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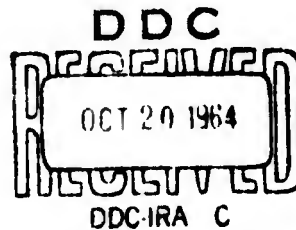
US ARMY NATICK LABORATORIES

TECHNICAL REPORT

TS-129

STUDY OF CHROMOTROPIC PROPERTIES
OF COLORANTS

449505



CLOTHING & ORGANIC MATERIALS DIVISION

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NATICK, MASSACHUSETTS

<p>AD- Div. 29-6 Accession No.</p> <p>UNCLASSIFIED</p> <ol style="list-style-type: none"> 1. Camouflage 2. Dyes 3. Clothing 4. Textiles 5. Colors 6. Photochromism 7. Thermochromism 8. Chromometry 9. Colorant 10. Coleman, Ralph A. 11. Foster, Walter H., Jr. 12. Donohue, Hugh C. 13. Mason, Marion 14. American Cyanamid Co. 15. Central 16. Title 17. Series 	<p>UNCLASSIFIED</p> <p>U. S. Army Natick Laboratories, Natick, Mass. STUDY OF CHROMOTROPIC PROPERTIES OF COLORANTS by Ralph A. Coleman, Walter H. Foster, Jr., Hugh C. Donohue and Marion Mason, February 1964, 71 pp illus (Textile Series Report 129).</p> <p>In order to explore technical feasibility regarding the use of chromotropic colorants for a "chromosome" type camouflage system, photochromic, thermochromic, and photochromic systems have been studied. Where possible, simple theoretical models for the various systems were analyzed mathematically to establish the thermodynamic and kinetic parameters which a suitable system must possess. Known compounds, representative of the three chromotropic classifications, were examined experimentally in both solution and polymer media. Consideration of the theoretical analyses and experimental results indicates that photochromic systems presently offer the most feasible approach for a chromotropic camouflage system. Of the presently available photochromic systems which were examined, the system based upon dibutone and its metal complexes--particularly HyGID--showed the most promising results. The dibutone system should provide a useful model system for future synthetic and physical chemical work in this area.</p>	<p>UNCLASSIFIED</p> <p>U. S. Army Natick Laboratories, Natick, Mass. STUDY OF CHROMOTROPIC PROPERTIES OF COLORANTS by Ralph A. Coleman, Walter H. Foster, Jr., Hugh C. Donohue and Marion Mason, February 1964, 71 pp illus (Textile Series Report 129).</p> <p>In order to explore technical feasibility regarding the use of photochromic, thermochromic, and photochromic systems, where possible, simple theoretical models for the various systems were analyzed mathematically to establish the thermodynamic and kinetic parameters which a suitable system must possess. Known compounds, representative of the three chromotropic classifications, were examined experimentally in both solution and polymer media. Consideration of the theoretical analyses and experimental results indicates that photochromic systems presently offer the most feasible approach for a chromotropic camouflage system. Of the presently available photochromic systems which were examined, the system based upon dibutone and its metal complexes--particularly HyGID--showed the most promising results. The dibutone system should provide a useful model system for future synthetic and physical chemical work in this area.</p>
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**U. S. ARMY NATICK LABORATORIES
Natick, Massachusetts**

CLOTHING & ORGANIC MATERIALS DIVISION

**Textile Series Report
No. 129**

STUDY OF CHROMOTROPIC PROPERTIES OF COLORANTS

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FOREWORD

Protection of military personnel from visual observation is still a most critical aspect of field camouflage, despite the development of new electronic detection systems, all of which require bulky equipment and special manipulation to cover a given area of the terrain.

Only a few colors of field uniforms are practical from a logistic standpoint, yet they must cover the whole spectrum of foliage and terrain background which nature provides. Accordingly, the possibility of using a color in combat clothing having some of the characteristics of a chameleon which could change to some degree against different backgrounds, has a great appeal to those concerned with providing protection to the soldier by camouflage coloration of his uniform and equipment.

The study being reported upon was designed to determine whether chromatropy of one form or another might provide an avenue to a possible chameleon-type system. As such, the work reported covers an analysis of potential systems, their rate constants, the influence of substrate, and a number of other factors. This is only the beginning of a much more extensive study which should include synthesis.

If and when a final chameleon-type chromotropic system is developed, it will unquestionably involve a great deal more than is possible by virtue of colorants alone. However, the work being reported at least gives encouragement to the idea that a chameleon-type system may become possible with further research.

The research described in this report was performed by the American Cyanamid Company, Organic Chemicals Division, Bound Brook, New Jersey, from October 29, 1962 to January 28, 1964, under Contract No. DA 19-129-AMC-19(X) (OI 9011), Project No. 1KO 24401A113 (09), sponsored by the U. S. Army Natick Laboratories, Clothing and Organic Materials Division, Natick, Massachusetts. Mr. F. J. Rizzo of the Textile Dyeing Branch, Natick Laboratories, was project officer.

At American Cyanamid, the project leader was Dr. Ralph A. Coleman. The research chemists who were assigned to the project and are the authors of this report are Dr. Walter H. Foster, Jr., Dr. Haig C. Donoian, and Mrs. Marion Mason.

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ABSTRACT

In order to explore technical feasibility regarding the use of chromotropic colorants for a "chameleon" type camouflage system, photochromic, thermochromic, and chemochromic systems have been studied. Where possible, simple theoretical models for the various systems were analyzed mathematically to establish the thermodynamic and kinetic quantities which a suitable system must possess. Known compounds, representative of the three chromotropic classifications, were examined experimentally in both solution and polymer media. Consideration of the theoretical analyses and experimental results indicates that photochromic systems presently offer the most feasible approach for a chromotropic camouflage system. Of the presently available photochromic systems which were examined, the system based upon dithizone and its metal complexes--particularly Hg(II)--showed the most promising results. The dithizonate system should provide a useful model system for future synthetic and physical chemical work in this area.

STUDY OF CHROMOTROPIC PROPERTIES OF COLORANTS

I. Introduction and Statement of Problem

The studies described in this report were carried out as part of a technical feasibility study on the utility of chromotropic colorants in the development of a camouflage system which would emulate the chameleon by adapting its color to the prevailing background.

Presumably the mechanism by which the chameleon blends into its surroundings is a neuromechanical one in which the proportion of the body surface covered by various colored cells is changed by expansion or contraction of the cells.¹

Conceptually a chameleon camouflage system based on chromotropic colorants would consist of colorant molecules in a polymer matrix, associated with a sensing system which would "pick up" a change in background color and translate this into a signal which would cause the chromotropic colorant to change its spectrum in order to match the new background color. The change in spectrum of the colorant would have to be brought about via regulation of some activating energy source (e.g., light, temperature, or electrical potential).

In the terminology of this report, the general phenomenon of color change induced by some stimuli will be referred to as chromotropism (color turning). The specific areas concerned with the various activating stimuli will be named as; photochromism for light-induced changes, thermochromism for temperature-induced changes, and chemochromism for "chemically" induced changes. The term "phototropism" frequently used for light-induced changes will not be used since this term already has a well established meaning in biology to describe the turning of a plant toward light.

Technical feasibility is probably most easily explored by setting up theoretical models and calculating, from these models, the particular thermodynamic and kinetic quantities which a system must have in order to satisfy the functional requirements which the particular application dictates. If rather well defined functional requirements can be set up, real systems can be studied experimentally and the results compared to the quantities calculated from the theoretical models.

An example of a feasibility study for which rather well defined functional requirements could be established is that carried out by O'Brien and Weissbein on "Attenuation of Thermal Radiation with Phototropic Colorants."² The specific functional requirements for this system were established so that the colorant would be nonphotochromic in sunlight and yet transform under thermonuclear radiation to increase the reflectance of a fabric from 10% to 80% of the incident radiation in 0.1 seconds.

In exploring the feasibility question with regard to chromotropic camouflage, two questions which must be answered before rigid functional requirements can be set up are:

1. What background colors will our system have to match?
2. How rapidly must the match be made?

Universal matching and instantaneous response can easily be set as the functional requirements for a perfect system, but since perfect systems undoubtedly do not exist, we probably will be better off if we try to establish what functional requirements can be met by presently available systems.

The approach adopted in this study was therefore primarily involved with experimental examination of some representative existing chromotropic colorants in solution and polymer media. These experimental results are analyzed to define the performance characteristics presently available and unique effects, as well as trends in the data, are used to recommend what directions future research in this area should take.

II. Photochromic Systems

A. Theoretical Considerations

In the following section, a simple working model is set up for a photochromic system. The equations developed are not completely rigorous and will strictly apply only under certain limited conditions. They can, however, aid in the estimation of optimum values for the various rate constants in the system.

Let us consider a photochromic system based on a reversible photoequilibrium between two species A and B where,



In this model the change from A to B is photoinduced and the B form is reconverted to the A form by a thermal process.

We can set up the following differential equation to describe the rate of this photochemical reaction,

$$\frac{-d(A)}{dt} = \frac{+d(B)}{dt} = \phi_{A \rightarrow B} I_{\text{abs}} - k_R(B) \quad (2)$$

where, (A) = concentration of form A in moles cm^{-2}

(B) = " " " " B " " "

t = time in sec.

$\phi_{A \rightarrow B}$ = quantum efficiency for the A to B phototransformation
moles einstein^{-1}

I_{abs} = intensity of light absorbed by the A form (over a specified wavelength band) einsteins $cm^{-2} sec^{-1}$

k_R = rate constant for the reverse thermal process sec^{-1}

In this equation, the rate of the photoforward process is taken to be proportional to the intensity of the light absorbed by (A), i.e. I_{abs} , since, from the Grotthus-Draper law, only the absorbed radiation can cause chemical change.³ The reverse thermal process is assumed to be unimolecular.

If I_0 is the incident light intensity, then for a thin, non-scattering film,

$$I_{abs} = I_0 - I_T \quad (3)$$

where, I_T = transmitted intensity.

For a scattering textile fabric,

$$I_{abs} = I_0 - I_R \quad (4)$$

where, I_R = reflected intensity
(diffuse reflectance)

For a camouflage fabric, equation (4) will have to be developed and used in the general rate expression given in equation (2). However, since all the quantitative work presented in this report was carried out on solutions or non-scattering films, equation (3) can be used in conjunction with Beer's law,

$$I_T = I_0 10^{-\epsilon C} \quad (5)$$

where, ϵ = molar absorptivity $cm^2 mole^{-1}$

C = concentration moles cm^{-2}

therefore,

$$I_{abs} = I_0 (1 - 10^{-\epsilon C}) \quad (6)$$

$$= I_0 (1 - 10^{-Abs}) \quad (7)$$

$$= I_0 (1 - T) \quad (8)$$

where, $T = \frac{I_T}{I_0}$ = transmittance (9)

Abs = absorbance

Placing the expression for I_{abs} from equation (6) in equation (2) gives us

$$\frac{-d(A)}{dt} = \frac{+d(B)}{dt} = \phi_{A \rightarrow B} I_0 (1 - 10^{-\epsilon(A)}) - k_R(B) \quad (2a)$$

This equation would apply rigorously if we were dealing with monochromatic radiation of wavelength λ . Then Beer's law [equation (5)] would be valid with $\epsilon = \epsilon$ at λ . However, since we are dealing with a light source which emits a continuous spectrum (sunlight), I_0 in equation (2a) will be the incident intensity within a specified wavelength band and ϵ will be an integrated value within the wavelength band. $\phi_{A \rightarrow B}$ will be an integrated or average value.

If our system is highly absorbing (i.e., $\epsilon(A) = \text{Abs} = \text{large number}$) then, from equation (6),

$$I_{\text{abs}} \approx I_0 \quad (10)$$

and equation (2a) reduces to

$$\frac{-d(A)}{dt} = \frac{+d(B)}{dt} = \phi_{A \rightarrow B} I_0 - k_R(B) \quad (2b)$$

If our system is weakly absorbing (i.e., $\epsilon(A) = \text{small}$), then, letting $\epsilon' = 2.303 \epsilon$

$$I_{\text{abs}} \approx I_0 \epsilon'(A) \quad (11)$$

and equation (2a) reduces to

$$\frac{-d(A)}{dt} = \frac{+d(B)}{dt} = \phi_{A \rightarrow B} \epsilon' I_0 (A) - k_R(B) \quad (2c)$$

Equation (2c) is identical to the expression used by Weissbein⁴ to describe attenuation of nuclear flash radiation with photobleaching dyes, with his value for k_F , the rate constant for the photoreaction, being given by:

$$k_F = \phi_{A \rightarrow B} \epsilon' \quad (12)$$

The approximation given in equation (11) holds best at values of $T > 0.7$ or $\text{Abs} < 0.155$, and is therefore reasonable to use in a photobleach system. It is also convenient to use equations (11) and (2c) in the present work since they lend themselves to simple mathematical manipulation.

