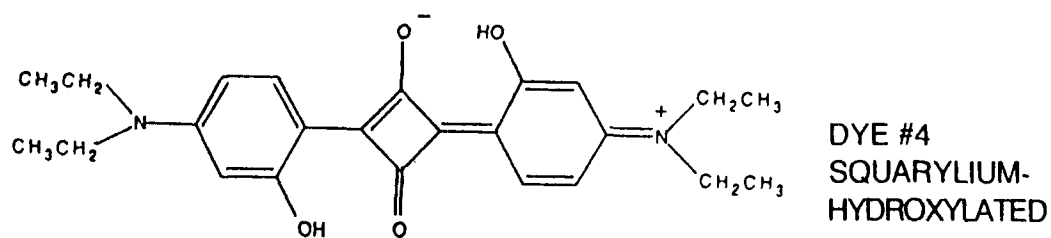
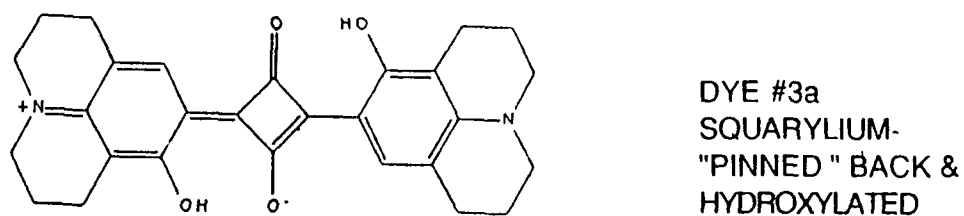
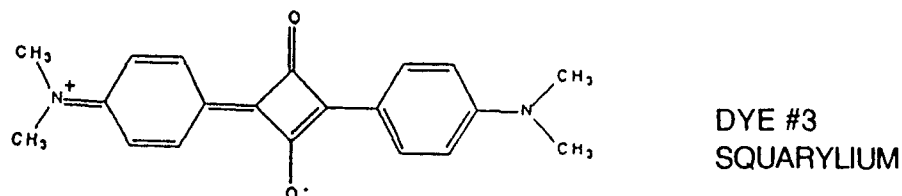
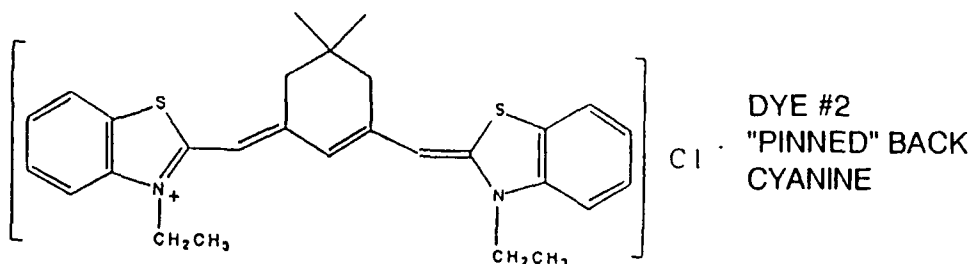
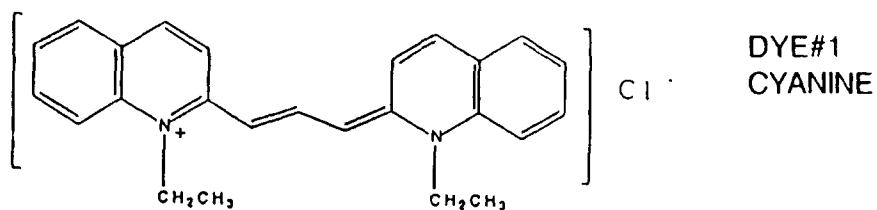