If our system reaches a photostationary state or photo-equilibrium, with the forward rate equal to the reverse rate, then from equation (2c)

$$\phi_{A \rightarrow B} \epsilon' I_0 (A) = k_R (B) \quad (13)$$

and a photoequilibrium constant $K(\text{p.e.})$ can be defined as.

$$K(\text{p.e.}) = \frac{(B)}{(A)} = \frac{\phi_{A \rightarrow B} \epsilon' I_0}{k_R} = \frac{k_F I_0}{k_R} \quad (14)$$

During photoequilibration, since the concentration of (A) will be changing, I_{abs} will be a function of time,

$$I_{\text{abs}} = I_0 \int_0^t [1 - T(t)] dt \quad (15)$$

However, if we consider a differential change in I_0 , assume that I_{abs} is reasonably constant and that equation (11) holds, we can derive an expression for the response time of our model photochromic system. In this case our model system corresponds to opposing first order processes.



The following derivation leads to an equation which permits estimation of the photoequilibration half life $t_{1/2}(\text{p.e.})$ exhibited by a system in changing from one photostationary state at some initial intensity to a new photostationary state at intensity I_0 . From equation (2c)

$$\frac{d(B)}{dt} = k_F I_0 (A) - k_R (B) \quad (17)$$

If $(A)_D$ = concentration of (A) reached in the dark, i.e., total concentration of colorant = $(A) + (B)$.

$$\frac{d(B)}{dt} = k_F I_0 [(A)_D - (B)] - k_R (B) \quad (18)$$

at photoequilibrium,

$$k_F I_0 \int (A)_{D-(B)_e} = k_R (B)_e \quad (19)$$

or

$$k_R = \frac{k_F I_0 \int (A)_{D-(B)_e}}{(B)_e} \quad (20)$$

Placing the value for k_R from (20) in (18)

$$\frac{d(B)}{dt} = k_F I_0 \int (A)_{D-(B)} - \frac{k_F I_0 \int (A)_{D-(B)_e} (B)}{(B)_e} \quad (18a)$$

$$= \frac{k_F I_0 (A)_{D-(B)_e} - (B)}{(B)_e} \quad (18b)$$

$$\int_{(B)=(B)_0}^{(B)=(B)_t} \frac{d(B)}{\int (B)_e - (B)} = \frac{k_F I_0 (A)_D}{(B)_e} \int_{t=0}^{t=t} dt \quad (21)$$

$$\left[-\ln \int (B)_e - (B) \right]_{(B)_0}^{(B)_t} = \frac{k_F I_0 (A)_D}{(B)_e} \left[t \right]_0^t \quad (22)$$

$$\frac{k_F I_0 (A)_D}{(B)_e} = \frac{1}{t} \ln \frac{(B)_e - (B)_0}{(B)_e - (B)_t} \quad (23)$$

from equation (19)

$$\frac{k_F I_0 (A)_D}{(B)_e} = k_F I_0 + k_R \quad (24)$$

therefore, from (23)

$$k_F I_0 + k_R = \frac{1}{t} \ln \frac{(B)_e - (B)_0}{(B)_e - (B)_t} \quad (25)$$

for a photoequilibration half life, $t = t_{1/2}$ (p.e.)

$$\frac{(B)_e - (B)_o}{(B)_e - (B)_t} = 2 \quad (26)$$

$$t_{1/2} \text{ (p.e.)} = \frac{2.303}{k_F I_o + k_R} \log 2 \quad (27)$$

$$t_{1/2} \text{ (p.e.)} \approx \frac{0.693}{k_F I_o + k_R} \quad (28)$$

The more general form of equation (28) is,

$$t_f = \frac{2.303}{k_F I_o + k_R} \log \frac{1}{(1-f)} \quad (29)$$

where f = fraction toward attainment of the new photoequilibrium at I_o .

Equations (14) and (28) can therefore be used to characterize our simple system with regard to -

- a - The position of photoequilibrium at intensity I_o .
- b - The time required for the system to change from one photostationary state to another.

Since a, depends on the ratio of the rate constants while b, depends upon the sum of the rate constants, at any value for I_o , specification of both a and b is required in order to uniquely define a system with particular values of k_F and k_R . For example, if we require the photoequilibration half life to be 5 seconds and also require that the system be 90% converted from A to B in full sunlight ($I_o \approx 6 \times 10^{-8}$ einsteins $\text{cm}^{-2} \text{sec}^{-1}$),

$$k_F (6 \times 10^{-8}) + k_R \approx 0.693/5 \quad [\text{From equation (28)}]$$

$$\frac{k_F (6 \times 10^{-8})}{k_R} = \frac{.9}{.1} = 9 \quad [\text{From equation (14)}]$$

$$\text{and } k_F = 2.06 \times 10^6 \text{ cm}^2 \text{ einstein}^{-1}$$

$$k_R = 1.38 \times 10^{-2} \text{ sec}^{-1} \quad (t_{1/2} = 50 \text{ sec.})$$

However, this system will still be over 50% converted in weak sunlight ($I_0 \approx 1 \times 10^{-6}$ einsteins $\text{cm}^{-2} \text{sec}^{-1}$)

$$\frac{(2.06 \times 10^6) (1 \times 10^{-8})}{(1.38 \times 10^{-2})} = K(\text{p.e.}) = 1.45 = 59\% \text{ converted}$$

therefore % conversion from A to B (and the color of the fabric) will change abruptly at low light levels.

Using the range of sunlight intensity values given in the following section (1 to 6×10^{-8} einsteins $\text{cm}^{-2} \text{sec}^{-1}$), a series of calculations similar to the above was generated to establish optimum values for k_F and k_R which would satisfy the response time requirement $t_{1/2}$ (p.e.) ≤ 5 sec. and yet produce a noticeable change in the position of photoequilibrium over the range of intensity values found in sunlight. The results of these calculations indicate that k_F and k_R should be within the following ranges:

$$1 \times 10^6 \leq k_F \leq 5 \times 10^6 \text{ cm}^2 \text{ einstein}^{-1}$$

$$.01 \leq k_R \leq .05 \text{ sec}^{-1} \text{ (half lives of 69 and 14 seconds, respectively)}$$

Note that a typical dye which might have a value of $\Sigma = 6 \times 10^7 \text{ cm}^2 \text{ mole}^{-1}$ should have ϕ values ranging from

$$\phi_{A \rightarrow B} = \frac{5 \times 10^6 \text{ cm}^2 \text{ einstein}^{-1}}{(2.303) 6 \times 10^7 \text{ cm}^2 \text{ mole}^{-1}} = 0.036$$

to

$$\phi_{A \rightarrow B} = \frac{1 \times 10^6 \text{ cm}^2 \text{ einstein}^{-1}}{(2.303) 6 \times 10^7 \text{ cm}^2 \text{ mole}^{-1}} = 0.0072$$

Equations (14) and (28) are also used in the experimental sections to show the operating characteristics which presently available photochromic systems possess.

B. Sunlight Intensity and Variation

The available literature was searched for data on variations of sunlight intensity with time of day and time of year for both full sunlight and skylight. Most references reported values in terms of luminous flux or other units relating to human vision.^{5,6,7,8} Since translation of these values into absolute energy units is rather inaccurate, they are not included in this survey.

Three references did report values for sunlight spectral distribution in absolute energy units.^{9,10,11} From these data, distributions in terms of einsteins/sec./cm² have been calculated and plotted. (Figure 1 and accompanying table in Appendix)

Only one source⁹ gave values for both direct sunlight and sky light. These were recorded in July. Hirt, et al¹⁰ gave variations of direct sunlight in the UV region with time of year at noon.

There are no available data on the variation of total sunlight and sky light with the seasons and time of day. This is an area in which more data would be valuable.

Some calculations were made on changes in full sunlight intensity with air mass from the data available, using the formula,

$$I = I_0 a^m$$

where,

I_0 = intensity at 0 air mass

m = air mass

a = attenuation or scattering coefficient

Assuming an air mass of 1.02 for the Luckiesh⁹ data (July, Cleveland) a was calculated for two wavelength regions: ($500 \pm 20 \text{ m}\mu$, $a = 0.81$), ($350 \pm 20 \text{ m}\mu$, $a = 0.56$). Table I shows the calculated variation of sunlight intensity with time of day in summer and winter at 40° latitude.

TABLE I

Calculated Variation in Sunlight Intensities

	<u>Time of Day</u>	<u>Solar Altitude</u>	<u>Air Mass (m.)</u>	<u>500±20 mμ² ein./sec/cm²</u>	<u>350±20 mμ² ein./sec/cm²</u>
<u>July</u>	Noon	90°	1.02	2.38 x 10 ⁻⁸	0.73 x 10 ⁻⁸
	10:00 a.m. or 2:00 p.m.	60°	1.15	2.32 x 10 ⁻⁸	0.67 x 10 ⁻⁸
	8:00 a.m. or 4:00 p.m.	38°	1.6	2.10 x 10 ⁻⁸	0.514 x 10 ⁻⁸

TABLE I (cont'd)

	Time of Day	Solar Altitude	Air Mass (m.)	500±20 m μ ein./sec/cm ²	350±20 m μ ein./sec/cm ²
Jan. 20	Noon	30°	2.0	1.95 x 10 ⁻⁸	0.41 x 10 ⁻⁸
	10:00 a.m. or 2:00 p.m.	25°	2.4	1.79 x 10 ⁻⁸	0.32 x 10 ⁻⁸
	8:00 a.m. or 4:00 p.m.	10°	5.6	0.905 x 10 ⁻⁸	0.052 x 10 ⁻⁸

From the data available it is not possible to calculate corresponding changes in skylight alone. However, measurements given in luminous units and measurements of UV below 300 m μ indicate that at times other than noon in the summer, skylight contributes a considerable portion of the total sunlight.

C. Experimental Studies

In order to explore the feasibility of using photochromic colorants for chromotropic camouflage, some systems representative of those presently available have been studied experimentally in both solvent and polymeric media. The major emphasis has been on studies in polymers since considerable information on photochromism in solution is available in the literature.

The bulk of the experimental work was carried out on two classes of photochromic compounds.

- a. Dithizone and its metal complexes (particularly Hg^{II}).
- b. Spiropyrans.

Several other systems were briefly examined, but since the above two appeared to offer the most promise for the intended application, work was concentrated upon them.

1. Dithizone and Its Metal Complexes

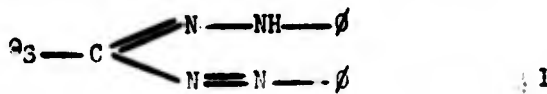
Dithizone (diphenyl thiocarbazono) (HDz)* is a well known analytical reagent used for the colorimetric determination of trace amounts of metals. It forms strong, highly colored complexes with a large number of

* As per the recommendation of Irving et al.¹³ we use the symbol HDz to represent the acidic reagent (C₁₃H₁₂N₄S) and Dz for the monovalent ligand (C₁₃H₁₁N₄S).

metals, including Hg(II), Cu, Pb, Bi(III), Pd, Ag, Au, Zn, and Cd. Despite its widespread use for this purpose, photochromism in this system has only been briefly mentioned and no detailed studies have appeared.

During the present research and through studies carried out at Cyanamid's Stamford Laboratories by Meriwether and co-workers,¹² it has been shown that dithizone itself and several of its metal complexes are photochromic.

The spectrum of dithizone is markedly dependent upon solvent and pH. The absorbing species responsible for the various bands have not been definitely established. The spectrum of dithizone in benzene is shown in Figure 2. This green solution, with peaks at 450 mμ (ε=18,800) and 620 mμ (ε=35,000), turns orange (λ_{max}=465 mμ) upon extraction into aqueous base. Irving et al¹³ have shown that dithizone is a monobasic acid with pK_a of about 5. The orange solution in base is therefore due to the dithizonate anion, Dz⁻(I)



but the green solution can be due to one or both of the following tautomers II:



It has not been possible to definitely establish which tautomer is responsible for which band in the absorption spectrum of dithizone. Attempts to examine the NMR spectrum were unsuccessful due to the limited solubility of dithizone in solvents suitable for NMR.

Dithizone has been found to be photochromic,

a. In toluene at room temperature by flash photolysis (De Bruyne¹⁴),

b. During the present work, in hexane and polystyrene film.

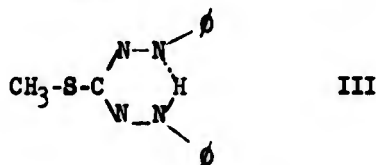
At room temperature the thermal returns were very rapid and it was necessary to use intense light sources in order to build up appreciable concentrations of the B form. Figure 3 shows the spectrum of dithizone in hexane before and during illumination, at low temperature, using the Cary 14 near infrared source. Figure 4 shows the spectrum in polystyrene film at low temperature. These spectra clearly show that the original green color, with two peaks, changed to pink with a λ_{max} at about 530 mμ.

In Figure 3, the curve which was run after prolonged irradiation shows that a species absorbing at 410-420 $m\mu$ is beginning to form. To see if this was caused by oxygen, the hexane solution was vacuum pumped and sealed in a glass cell suitable for spectrophotometry. Figure 5 shows the spectra for unirradiated and irradiated solutions. Note that the 410-420 $m\mu$ species did not form when oxygen was excluded. (the relative intensities of the unirradiated and irradiated curves may have been influenced somewhat by moisture condensation on the cell walls).

Further evidence for the photodecomposition (photooxidation) of dithizone was obtained when the solution of dithizone and polystyrene in benzene, used to cast the film whose spectrum is shown in Figure 4, was allowed to stand on the bench top, exposed to sunlight and room light from fluorescent bulbs. After two months a film cast from the same solution gave the spectra shown in Figure 6. This sample was still photochromic but no 530 $m\mu$ species was produced. Only the absorbance at 430 $m\mu$ was decreased upon irradiation.

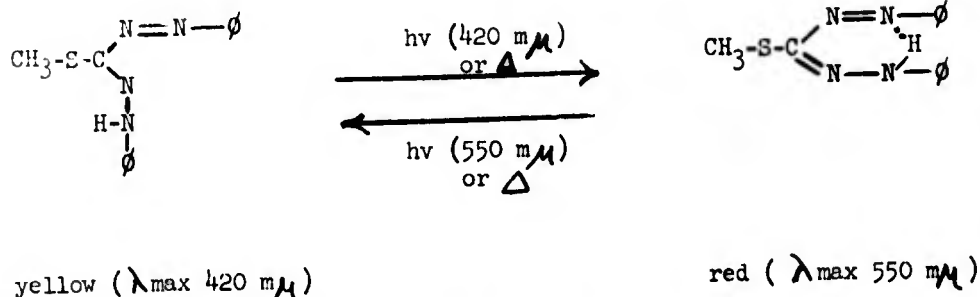
The sample of dithizone in polystyrene film, originally used to obtain Figure 4, was left in a yellow envelope in a desk drawer for well over two months and the spectrum was essentially unchanged from Figure 4, indicating that the decomposition was light-initiated.

During the course of this research, the S-methyl analog of dithizone (3-methylthio-1,5-diphenylformazan) was synthesized and examined for photochromism.

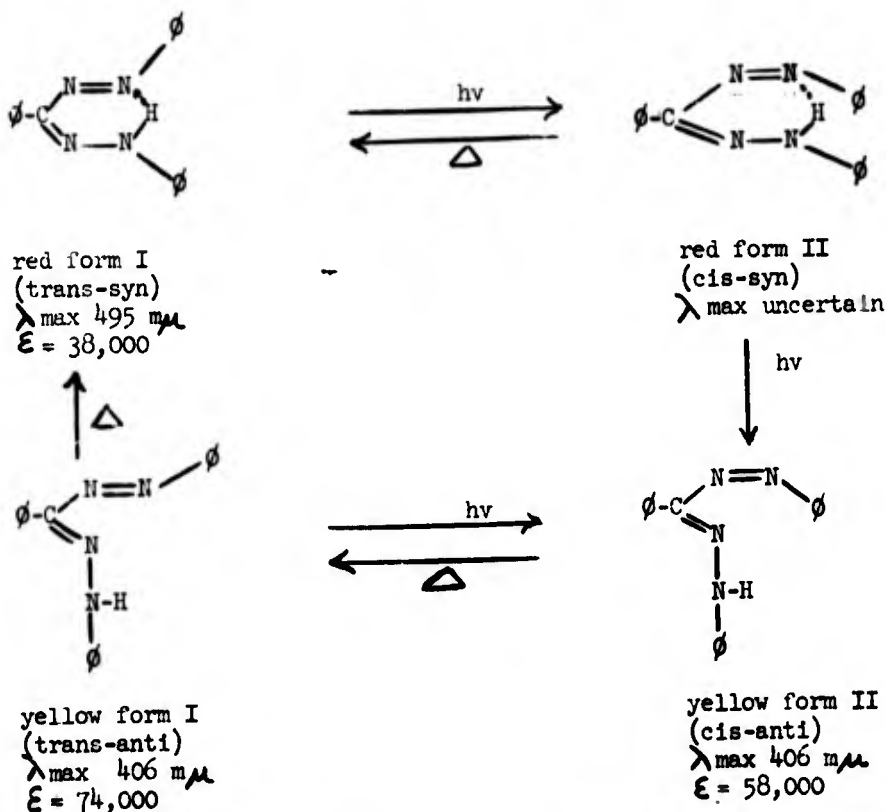


This material is photochromic in cellulose acetate, the spectra being given in Figure 7. The spectrum of the system in the dark consisted of two peaks, one at 420 and another at 550 $m\mu$. This system was found to have photoforward and photoreverse steps, the thermal return steps being very slow. The photo-photo nature of this system is illustrated in Figure 7. Curve B was taken after the cellulose acetate film sample was irradiated with the Cary 14 near infrared tungsten lamp, through a Corning CS 5-56 band pass filter peaking at 440 $m\mu$ and a KG-3 infrared absorbing filter. When the sample was thus irradiated with light of the lower wavelength peak, the system was shifted in favor of the long wavelength species. When the irradiation was carried out through a filter which transmitted light from 520 to 900 $m\mu$, using a 520 $m\mu$ cut-off filter, along with the KG-3, curve C was produced. Thus, irradiation with long wavelength light pushed the equilibrium back to the short wavelength absorbing species. The two species may involve cis-trans isomerization about the C=N double bond with the cis form being in a formazan type structure, hence the long wavelength shift of 130 $m\mu$.

* Fish Schurman Corporation, New Rochelle, New York.



The above type of photochromism has been observed for triphenylformazan by Kuhn and Weitz¹⁵. They found triphenylformazan to be photochromic in toluene at 0°C going from red to yellow. They gave the following scheme for the photochromism.



Following up literature reports that Hg(II) bisdithizonate (HgD_2) was photochromic,^{50,51} Meriwether and co-workers¹² synthesized and examined the photochemistry of a number of metal complexes of dithizone. The complexes were examined over a wide temperature range in solvents

such as methylene chloride, chloroform, and tetrahydrofuran. Of those found to be photochromic under steady illumination with visible light, the thermal return rates of all but $\text{Hg}(\text{Dz})_2$ and $\text{Pd}(\text{Dz})_2$ were very rapid at room temperature. During the present research PdDz_2 , AgDz , CdDz_2 , and several mercury (II) dithizonates were studied.

The spectrum of PdDz_2 dissolved in tetrahydrofuran (THF) is shown in Figure 8. The solid curve is for the unirradiated solution (peaks at λ_{max} 450 $\text{m}\mu$, $\epsilon = 41,800$ and λ_{max} 650 $\text{m}\mu$, $\epsilon = 35,600$). Upon irradiation with the Cary 14 near infrared source at room temperature, the steady state spectrum (dashed line) was obtained. Both peaks at 450 and 650 $\text{m}\mu$ decreased in intensity while increased absorption is evident at about 500 $\text{m}\mu$.

When PdDz_2 was incorporated in polymers the photochromism was similar to that observed in THF solution. Figure 9 shows unirradiated and steady state irradiation curves for PdDz_2 in cellulose acetate film at low temperature. The photochromic form (pink) has a peak at λ_{max} 485 $\text{m}\mu$. The $t_{1/2}$ for thermal return at room temperature was about 2-3 minutes. The behavior of PdDz_2 in other polymers such as poly(methyl methacrylate) and polystyrene was similar to cellulose acetate although some degree of irreversibility was observed in PMMA.

Cadmium bisdithizonate (CdDz_2) was a highly insoluble orange-red compound with λ_{max} 510 $\text{m}\mu$ ($\epsilon = 68,000$) in THF. It did not show any signs of photochromism at room temperature, ice or dry ice temperature.

The silver monodithizonate (AgDz) was also extremely insoluble. A saturated solution in benzene had an absorbance of 0.3233 (1 cm. cell) at λ_{max} 470 $\text{m}\mu$. It did show photochromism at room temperature in benzene, CH_2Cl_2 , and THF with conversions of 42%, 31%, and 46% respectively. In cellulose acetate the conversion to the blue form was approximately 15% when irradiated with the Cary 14 near infrared source. The return rate was not measured but appeared slow by visual observation.

In addition to mercury bisdithizonate (HgDz_2), it is possible to synthesize complexes of dithizone with an organomercury compound (i.e., CH_3HgX , $\text{O}(\text{HgX})$) to obtain mercury monodithizonates of the form RHgDz and ArHgDz . The general characteristics of the mercury dithizonates are as follows:

- a. Initial unirradiated colors of yellow to red
(λ_{max} 475 $\text{m}\mu$ - 510 $\text{m}\mu$)
- b. Irradiated colors of blue (λ_{max} 590 $\text{m}\mu$ - 605 $\text{m}\mu$)

The photochemistry of two compounds, HgDz_2 and CH_3HgDz , was studied quite thoroughly in solution and polymeric media.

Figure 10 presents spectra for HgDz_2 in benzene solution. The A or dark form has $\lambda_{\text{max}} = 490 \text{ m}\mu$; $\epsilon = 64,200$ and the irradiated or light (B) form (dashed line) has $\lambda_{\text{max}} = 605 \text{ m}\mu$.

Figure 11 presents spectra for CH_3HgDz in benzene. The dark A form has $\lambda_{\text{max}} = 475 \text{ m}\mu$; $\epsilon = 33,500$ and the B form has $\lambda_{\text{max}} = 600 \text{ m}\mu$.

It was difficult to obtain 100% conversion from A to B in order to evaluate ϵ for the B form. However, in those cases where conversion appeared to be almost 100% (e.g., Figure 11), the molar absorptivity of the B form appeared to be one-half that of the A form. Assuming this to be true, the molar absorptivities would be as given by Table II.

TABLE II
Molar Absorptivities of A and B
Forms of CH_3HgDz and HgDz_2 in Benzene

	<u>ϵ_A</u>	<u>ϵ_B</u>
HgDz_2	64,200	32,100
CH_3HgDz	33,500	16,800

The thermal return rates for both HgDz_2 and CH_3HgDz were markedly dependent upon inherent solvent polarity and the presence of water, acids, or bases in the solvent. Figures 10 and 11 are for HgDz_2 and CH_3HgDz dissolved in "as is" benzene as taken from the reagent bottle. In this benzene the thermal return $t_{1/2}$ values were 30-90 seconds for HgDz_2 and 3-10 minutes for CH_3HgDz . The behavior of HgDz_2 in "wet," "as is," and "dry" benzene is illustrated in Table III and Figures 10, 12, and 13. "Wet" benzene was prepared by adding 10 μl . of water, via microsyringe, to 10 ml. of "as is" benzene. "Dry" benzene was prepared by storing "as is" benzene over molecular sieves.

TABLE III
Photochromism of Mercurybisdithizonate in Benzene

<u>Type of Benzene</u>	<u>%Conversion*</u>	<u>$t_{1/2}$ (thermal return)</u>
"dry"	82.4	19 minutes
"as is"	76.4	73 seconds
"wet"	50.9	9 seconds

*All percent conversion values are calculated assuming the molar absorptivity (ϵ) for the A form is twice the value for the B form.

When HgDz_2 was photochromed in ethyl alcohol, the thermal return rate was so fast that only about 10% conversion was obtained in the photo-stationary state.

The effect of water on the thermal return rate was strikingly evident when HgDz_2 and CH_3HgDz were studied in polymers. The thermal return rates for these compounds in cellulose acetate films were found to vary, depending upon the relative humidity in the laboratory.

Figures 14 and 16 show spectra taken on cellulose acetate films containing HgDz_2 and CH_3HgDz respectively. These films were freshly prepared by the method described in the experimental details section and had been equilibrated at room temperature and relative humidity. Figures 15 and 17 show spectra taken on these same film samples, with the films actually immersed in distilled water at room temperature. The measured thermal return rates and % conversion values were as follows:

TABLE IV
Effect of Moisture on Photochromes in Cellulose Acetate Films

	HgDz_2		CH_3HgDz	
	<u>% Conv.</u>	<u>$t_{1/2}$ (thermal return)</u>	<u>% Conv.</u>	<u>$t_{1/2}$ (thermal return)</u>
"Dry" (Atmosphere equilibrated)	65	14 mins.	96	6-10 mins.
"Wet" (Immersed in water)	64	32 secs.	42	~12 secs.

When the films were immersed in water, the thermal return rates for both HgDz_2 and CH_3HgDz became very rapid. Similar "water effects" were observed when HgDz_2 and CH_3HgDz in other polymers (e.g., T-61 acrylic polymer, Mylar, Cyanocel), were immersed in water. Also, immersion of cellulose acetate films in other solvents, such as benzene and alcohol, produced photostationary conversions and thermal return rates characteristic of the photochromic compound in benzene or alcohol.

From the results presented in Table IV, it can be observed that the large increase in thermal return caused by water was accompanied by a sizeable reduction in the photostationary conversion for CH_3HgDz , but essentially no change for HgDz_2 .

Similar behavior by HgDz_2 was also observed when cellulose acetate films were run at various temperatures as shown in Table V.

TABLE V

Effect of Temperature on Photochromes in Cellulose Acetate Films

<u>Temperature</u>	<u>HgDz₂</u>		<u>CH₃HgDz</u>	
	<u>% Conv.</u>	<u>t_{1/2} (thermal return)</u>	<u>% Conv.</u>	<u>t_{1/2} (thermal return)</u>
Low (~4°C)	66	very slow	99	very slow
Room	62	3.3 mins.	92	6 mins.
High (~54°C)	72	2.7 mins.	87	1.6 mins.