Figure 3
Absorption spectra of Dyes Studied in Phase I

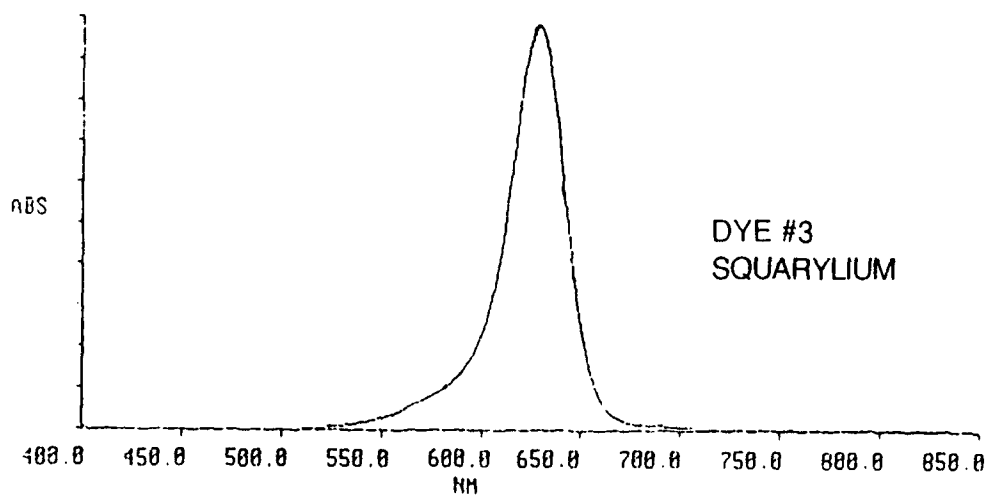
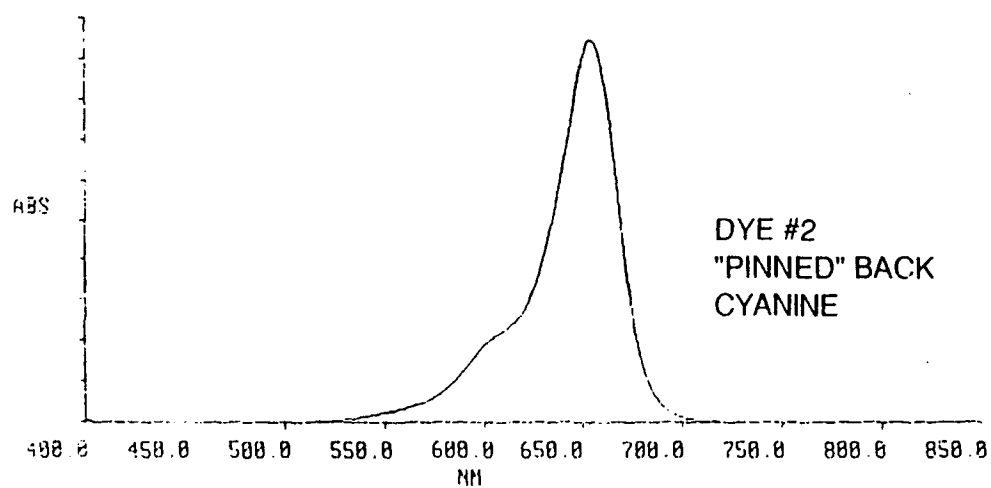
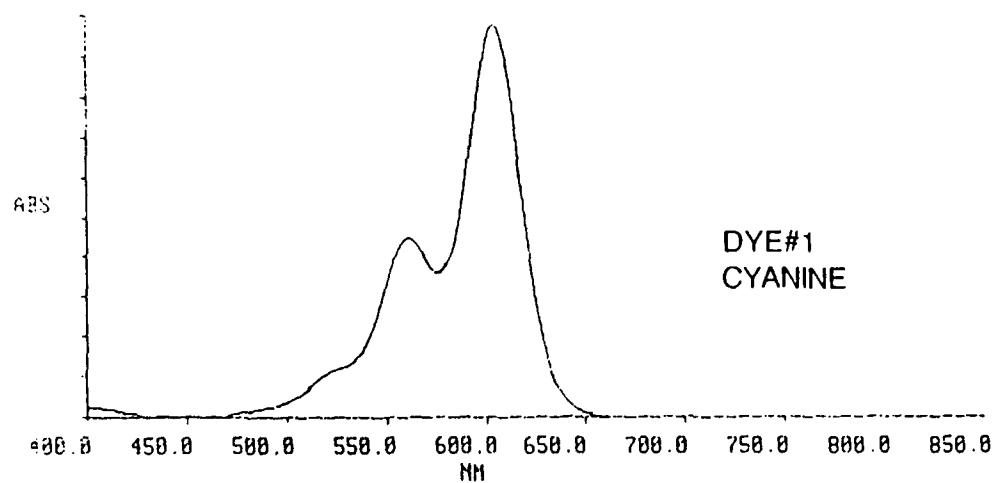