Here also, the compound containing one dithizone ligand per mercury atom exhibited decreasing photostationary conversions as the thermal return rate increased. The behavior of the bis compound is not as clear-cut.

A rough estimate for ΔE^* the activation energy for the thermal return process, using the thermal return rates for CH₃HgDz in cellulose acetate at room temperature and ~54°C, gave a value of $\Delta E^* \approx 14$ kg.cal mole⁻¹.

These two compounds were examined in some other polymers, with the results obtained being listed in Table VI. For each of these polymers the return rates were sensitive to the presence of moisture so the t_{1/2} values must be considered to be estimates.

TABLE VI

Photochromes in Various Polymers

<u>Polymer</u>	<u>HgDz₂</u>		<u>CH₃HgDz</u>	
	<u>% Conv.</u>	<u>t_{1/2} (thermal return)</u>	<u>% Conv.</u>	<u>t_{1/2} (thermal return)</u>
Cellulose Acetate	62	1.6-14 mins.	96	6-10 mins.
Cyanoethylated Cotton ("Cyanocel")	57	2.0 mins.	82	17.6 mins.
Type 61 Cyanamid Acrylic Fiber	47	3.7 mins.	76	6.2 mins.

In addition, HgDz₂ was tested in poly(methyl methacrylate), polystyrene, and Mylar[†]. The thermal returns in all three polymers were very slow. Since photoequilibration was very slow for these samples, reliable photostationary percent conversions were difficult to obtain.

[†] Dyed in as a disperse dye.

Some experiments were carried out where an acid (salicylic acid) and also a base (2,6-lutidine) were added to samples of CH_3HgDz in cellulose acetate. In the initial experiments the amounts of CH_3HgDz and acid or base added were quite arbitrary. These initial experiments served to confirm that the thermal return rate in polymers was, in fact, very sensitive to acids and bases. The photostationary conversions were decreased for both HgDz_2 and CH_3HgDz as the thermal return was increased by the acid or base added.

Some further experiments were carried out where known amounts of salicylic acid were added to a cellulose acetate film containing 0.1% CH_3HgDz . The results obtained at room temperature and relative humidity are shown in Table VII.

TABLE VII

Influence of Salicylic Acid Addition
on Photochromism of CH_3HgDz in Cellulose Acetate

<u>Added Acid*</u>	<u>% Conversion</u>	<u>$t_{1/2}$ (thermal return)</u>
None	94	11 mins.
25%	92	4 mins.
50%	84	2 mins.
100%	80	1 min.

*Based on the weight of CH_3HgDz .

The thermal return rates for all these samples decreased upon aging of the films. It was not clear whether this was due to chemical effects or changes in the moisture content of the films.

In any particular medium, the changes in photostationary conversion obtained from samples of varying return rates are obviously not as simple as those predicted by equation 14, particularly for HgDz_2 . It may be that a more complex expression is required (e.g., equation 2a) or perhaps the photoforward rate depends somewhat on temperature and the presence of proton carriers.

It was therefore of interest to estimate a value for $\phi_{A \rightarrow B}$ the quantum yield for the photo process. Since ϕ is defined as the number of moles converted from A to B per unit time, divided by the number of einsteins of radiation absorbed by A per unit time, there appear to be three ways in which ϕ can be evaluated:

- a. From a photoequilibration rate measurement.
- b. From a photo rate measurement at very low temperatures, where the thermal return is eliminated.
- c. From a thermal return rate measurement at the photostationary state.¹⁶

Method c appears to be the most convenient method to use. Method a involves some complex mathematics (since I_{abs} is a function of time). Method b requires very low temperatures and ϕ may itself be temperature dependent. With method c, the system is evaluated at the temperature of interest and I_{abs} is constant.

The major difficulty in defining ϕ for a photochromic system is in defining I_{abs} . A quantum yield is strictly valid only for monochromatic radiation of wavelength λ . For our system we must consider radiation within a wavelength band, since we are irradiating our sample with a continuous light source. We can use the wavelength band defined by the half wave band of the absorption peak of the A form, but ϕ may be different for each wavelength within this band. At best, then, we can only calculate an integral or average quantum efficiency.

If we use method c, then from equation 2, in the photo-stationary state,

$$k_F I_{abs} = k_R (B)$$

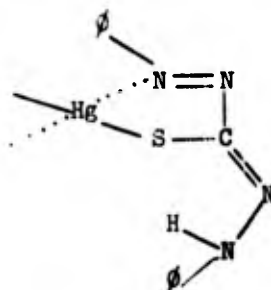
then,

$$\phi_{A \rightarrow B} = \frac{k_F I_{abs}}{I_{abs}} = \frac{k_R (B)}{I_{abs}}$$

$$\phi_{A \rightarrow B} = k_F$$

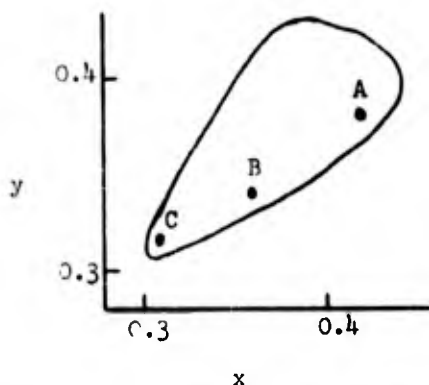
Defining I_{abs} as the fraction of the total energy, within a given wavelength band, absorbed by the A form, some preliminary calculations for $\phi_{A \rightarrow B}$, using photostationary measurements for $HgDz_2$ and CH_3HgDz in cellulose acetate film, lead to values of ca 10^{-2} to 10^{-4} .

The exact mechanisms operative in the photochromism of dithizone and its metal complexes are not presently known. Isomerization about double bonds is known to lead to spectral changes and the thermal processes in such systems are frequently sensitive to medium polarity and acid or base catalysis, (e.g., azo dyes^{16a, 16b} and formazans¹⁵). In the dithizonate systems, cis-trans type isomerization may be accompanied by tautomerism involving a proton transfer. The structure of $HgDz_2$ in the solid state, as the pyridine complex (see structure on next page), is available from published work.^{16c} However, even if this structure is assigned to the A form in solution, considerable difficulty is encountered in assigning a structure to the B form which will account for the intense long wavelength absorption (λ_{max} 605 m μ , $\bar{\epsilon}$ = 32,100). This problem is apparently also involved in accounting for the long wavelength peak (λ_{max} 620 m μ , $\bar{\epsilon}$ = 35,000) in the spectrum of dithizone itself. Further work will obviously be required to establish the molecular species responsible for the long wavelength absorption in the dithizonate systems.



Since the mercury dithizonates appeared very promising as chromotropic camouflage colorants, some preliminary attempts were made to apply them to textile fabrics. Both HgDz_2 and CH_3HgDz were successfully applied (as disperse dyes) to cellulose acetate and nylon fabrics.

The reflectance spectrum of one dyeing of HgDz_2 on cellulose acetate fabric was examined before and after exposure to sunlight. The following plot shows the change in tri-stimulus values, calculated from the reflectance curves, plotted on an ICI color diagram. The portion of the color diagram shown includes (within the triangular shaped area) most of the colors encountered in camouflage.^{16d}

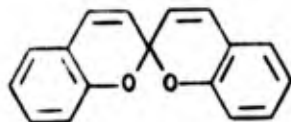


- A = Unexposed fabric.
- B = After approximately 10 minutes exposure to sunlight.
- C = ICI source "C".

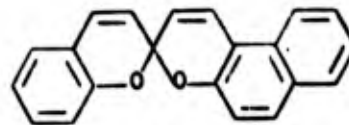
These results indicate that the color changes achievable with mercury dithizonate photochromic colorants (in conjunction with suitable nonphotochromic dyes) are probably sufficient to encompass most of the standard camouflage shades.

2. Spiroprans

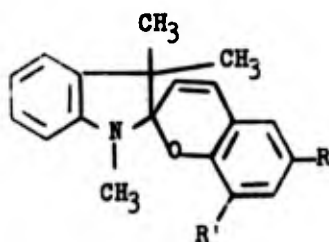
The spiroprans are a large class of compounds found to exhibit pronounced color changes under the influence of radiation. They have been extensively studied by Hirschberg, Fisher and others,^{17, 18, 19, 20} (primarily at low temperatures). The class includes:



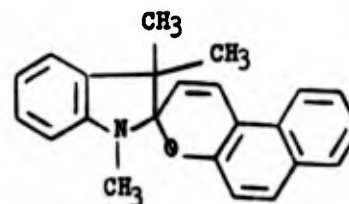
IV



V



VI



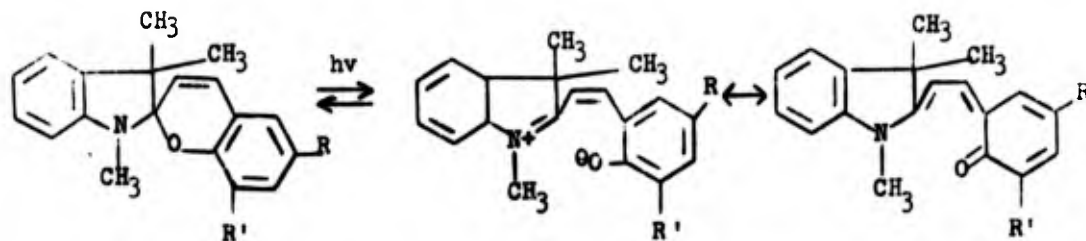
VII

For this study, two derivatives of VI were chosen.

VIa - R = NO₂, R' = H

VIb - R = Cl, R' = NO₂

The postulated mechanism for the photochromic behavior of these compounds is as follows:



spiropyran
(colorless)

"merocyanine"
(colored)

Both VIa and VIb were colorless in solvents except for alcohols. VIa was red (λ_{\max} 540 m μ) and VIb was blue (λ_{\max} 590 m μ) in alcohol, and both were thermochromic in this solvent. On irradiation with ultraviolet in solvents such as butyl acetate or benzene, the colorless solutions became blue (λ_{\max} 590 m μ). VIa had a thermal return rate with $t_{1/2}$ of 13 seconds in butyl acetate.

The molar absorptivity of the colorless forms of both compounds in the ultraviolet was easily determined, VIa, $\epsilon = 10,100$ at 330 m μ and VIb, $\epsilon = 3,500$ at 350 m μ . No satisfactory method for determining the molar absorptivity of the colored form in the visible was found. A literature value²¹ for VIa in ethanol gave limits of 4.68×10^4 to 2.40×10^4 (liter moles⁻¹ cm⁻¹).

In polymethyl methacrylate and polystyrene, polymers VIa and VIb were colorless or almost colorless. In cellulose acetate they had the same colors as in alcohol solutions (VIa absorbed at 550 m μ and VIb absorbed at 590 m μ , latter shown in Figure 18). Both were thermochromic in cellulose acetate (see Thermochromic Systems section for discussion).

Three rates in polymers were investigated:

- a. Photocolor (ultraviolet activated)
- b. Photobleach (visible activated)
- c. Thermal return to "dark" form.

The thermal return rates in all cases were slow. The shortest $t_{1/2}$ measured was 40 minutes.

The rates primarily determining absorption changes were photocolor and photobleach. This is best illustrated by the difference in absorption caused by skylight and full sunlight. Dipped slides were exposed to sky light with a ratio of 1:1.49 (einsteins/sec/cm² of 350 \pm 20 m μ to 590 \pm 20 m μ) and to full sunlight with a ratio 1:2.91. The slides were irradiated for 3-5 minutes before readings were made. The irradiations were made near solar noon at the end of May. Figures 19, 20 and 21 show the results obtained for VIa in cellulose acetate and polymethyl methacrylate and for VIb in cellulose acetate. In all three cases full sunlight gave less coloration than skylight. In the case of VIb in cellulose acetate, the absorption at 590 m μ in skylight was less than the "dark" value.

Table VIII summarizes thermal and photo rate measurements using an Hanovia mercury arc lamp with a 365 m μ band pass filter (transmitting 36% of the available light), and the Cary 14 near infrared source with an ultraviolet filter. This latter source is extremely intense in the 590 m μ region (over 20×10^{-8} einstein/sec/cm²).

TABLE VIII

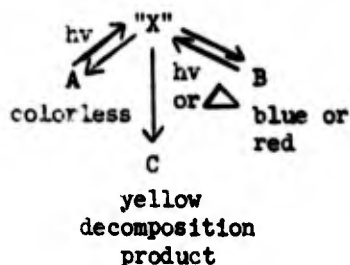
Photo and Thermal Rates for Benzospiropyrans in Polymers

<u>Rate Measured</u>	<u>Polymer</u>	<u>Via</u>			<u>Vib</u>		
		<u>λ (mμ)</u>	<u>Remarks</u>	<u>t$_{1/2}$</u>	<u>λ (mμ)</u>	<u>Remarks</u>	<u>t$_{1/2}$</u>
<u>Thermal</u>	CA	550	colored to colorless	55 min.	590	colorless to colored	70 min. 40-1/2 min.
	PMMA	590	colored to colorless	57 min.	590	colored to colorless	100 min.
<u>Photocolor</u>	Acrylic T-61	-	-	-	590	ditto	245 min.
	Cyanoceel	-	-	-	590	ditto	102 min.
	CA	550	Hanovia with 365 m μ band pass filter	29 sec.	590	Hanovia with 365 m μ band pass filter	3.2 min.
	PMMA	590	ditto	23 sec.	590	ditto	5.1 min.
<u>Photobleach</u>	CA	550	Ca γ 14 NIR source + UV filter	4.2 sec.	590	Ca γ 14 NIR source + UV filter	5 sec.
	PMMA	590	ditto	5.5 sec.	590	ditto	9 sec.

CA = cellulose acetate
 PMMA = poly(methyl methacrylate)

The greatest deficiency of the spiropyrans was their photo-instability. After only one or two cycles of photocolor-photobleach, the yellowing was considerable. In the case of VIb in PMMA only one cycle of readings could be made before decomposition interfered.

A limited attempt was made to identify the decomposition product from benzene solution, with no success. It was established from a sealed tube experiment that oxygen was not involved in the photodecomposition. The following scheme is suggested as the possible route of photodecomposition.

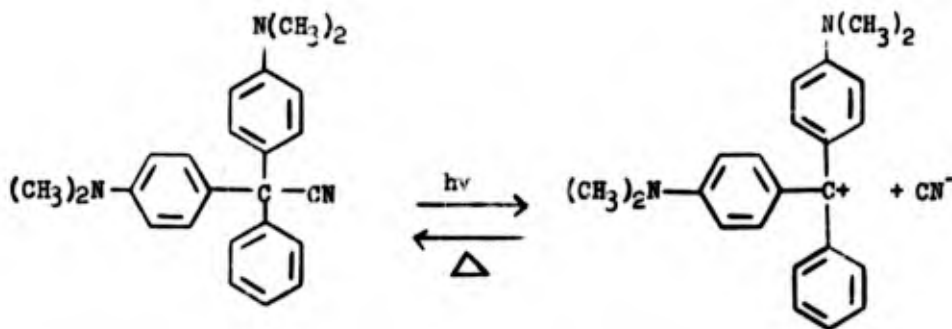


3. Other Systems

The following compounds have been reported as photochromic in the literature.^{22, 23} They were examined briefly. Full scale investigations of their behavior was not made for the reasons given with each compound.

a. Triphenylmethane Leuconitriles

Malachite Green leuconitrile



VIII

Since this type of compound has been extensively investigated in solution by other workers,^{24, 25, 26} it was examined only briefly in polymers.

The leuconitrile was incorporated into poly(methyl methacrylate), cellulose acetate, and polystyrene by milling and molding techniques. In polystyrene it was colorless and nonphotochromic. In both cellulose acetate and poly(methyl methacrylate), it turned green irreversibly on dispersion in the plastic.

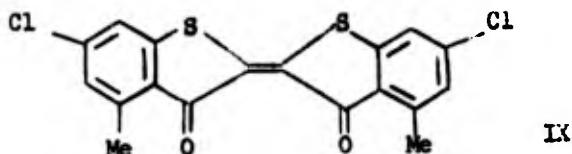
From the limited work done, it seems that the resultant color was largely influenced by the nature of the polymeric media. Since the photochromic mechanism postulated for these compounds involves separation of charged species, it was not surprising that, in rigid media where diffusion from a reaction site is limited, photochromism did not occur.

Dreyer²⁷, in attempting to develop a device to protect against flash blindness, found it necessary to use this photochrome in a gel system since very slow thermal returns prevailed in polymers.

b. Thioindigoid Dyes

4,4'-Dimethyl-6,6'-dichlorothioindigo

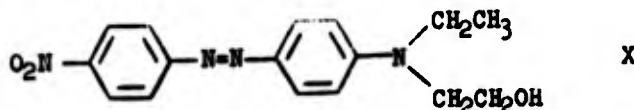
(Calcophyl Pink FF Conc., Color Index No. 73360.)



This compound found to be photochromic by Brode et al,²⁸ has two absorption peaks in benzene solution, 500 and 540 m μ . Irradiation with ultraviolet light, daylight, or Cary 14 near infrared source produced no observable changes, by eye or in the spectra. A decrease in 540 m μ peak could be seen if the solution was irradiated through filter cutting off at 510 m μ . Under normal conditions of illumination (i.e., sunlight) this dye was not usefully photochromic.

c. Azo Dyes

(Calcosyn Brilliant Scarlet BN, Color Index No. 11110.)

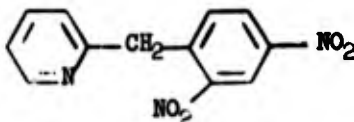


This dye was among those found to bleach under conditions of high intensity light by O'Brien and Weissbein.² When examined in acetone solution and cellulose acetate films (at room temperature), no

decrease in absorption in the visible was found on illumination with the Cary 14 near infrared source.

d. Nitrobenzyl Compounds

2(2',4'-Dinitrobenzyl)pyridine^{29, 30, 31}



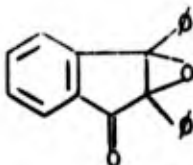
XI

The ultraviolet spectra were recorded in butyl acetate. No distinct λ_{\max} was seen from 320 to 400 $m\mu$. At 330 $m\mu$, ϵ was 533; at 350 $m\mu$, ϵ was 372. At dry ice temperature the butyl acetate solution was slightly photochromic.

Dipped slides containing 4%/wt. on cellulose acetate were prepared. At room temperature no photochromic behavior was seen. Chilled in dry ice, the solution cast films exhibited a slight color change when exposed to ultraviolet radiation.

A poly(methyl methacrylate) chip prepared by milling and molding was found to be quite photochromic upon irradiation with ultraviolet light. The thermal return at 575 $m\mu$ was measured on the Cary 14. A plot of $\log(Abs_t - Abs_{\infty})$ versus time was nonlinear indicating the thermal return was not first order. A $t_{1/2}$ in the initial portion of the curve was determined as 72 seconds. A repeat gave 80 seconds. In addition to the thermal return, a photobleach was established. Irradiation by full light of Cary 14 near infrared source gave a $t_{1/2}$ for bleach reaction of 11 sec.

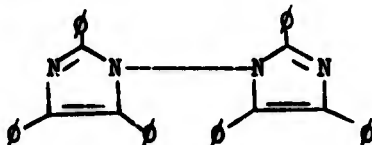
e. Diphenylindaneone Oxide



XII

This compound had an $\epsilon = 795$ at λ_{\max} 300 $m\mu$ in butyl acetate. In sunlight only a faint color was developed although irradiation with the full light of a Mercury arc lamp (Hanovia) generated a decidedly pink color.

f. Lophine Dimer



XIII

This compound had a λ_{\max} at 345 μ with an $E = 3,000$. The low molar absorption coupled with the fact the color producing mechanism was free radical generation.²² did not make work in rigid media promising.

g. Anils

A series of five anils of salicylaldehyde were synthesized.^{32, 33} None showed any signs of photochromism in solution or plastic at room to dry ice temperatures.

However, they exhibited solid state photochromism going from yellow to orange with ultraviolet radiation and orange to yellow with visible radiation.

h. Heteropoly Acids

Phosphomolybdic acid and phosphovanadomolybdic acid.

Samples of the above acids (submitted by the Natick Laboratories, as per letter from A. O. Ramsley, dated 4/9/63), were found to be non-photochromic in alcohol and water solutions and in the solid state.

III. Thermochromic Systems

A. Theoretical Considerations

Just as photochromism involves reversible light-induced changes in spectra, thermochromism is the term applied to reversible spectral changes induced by temperature change. Many substances exhibit thermochromism, most in the solid state. 34

Thermochromism may be due to several causes, but the simplest model which can be used to represent a thermochromic system is:



The rate expression for this process would be

$$\frac{-d(A)}{dt} = k_F(A) - k_R(B) \quad (31)$$

and at thermal equilibrium

$$k_F(A) = k_R(B) \quad (32)$$

$$\frac{(B)}{(A)} = \frac{k_F}{k_R} = K \text{ (t.e.)} \quad (33)$$

where k_F = thermal rate constant for $A \rightarrow B$ process sec^{-1}

k_R = thermal rate constant for $A \rightarrow B$ process sec^{-1}

$K(\text{t.e.})$ = thermal equilibrium constant.

The variation of $K(\text{t.e.})$ with temperature will be dependent upon the activation energies for the forward and reverse rate constants, and will be given by the equation

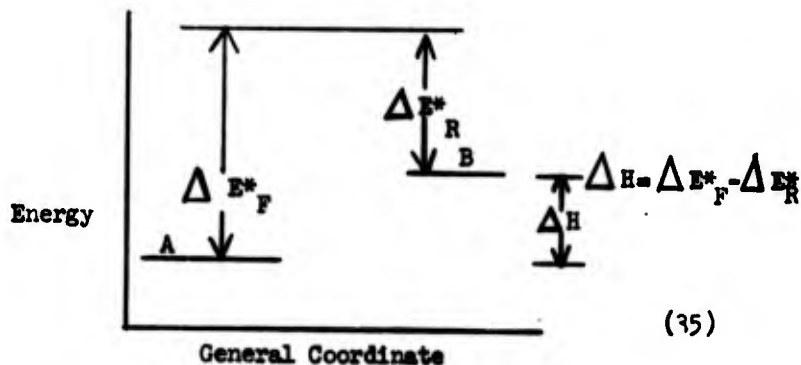
$$\frac{d \ln K(\text{t.e.})}{dt} = \frac{\Delta E}{RT^2} \quad (34)$$

where R = gas constant

T = absolute temperature

ΔH = enthalpy for the thermochromic process.

ΔH will be equal to the difference between the activation energies for the forward and reverse steps as shown in the following energy diagram:



While the sensitivity of the thermal equilibrium to temperature changes is given by ΔH , the absolute value of K (t.e.) is given by

$$\Delta F = \Delta H - T\Delta S = -RT \ln K(\text{t.e.}) \quad (36)$$

where ΔF = free energy change

ΔS = entropy change

or

$$-RT \ln K = \Delta H - T\Delta S$$

$$-2.303 \log K = \frac{\Delta H}{T} - \Delta S$$

$$\log K = \frac{\Delta S}{4.57} - \frac{\Delta H}{4.57T} \quad (37)$$

The entropy change therefore determines the value for K at a particular temperature and hence the extent of conversion from A to B.

The integrated form of equation (34) with $K=K_1$ at $T=T_1$ and $K=K_2$ at $T=T_2$ is,

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{4.57} \frac{T_2 - T_1}{T_2 T_1} \quad (38)$$

If we tentatively establish 20°-65°C (68°-149°F.) as our usable temperature range, then from equation (38),

$$\Delta H = 10,060 \log \frac{K_2}{K_1} \quad (39)$$

If we allow K_2/K_1 to vary from 2 to 10 we obtain ΔH values of 3,030 to 10,060 cal. mole⁻¹. However, $K_2/K_1 = 2$ can, of course, be given by an infinite number of equilibrium constants. Table IX illustrates how various absolute values for K_1 and K_2 affect the conversions from A to B at 20° and 65°C. In this table $K_2/K_1 = 2$, hence $\Delta H = 3,030$ cal mole⁻¹ and ΔS is calculated from equation (37a).

$$\Delta S = \frac{\Delta H}{T} + 4.57 \log K \quad (37a)$$

TABLE IX

Change in Entropy and Percent Conversion of A Thermochromic System
At Two Temperatures When $K_2/K_1 = 2$ and $\Delta H = 3,030$ cal mole⁻¹

K_1	% Conv. at 20°C	K_2	% Conv. at 65°C	ΔS
0.005	0.5	0.01	1.0	-0.17 e.u.
0.055	5.2	0.11	10.0	+4.59
0.5	34.0	1.0	50.0	+8.87
1.5	60.0	3.0	75.0	+11.2
4.5	82.0	9.0	90.0	+13.3

We can see from this table that a system with $K_2/K_1 = 2$ and $\Delta H = 3,030$ cal mole⁻¹ will show a relatively small change in percent conversion between the two temperature extremes (i.e., small color change). Also, as the values for K_2 and K_1 increase, the entropy changes become large. As higher ΔH values are considered, the ΔS value (for a particular value of K) will increase. If $\Delta H = 10,060$ cal mole⁻¹ (i.e., $K_2/K_1 = 10$), the value of ΔS for 50% conversion at 65°C will be 29.8 e.u. Such large entropy changes would require rather drastic structural changes and such changes would be very difficult for highly conjugated species in a solid polymeric matrix.

The above considerations apply to the thermodynamics of the thermal equilibrium represented by equation (30). The kinetics of the system, i.e., how rapidly the system responds to a given change in temperature, will depend upon the absolute values of k_F and k_R (i.e., the "chemical reversibility" of the system).

In the following experimental sections, some representative thermochromic systems are discussed. The discussion is limited to a consideration of feasibility on thermodynamic grounds as introduced above. If a system is not capable, thermodynamically, of bringing about the desired change, then the kinetics are immaterial.