Figure 4
Absorption spectra of Dyes studied in Phase I

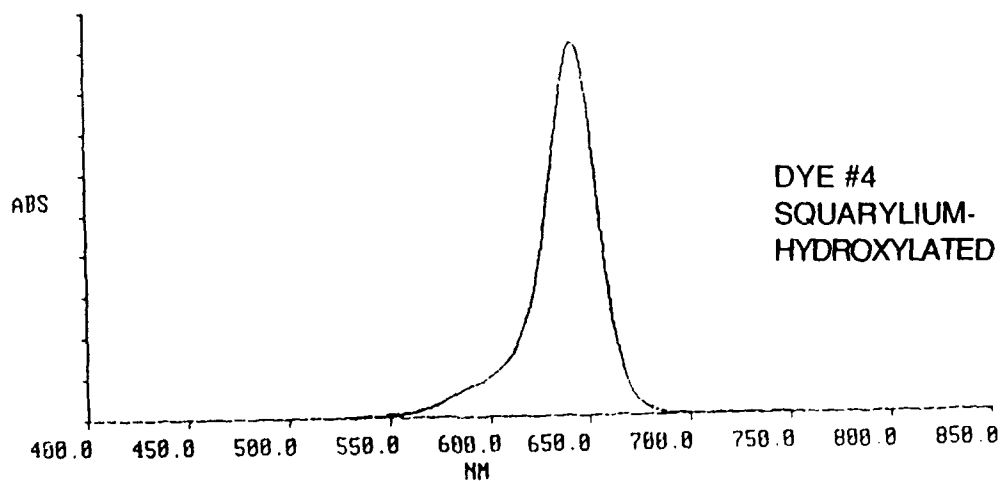
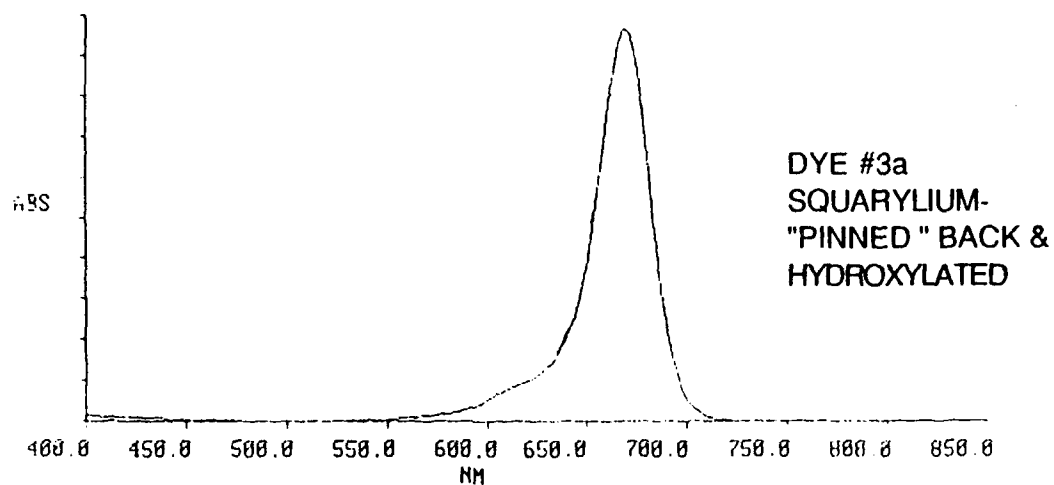
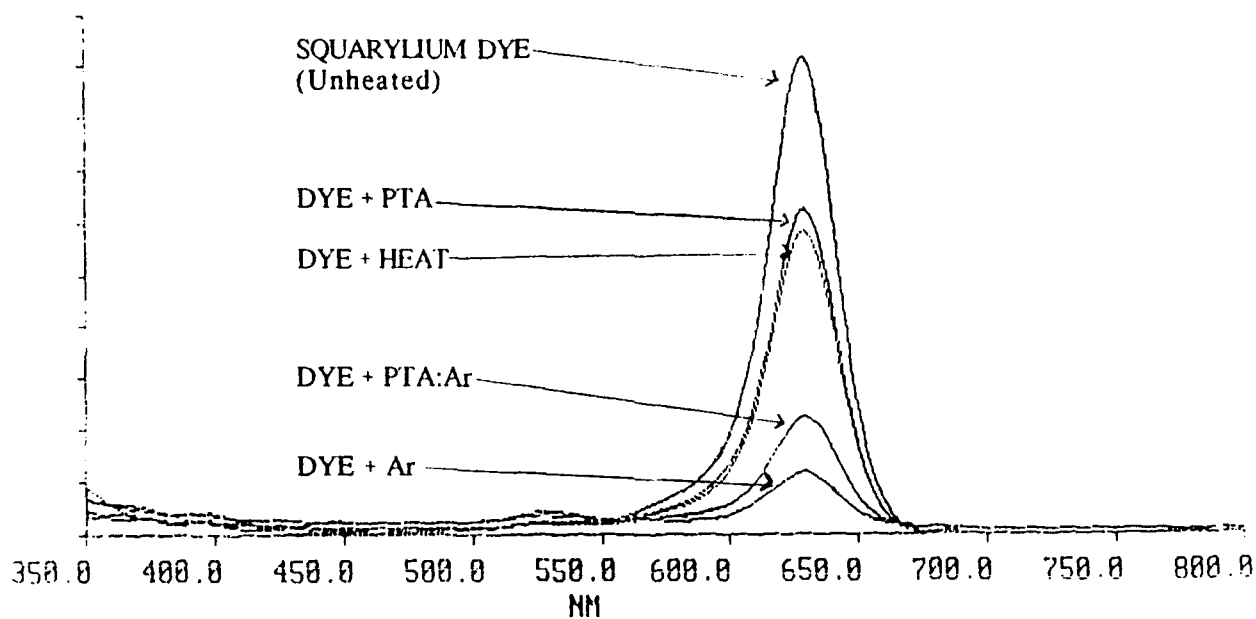


FIGURE 5

ABSORPTION SPECTRA OF HEAT TREATED (AT 290°C) SQUARYLIUM DYE
(DYE # 3 of Figure 2) AND DYE/ADDITIVE COMBINATIONS



ABBREVIATIONS : PTA - Phosphotungstic Acid
Ar - Arquad 218