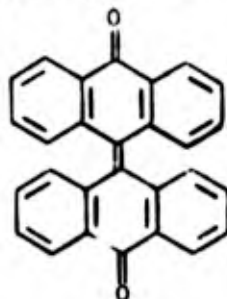
A unique type of thermochromism is that caused by the influence of temperature on a Christiansen filter^{52,53}. These filters depend upon the relative magnitudes and shapes of the curves of refractive index (n) versus wavelength (λ) of a medium (n_0) and of insoluble particles (n_p)

suspended in it. The "Christiansen wavelength" λ_c , (linearly transmitted radiation) occurs at the wavelength where the two (n vs. λ) curves cross ($n_o = n_p$). The variation of the two (n vs. λ) curves with temperature causes a shift in λ_c , and a resultant change in color. Attenuation of radiation is achieved by scattering or diffuse reflection. Some exploratory studies on this type of thermochromism were carried out and are briefly described under the experimental studies.

B. Experimental Studies

Of the large number of compounds reported to be thermochromic, a sizeable number show the effect in the solid state. The changes in crystal form occurring in the solid apparently produce the large ΔS values required, as discussed in the theoretical section.

1. Bianthrone is one of the most well known and frequently studied thermochromic compounds, ^{35,36}.



XIV

This substance exists as a yellow solid which turns green, irreversibly, above 250°C. In solution the yellow to green color change is reversible but rather weak in the temperature range 25 to 65°C (see Figure 22). Grubb and Kistiakowsky ³⁶ studied the spectrum of bianthrone in acetophenone and decalin. From a "heat of transformation" plot they obtained a value for ΔH of 3.5 kg-cal. mole⁻¹. Their measurements were carried out over the temperature range 25-145°C. A "heat of transformation" plot is a plot of the area under an absorption curve, the absorbance at λ_{max} or the molar absorptivity at λ_{max} vs. the reciprocal of the absolute temperature.

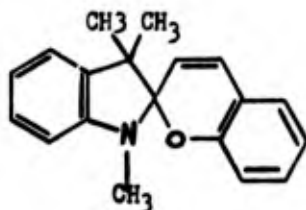
In the present research, the thermochromism of bianthrone was studied in polymeric media. Bianthrone was incorporated in cellulose acetate and polymethyl methacrylate films. Little or no change in spectrum could be observed over the temperature range 25-65°C. Incorporating a dibutyl phthalate plasticizer, along with the bianthrone, in cellulose acetate did not lead to any improvement.

2. Spiroprans - Several of the spiroprans have been reported to be thermochromic as well as photochromic. ⁴⁴ ΔH values in solution media, determined from heat of transformation plots, ranged from 3 to 7 kg-cal mole⁻¹. For indolinospiroprans, Hirschberg and Fischer ³⁷ found 7.0 kg-cal mole⁻¹ for (XV) in dimethylphthalate and values for (XVI) which depended upon solvent (see Table X).

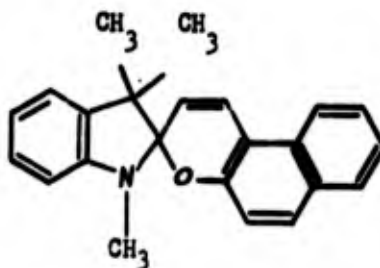
TABLE X

Influence of Solvent Media on Enthalpy of Indolinospiropyrans

<u>Solvent</u>	<u>Compound</u>	<u>ΔH (kg-cal mole⁻¹)</u>
Dimethyl phthalate	XVI	4.9
Diphenyl ether	XVI	5.4
Decalin	XVI	7.2

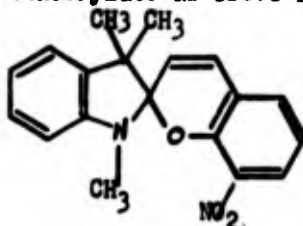


XV



XVI

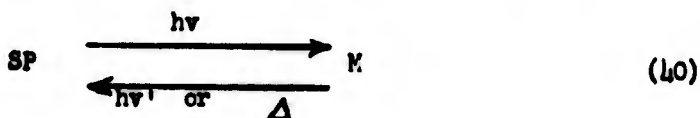
In the present research, indolinospiropyran (XVII), which was also studied under photochromism, was incorporated in cellulose acetate and polymethyl methacrylate as above for bianthrone.



Cl

XVII

As discussed in the section on photochromism, the spiropyrans have been shown to exist in colorless spiropyran (SP) and highly colored merocyanine (M) forms.



In nonpolar solvents and polymers, the spiropyrans exist completely in the colorless SP form in the dark at room temperature. Ultraviolet light ($h\nu$) produces the colored merocyanine which can return thermally to the SP form or can be converted by visible light ($h\nu'$) to SP.

In polar solvents and polymers, the polar merocyanine form (M) is appreciably stabilized at room temperature so that a thermal component exists in both the SP \rightarrow M and M \rightarrow SP steps (i.e., the system exhibits thermochromism).

When (XVII) was incorporated in polymethyl methacrylate and cellulose acetate, the colored forms were stabilized in both, but considerably more in cellulose acetate. Temperature variation in the dark from 35 $^{\circ}$ -36 $^{\circ}$ C, for XVII in cellulose acetate, indicated that this sample was thermochromic and an attempt was made to estimate ΔH for the process. The spectra shown in Figure 23 indicate that ΔH for the SP \rightarrow M process is negative since the SP form is favored at higher temperatures. From a plot of absorbance at 590 $m\mu$ vs. T^{-1} , an approximate ΔH value of -2050 cal mole $^{-1}$ was calculated. This is extremely small and indicates that the polymer matrix has decreased the energy difference between the SP and M forms as compared to solution media.

3. Christiansen Filters - The change in index of refraction per degree centigrade in polymers is about ten times larger than those of glass or alkali metal halides.^{54, 55, 56} Therefore a limited amount of work was done with potassium chloride (325 mesh) dispersed in poly (methyl methacrylate) by milling and molding (33% KCl/wt.). When the temperature of an eighth-inch panel of the potassium chloride in poly (methyl methacrylate) was varied from 0 $^{\circ}$ to 100 $^{\circ}$ C, the color of a bright broad light source (viewed by transmitted light) changed from bluish-gray to yellowish-gray. An increase in the scattering of blue light was noted as well as an increase in opaqueness of the panel on heating. Quantitatively, these changes were difficult to measure. No discernable change in chroma could be seen when the sample was viewed by reflected light.

Although the Christiansen effect has been useful for light filters, it appears that considerable experimental work would be required to establish how the effect could be used to change the color (by reflected light) of a textile fabric. The literature indicates that such parameters as particle size and thickness are important in the efficiency of the filter.^{53, 57} Necessary index of refraction data for choosing the best combination of medium and insoluble particles is lacking in the literature. Because of the limited amount of information available on the Christiansen effect in textile fabrics, it does not appear to presently offer a feasible approach to chromotropic camouflage. Further research in this area might be fruitful, particularly since the Christiansen effect might prove useful in conjunction with one of the other chromotropic systems (e.g., photochromic).

IV. Chemochromism

A. Theoretical Considerations

The term "chemochromism" is used in this report to encompass spectral changes induced by variations in physical and chemical properties other than light and heat. This is a very broad area and includes effects involving redox potential, pH, solvent and electrical potential.

While photochromism and thermochromism usually involve monomolecular systems, the chemochromic systems are frequently bimolecular.

There is a multitude of information available in the chemical literature on colorants which change spectrum with pH, solvent, etc. However, as was true under photochromism and thermochromism, these effects have been studied almost exclusively in solution medium. To determine the effect which a rigid polymer matrix would have on such systems was one of the main objectives of the experimental work described in this report.

Also, in exploring feasibility for chemochromic colorants, the concept of a triggering or controlling mechanism becomes much more elusive. While regulation of light intensity and temperature would permit control for photochromic and thermochromic systems respectively, control of a chemochromic system would depend upon devising a method of changing the redox potential, acidity, dielectric constant, etc., of a polymeric medium. It would seem that control of these properties would still have to proceed via regulation of one or more of the three readily available sources of energy:

- a. Light intensity
- b. Temperature
- c. Electric potential

Therefore, in the case of chemochromism, we would actually be dealing with indirect photochromism, thermochromism, or electrochromism.

Rather than laboring the above points on theoretical grounds, it was decided to obtain some information, from exploratory experiments, on the way in which known chemochromic systems would behave in polymer media. The three general areas examined were:

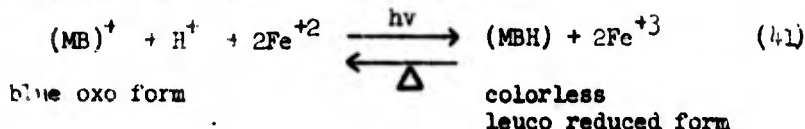
- a. Photoredox systems
- b. Solvatochromism
- c. pH sensitive colorants

B. Experimental Studies

1. Photoredox Systems

One of the most well known photoredox systems is the thiazine dye-ferrous iron system. This system has been extensively studied in aqueous solution by Rabinowich^{38, 39} in connection with utilization of solar energy.

If thionine (TH) or methylene blue (MB), in the presence of Fe^{+2} , is irradiated with visible light, the dye is reversibly bleached (reduced) according to the following equation:



In an aqueous system, the dye was bleached by visible light with $t_{1/2}$'s of 2 to 4 sec. The return rates were too fast to measure. The amount of bleach was dependent on the concentration of reducing agent and pH. The maximum amount of bleach occurred in a solution with 0.01 M $FeSO_4$ and 0.01 N H_2SO_4 $[(MB)^+ = 1.57 \times 10^{-5} M]$.

When $(MB)^+$ was incorporated in polyvinyl alcohol (PVA) film, the dye bleached upon irradiation, in the absence of any added reducing agent. These results are similar to those found by Brody.⁴⁰ The light-excited form of the dye apparently reacts directly with the hydroxyl groups in the polymer. When the PVA was partially crosslinked with dimethylol urea (DMU), the extent of photobleaching decreased as the extent of crosslinking increased. Typical spectra obtained for $(MB)^+$ in PVA film, before and after irradiation with the near infrared source of the Cary 14, are shown in Figure 24. These spectra show that the system was completely bleached with the intense Cary source, not reaching a photo-stationary state. The return rate to the blue form was very slow at room temperature and relative humidity. At 100% relative humidity (i.e., in steam atmosphere) the return rate was fairly rapid, ca. 2-3 min. Figure 24 also shows the spectrum for the sample after one photobleaching and recovery cycle. While the original spectrum shows peaks at 600 and 650 $m\mu$ (the latter presumably due to monomeric dye and the former to polymeric dye), after photobleaching and thermal return, only the 600 $m\mu$ polymer peak remains.

Various methods were investigated to find an additive (other than H_2O) which might increase the thermal return rate. The addition of oxidizing agents had little effect and in some cases (e.g., Fe^{+3}) led to complicating reactions (apparent complexation or aggregation). Addition of glycerin plasticizer to the films increased the thermal return somewhat, although still not enough to be practicable. One film containing $(MB)^+$ + 50% glycerin (based on weight of PVA) was run at about 50°C. in a constant temperature block, and a thermal return measurement at 640 $m\mu$ indicated that $t_{1/2}$ was approximately 15 min.

Long-term instability was noted with almost all of the PVA samples containing $(MB)^+$, even when the samples were stored in the dark. The dye did not photoreduce in polymers other than PVA.

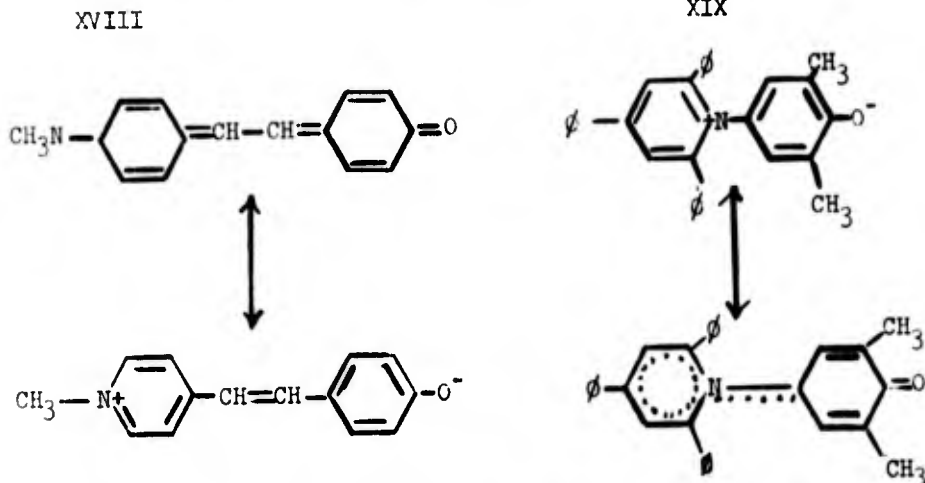
The slow reversibility, plus poor stability, of this system, indicates that it would probably not be a feasible approach for a chromotropic camouflage colorant system.

2. Solvatochromism

A number of classes of dyes are known to show wide spectral shifts in different solvents. Two classes, the merocyanines and betaines, have been extensively studied by Brooker et al.⁴¹ and Dimroth.^{42, 43} The

mechanism postulated for the solvatochromism generally involves the effect of the polarity of the solvent on the equilibrium of polar and nonpolar resonance species of the dye.

A representative dye of each of the above classes was synthesized.



Both dyes exhibited the reported spectral shifts in solvents.

TABLE XI

Solvatochromism of Typical Merocyanines and Betaines

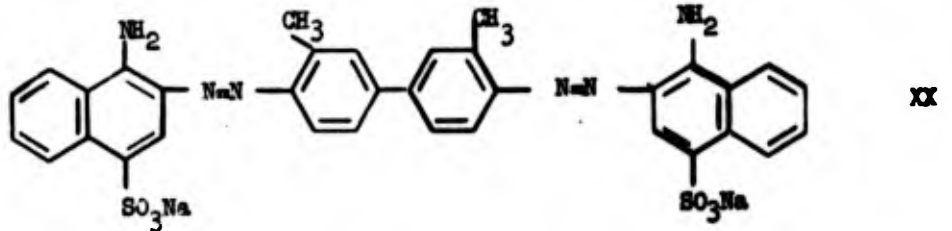
<u>Solvent</u>	<u>XVIII</u>	<u>XIX</u>
H ₂ O	pale yellow	pale orange
Methanol	orange-red	red
Ethanol	blue-red	blue-red
CHCl ₃	blue	blue

Both dyes, on incorporation into polymeric media (cellulose acetate, polystyrene, polyvinyl chloride, polyvinyl alcohol, and polyvinyl pyrrolidone), were either colorless or pale yellow or orange. Heating to 60° had no effect except in one case. Dye (XVIII) in polyvinyl pyrrolidone went from yellow to orange-red on heating (see Figure 25). This was established as an effect of reversible hydration on the color, since when films were cooled to room temperature in a desiccator, the sample remained orange-red.

The reason for the stabilization of the polar form of these dyes in media of apparently low polarity is not fully understood.

3. pH Indicators

The sensitivity of a pH sensitive colorant in a polymeric matrix was examined using benzopurpurine (XX) (Color Index No. 23500) in cellophane film,



In aqueous solution, this compound has a pK_a of approximately 3 (i.e., at pH 3 it exists half in the acid form [blue] and half in the base form [red]).

Since (XX) has a natural "affinity" or "substantivity" for cellulose, it can be dyed into cellophane film and the apparent pK_a , in the polymer, can be determined by equilibrating the dyed films in aqueous solutions of different pH values and recording their spectra.

When this was done for (XX) in cellophane, see Figure 26, the results obtained indicate that the apparent pK_a in the polymer phase is ≤ 1.0 , i.e., whereas $10^{-3} M H_3O^+$ will produce 50% conversion from red to blue, in water solution, $0.1 M H_3O^+$ is required when the chromophore is held in the cellulose polymer. Note that these are time-independent measurements since the H_3O^+ in the water solution was in equilibrium with that in the cellophane. Equilibrium was checked by raising the temperature of the system and no further changes in color of the films were observed.

While definitions of the activity of XX and H_3O^+ in the polymer phase become quite complex, the above results illustrate that chromophores, which are very sensitive to changes in hydronium ion activity in solution, will probably lose much of their sensitivity when they become imbedded in a polymer matrix.

V. Conclusions and Recommendations

Of the various types of chromotropic colorants studied, photochromism (with thermal return) presently represents the most feasible approach for a chromotropic camouflage system.

Presently available thermochromic systems show rather small spectral changes in polymers over the temperature range tolerable in clothing. It seems unlikely that the large ΔH and ΔS values which are theoretically required for a suitable thermochromic system can be achieved in a rigid polymeric medium.

Chemochromic systems usually have second-order kinetic processes and therefore diffusion in the polymer is usually a rate-limiting step. Although many of the systems have good color changes, they suffer from a lack of reversibility in polymers and those systems based on photoredox (e.g., Thiazine dyes) have rather poor stability.

Of the various known photochromic systems studied, the system which has shown the most promising results for the intended application is that based upon dithizone and its metal complexes [particularly Hg(II)]. None of the other systems examined possessed the combination of favorable properties found in the dithizonate system.

The spiropyrans showed good spectral changes but their photo-photo nature led to photostationary states in sunlight which were dependent upon the spectral distribution of the light.

In general, those systems which were photoactivated in the ultraviolet region of the spectrum showed rather poor photostability (e.g., spiropyrans, triarylmethane leuconitriles, and nitrobenzyl compounds). The dithizonate systems, since they are activated by visible light (475-510 m μ), absorb lower energy radiation and, when protected by an ultraviolet absorber (e.g., Cyasorb[®] UV24 light absorber) show good photostability.

Theoretical considerations (see Section IIA) indicated that a suitable photochromic system should have photo and thermal rate constants within certain ranges in order to provide a rapidly reversible photoequilibrium and one which would reach favorable photostationary states at various sunlight intensity levels. Of the photo rates measured for the various photochromic systems, the fastest were those given by photobleaching of spiropyrans and the A \rightarrow B photoprocess in the mercury (II) dithizonates. From photoequilibration measurements, and using known intensity values for the light sources, estimates for k_p calculated from equation (28) are:

ca. 0.6 to 0.8 $\times 10^6$ for spiropyrans in cellulose acetate,
ca. 1.0 to 3.0 $\times 10^6$ for HgDz₂ in cellulose acetate
(theoretical optimum values for k_p ; 1 to 5 $\times 10^6$).

Theoretical optimum values for thermal return rate constants were between 0.01 and 0.05 sec⁻¹ (half lives of 69 and 14 seconds, respectively). Only the dithizonates and the nitrobenzyl compound had thermal return rates in polymers which were of this order of magnitude. The nitrobenzyl compound was only photochromic under a limited set of conditions and suffered from severe photoinstability. The mercury dithizonate system also has a thermal return rate which can be regulated

by the controlled addition of proton-transfer agents (water, acids, and bases).

To summarize, the system based upon dithizone and its metal complexes [particularly Hg(II)], presently offers the most promising system for chromotropic camouflage, since it exhibits the following favorable properties;

- a. Large difference in spectrum of the A and B forms,
- b. Fast photo and thermal rates in polymers,
- c. Favorable photostationary conversions from A to B at sunlight intensity levels,
- d. Absence of complicating side reactions,
- e. Good photostability when protected with a near ultraviolet absorber,
- f. Thermal return rate which is adjustable by the use of proton transfer additives.

Further work, both synthetic and physical chemical, will be required to develop a chromotropic camouflage colorant based upon a photochromic system. Because of the promising results obtained with the mercury (II) dithizonates, study of this system can serve as a logical starting point for this future work. While such study will be fruitful in itself, the results obtained should also provide leads which will aid in the discovery of improved systems. These improved systems might be found within the dithizonate class (e.g., with metals other than Hg or with modifications of dithizone itself). They also might be obtained by suitable modification of other presently existing photochromic systems. Finally, they might be found in entirely new chemical classes.

Some specific changes and improvements which should be sought by synthesis are;

- a. Faster return rate,
- b. Greater spectral changes,
- c. Acid and disperse dye properties,
- d. Reactive groups for cellulose and nylon.

Further physical chemical work is also needed to help guide the above synthetic efforts and to improve our basic understanding of the photochromic process in polymers. Although thermal return rates in the dithizonate class can be adjusted, the extent to which the photoforward rate can be influenced is not clear. The answer to this question will come only when we have reliable information on such subjects as;

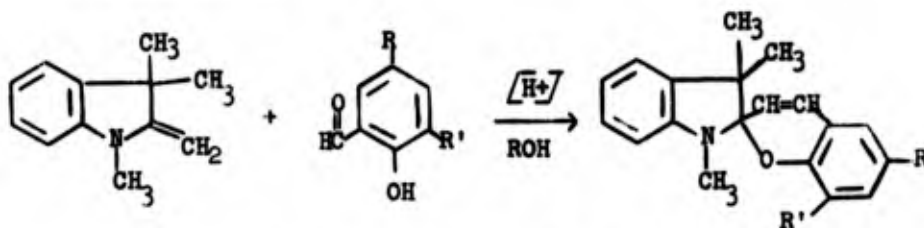
- a. The metastable excited state through which the photochromism proceeds,
- b. The quantum efficiency of the process.
- c. The temperature and medium dependence, if any, of the quantum yield.

Future physical chemical work will also be needed to successfully apply new photochromic colorants to textile fabrics. (Some very promising preliminary results have already been obtained by dyeing mercury dithizonates on cellulose acetate and nylon fabrics, as disperse dyes.)

VI. Experimental Details

A. Materials

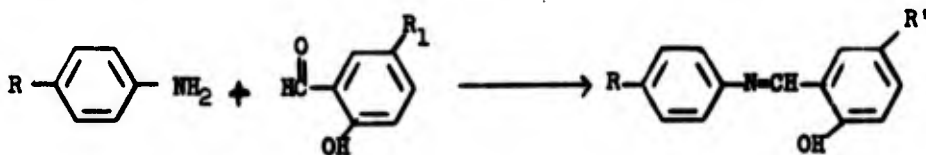
1. Benzospiropyrans ^{18, 45}



<u>R</u>	<u>R₁</u>	<u>Yield Recrystallized</u>	<u>M.P.</u>	<u>Lit</u>
H	H	60.3% colorless crystals	95-97	92-94
NO ₂	H	74.0% yellow needles	178-178-1/2	179-180
Cl	NO ₂	54.2% yellow crystals	134-135	134-135

The 1,3,3-trimethyl-2-methyleneindoline (0.1 M) (prepared by treatment of 1,2,3,3-tetramethylpseudindolium methyl sulfate with base, then extraction with ether) was reacted with the appropriate aldehyde (0.1 M) in isopropanol with a trace of phosphoric acid. After refluxing for 1 or 2 hours, the reaction was cooled and filtered. The product was then recrystallized from alcohol.

2. Anils^{32,33}

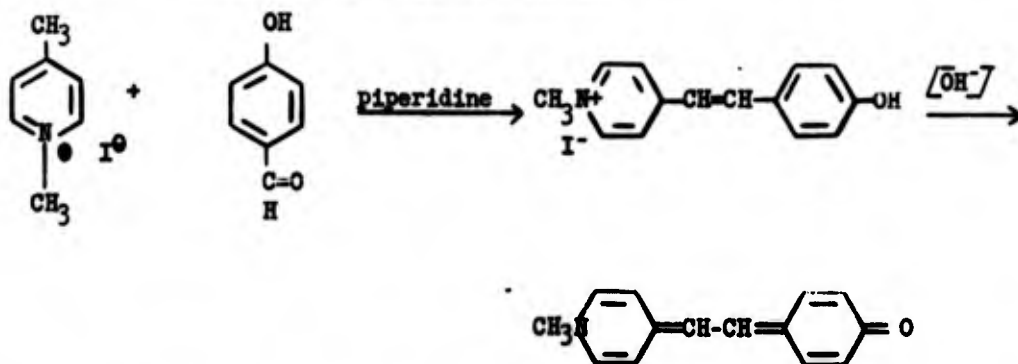


<u>R</u>	<u>R₁</u>	<u>% Recrystallized Yield</u>	<u>M.P.</u>	<u>Lit.</u>
H	H	50% (lt. yellow crystals)	53-53-1/2	50.5-51.0
Br	Br	80% (bright yellow plates)	174-175	178
Br	H	69% (sparkling yellow plates)	111-112	110
H	Br	79% (bright orange needles)	122-124	122.5
H	NO ₂	83% (orange-yellow needles)	132-133	133

The appropriate aniline and salicylaldehyde were mixed in equimolar quantities in a minimum amount of alcohol, then refluxed for about one hour. After cooling, the product was filtered and recrystallized from alcohol (alcohol and water for the unsubstituted anil).

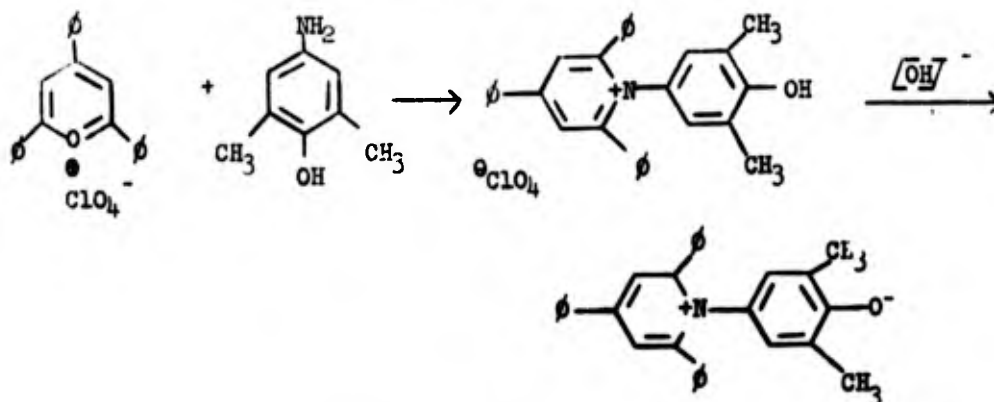
3. Solvatochromic Dyes

a. Merocyanine 1-methyl-4-(4-oxocyclohexadienylidene-ethylidene)-1,4-dihydropyridine⁴¹



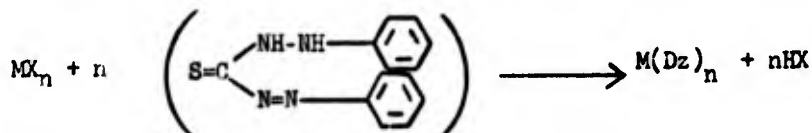
γ -Picoline N-methyl iodide, 5.0 g. (0.021 m.) and p-hydroxy benzaldehyde, 10.0 g., were refluxed together in 2B alcohol with a catalytic amount of piperidine for two hours. After cooling, a bright red product (5.4 g., m.p. 240°) was filtered off. This was slurried in water, then 10 ml. of 10% NaOH added and the slurry stirred for one-half hour. Filtering yielded 3.9 g. This was recrystallized from water, yield 2.5, m.p. 259-260°.

b. Betaine 1-(4-hydroxy-3,5-xyllyl)-2,4,6-triphenyl pyridinium hydroxide, inner salt⁴²



2,4,6-Triphenylpyrilium perchlorate (from condensation of benzaldehyde and acetophenone in conc. H_2SO_4) and 4-amino, 2,6-dimethylphenol (from nitrosation of 2,6-dimethylphenol followed by reduction) in 1:1.5 molar ratio, were refluxed in ethanol for 1/2 hour. Perchloric acid and water were added and yellow product filtered. The product was slurried in H_2O and NaOH added, then extracted with CHCl_3 to yield a dark blue product (50% theory). Recrystallization from alcohol and water yielded dark blue needles (25% theory), m.p. 168-170.

4. Metal Dithizonates



<u>M</u>	<u>X</u>	<u>n</u>	<u>Color</u>		<u>M.P. (Decomp.)</u>	<u>Lit.</u>
			<u>Solid</u>	<u>Soln.</u>		
Hg	Cl	2	red	orange	225-226	227-28
Ag	NO_3	1	orange	yellow-orange	237-238	
Pd	Cl	2	black	green	264-265	
Cd	Ac	2	orange	orange	273	
Cu	Ac	2	dark	violet	188-188-1/2	

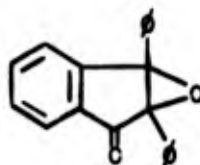
The metal salt was dissolved in a minimum amount of water, then stirred vigorously with toluene or benzene. Dithizone (Eastman reagent grade) was added in increments (with copper, it was necessary to add NaHCO_3

solution alternately). After stirring about an hour, the reaction was filtered and the product recrystallized. (DMF for cadmium, silver, and palladium compounds, benzene for mercury and copper.)

The methyl mercury dithizonate was made from methyl mercuric iodide and dithizone by the same procedure.

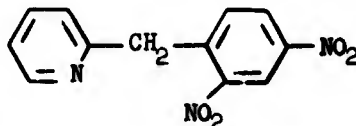
5. Miscellaneous Compounds

a. Diphenylindenoneoxide



From diphenylindenone⁴⁶ by treatment with H_2O_2 in an alkaline media, m.p. 140-140.5, lit. 141.

b. 2(2',4'-dinitrobenzyl)pyridine



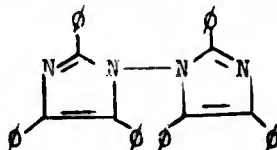
From nitration of 2-benzylpyridine,⁴⁷ m.p. 91-92-1/2, lit. 92-93.

c. 10,10'-bianthrone



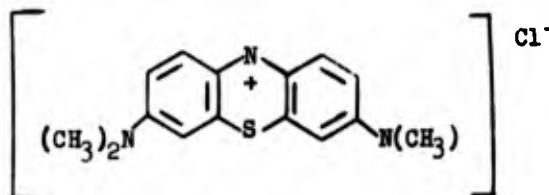
From oxidation of bianthryl with bromine,⁴⁸ m.p. above 300°, lit. above 300°.

d. Lophine dimer (bis-2,4,5-triphenylimidazole)



Prepared from lophine ⁴⁹ by oxidation of the silver salt of lophine with Br₂ in benzene. The silver salt was prepared by reaction of lophine and AgNO₃ in alcohol.

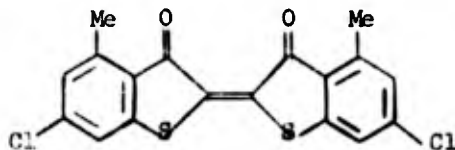
e. Methylene blue



Commercial (zinc free) sample, recrystallized from alcohol.

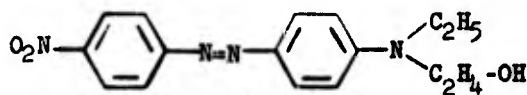
f. Calcophyl Pink FF Conc. (4,4'-dimethyl-6,6'-dichloro-thiaindigo)

Commercial sample.



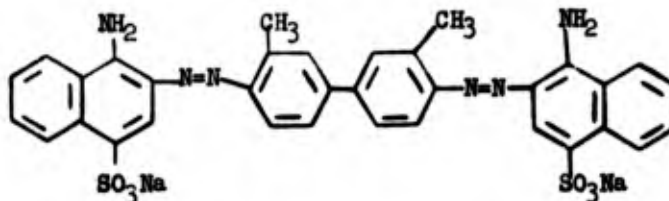
g. Calcocyn Brilliant Scarlet BN (4-nitro, 4'-ethyl, hydroxyethyl amino azo benzene)

Commercial sample.



h. Benzopurpurine

Commercial sample.



6. Polymers

The polymers used, their sources, and the solvents used in preparation of films are listed in the following table.

<u>Polymer</u>	<u>Commercial Name and Manufacturer</u>	<u>Solvent Used for Casting</u>
cellulose acetate	Tenite [®] (Eastman)	acetone
poly(methyl methacrylate)	Acrylite [®] (American Cyanamid)	acetone
polystyrene	Lustrex [®] (Monsanto)	benzene
cianoethylated cotton	Cyanoce [®] (American Cyanamid)	acetonitrile
acrylic polymer	Acrylic T-61 (American Cyanamid)	dimethyl formamide
polyvinyl alcohol	Elvanol 51-04 [®] (Dupont)	water
polyvinyl pyrrolidone	- (General Aniline)	water or alcohol
polyvinyl chloride	Geon [®] (B. F. Goodrich)	tetrahydrofuran

Disperse dyeings were carried out on;

- a. Delustered secondary cellulose acetate fabric,
- b. Delustered nylon (66) fabric,
- c. 2-mil Mylar film (du Pont).

B. Methods

Visible (and some ultraviolet) spectra were taken on most compounds in solvents and in polymer films. Most solution spectra were run on purified material in reagent grade solvent, especially when molar absorptivities were being determined.

Compounds of interest were incorporated in the polymers by one or more of the following methods:

- a. Solution casting,
- b. Milling and molding,
- c. Dyeing.

In a typical solution-casting experiment, 10 gms. of polymer were dissolved in enough solvent to make a 20-30% solution (by weight). The compound was then added to this polymer solution and thoroughly mixed. The resulting solutions were usually allowed to stand about one hour, before making films, to ensure homogeneity and to remove entrapped air bubbles. Films were made by (1) casting the solution on glass or metal plates with a doctor blade, or (2) dipping microscope slides in the solution and removing at a slow, even speed. The films were then dried in a steam-heated oven at approximately 50°C. The dipped slides were placed in a holder so they dried in a vertical position.

Milling was performed on a hot roll mill at about 180°C for 20 to 40 passes, followed by hot compression molding at 170°C. Thus 15- and 50-mil chips were prepared containing 0.01 to 0.04 percent compound.

Dyeing was used to incorporate some of the mercury dithizonates into Mylar film and on cellulose acetate and nylon fabrics. These compounds were applied as disperse dyes. The compound was dissolved (with heating, if necessary) in a small amount of acetone, followed by addition of a small amount of an aqueous solution of Dupanol WA^(R) (5%/wt.). Distilled water was added rapidly to produce a fine dispersion. Dyeings were carried out at 80-90°C for about one hour. These dyeings were not subjected to rigorous fastness tests (e.g., light, wash, Cl₂, etc.). The pH sensitive dye, benzopurpurine, was dyed from aqueous solution, with common salt, as a direct dye.

All of the spectra presented in this report were obtained as transmittance data on the Cary Model 14 recording spectrophotometer. The spectra taken in polymer films were generally run versus an air reference. Spectra of polymer films, immersed in solvents, were run in regular 1 cm. cells versus the solvent, using inserts to hold the film against the cell wall.

When visible spectra were recorded in the normal manner, the weak light beam emerging from the monochromator did not cause any spectral change in the photochromic samples. The spectra of the "dark" forms were therefore obtained in this manner. The photostationary spectra were obtained by using the reversed optics system of the instrument. Under these conditions, the full power of a strong tungsten lamp (a 108-watt projection lamp, GPR) was directed on the sample* and the transmitted light was sent through the monochromator to a lead sulfide detector. Identical spectra were obtained, by the two recording techniques, on a number of nonphotochromic samples. In some cases, particularly with highly scattering samples, the two techniques differed by 1 to 2 percent.

All rate measurements, thermal and photo, were carried out spectrophotometrically by following changes in absorbance, as a function of time, at a particular wavelength. In general, the kinetic data for the photo and thermal rates were not strictly first order. Some typical first-order rate plots are shown in Figure 27 for a spiropyran and in Figure 28 for HgDz_2 , both in polymeric media. The photo rates were so fast that they were difficult to measure accurately. The thermal return for the spiropyran is obviously not first order but the thermal return for HgDz_2 in cellulose acetate shows only a slight curvature. Since the bulk of the rate data was obviously of complex order and since time did not permit establishment of the exact order, all rates reported in this work are expressed as $t_{1/2}$ values, i.e., the time required for the absorbance (at λ) to go from some initial value (Abs_0) to one-half ($\text{Abs}_0 - \text{Abs}_\infty$) where Abs_∞ is a final or equilibrium absorbance at λ .

For spectral measurements above and below room temperature, solutions and polymer films were held in constant temperature cells. For solution work, regular 1 cm glass or silica cells were used in a Cary No. 144,300 thermostable cell adapter. Solution temperature was measured by inserting an ordinary thermometer into the solution. Polymer films were sandwiched between two aluminum blocks which were fitted with an opening for the light path. Temperatures were measured with a copper-constantan thermocouple. Temperature control for both of the above holders was obtained by circulating a constant temperature liquid through the holder. Distilled water was used for studies at room temperature and above, while a 50% ethylene glycol solution (in water) was used for low temperature work. Cooling of the ethylene glycol-water was accomplished with a separate refrigeration unit. When operating at low temperature (e.g., 0°C), a strong stream of dry nitrogen was kept flowing through the sample compartment of the Cary 14 to prevent moisture condensation on the cells or films.

Photochromic samples which were activated by ultraviolet light were irradiated with a Hanovia No. 30600 high pressure mercury vapor arc lamp (140 watts). This lamp was equipped with a Hanovia No. 6540 heat resistant filter and a Hanovia No. 16223 filter to isolate the 365 m μ Hg line.

* An infrared absorbing KG-3 filter (Fish Schurman Corp., New Rochelle, New York) was placed between lamp and sample to eliminate heating effects.

The intensity of the tungsten lamp in the Cary 14 was measured in the region of 440 to 460 $m\mu$ by actinometry. Potassium ferrioxalate was used as the actinometer following essentially the method of C. G. Hatchard and C. A. Parker.⁴⁵ A combination of Wratten No. 50 and Corning CS3-73 filters was used to obtain a narrow band pass. The integrated transmission values for this filter combination were as follows:

<u>Wavelength Band ($m\mu$)</u>	<u>% of Total Transmitted Light in each Wavelength Band</u>	<u>% Transmission of Incident Light in each Wavelength Band</u>
420-440	8.35	0.81
440-460	64.5	6.26
460-480	26.2	2.55
480-	0.62	0.06

Approximately 3 cc. of 0.15 N potassium ferrioxalate was used for each determination. While the experiments were being run it was necessary to change the lamp. A comparison of values for an old lamp and a new one is as follows:

TABLE XIII

	<u>Time Exposed</u>	<u>Calculated einsteins/sec/cm² (440-460 $m\mu$)</u>
New Lamp	8 min.	10.5×10^{-8}
	17 min.	10.8×10^{-5}
Old Lamp	4 min.	9.86×10^{-8}
	8 min.	9.60×10^{-8}

Values at other wavelengths were obtained from output of a standard lamp plotted in einsteins/sec./cm² vs. wavelength.⁴⁶ Assuming the difference in color temperature between the two lamps would not materially affect the shape of the curves, the areas under the curve at various wavelengths were taken as proportional.

TABLE XIV

<u>Wavelength Band ($m\mu$)</u>	<u>Intensity (einsteins/sec/cm²)</u>
400-420	4.46×10^{-8}
420-440	6.9×10^{-8}
440-460	9.8×10^{-8}
480-500	18.3×10^{-8}
580-600	60.3×10^{-8}

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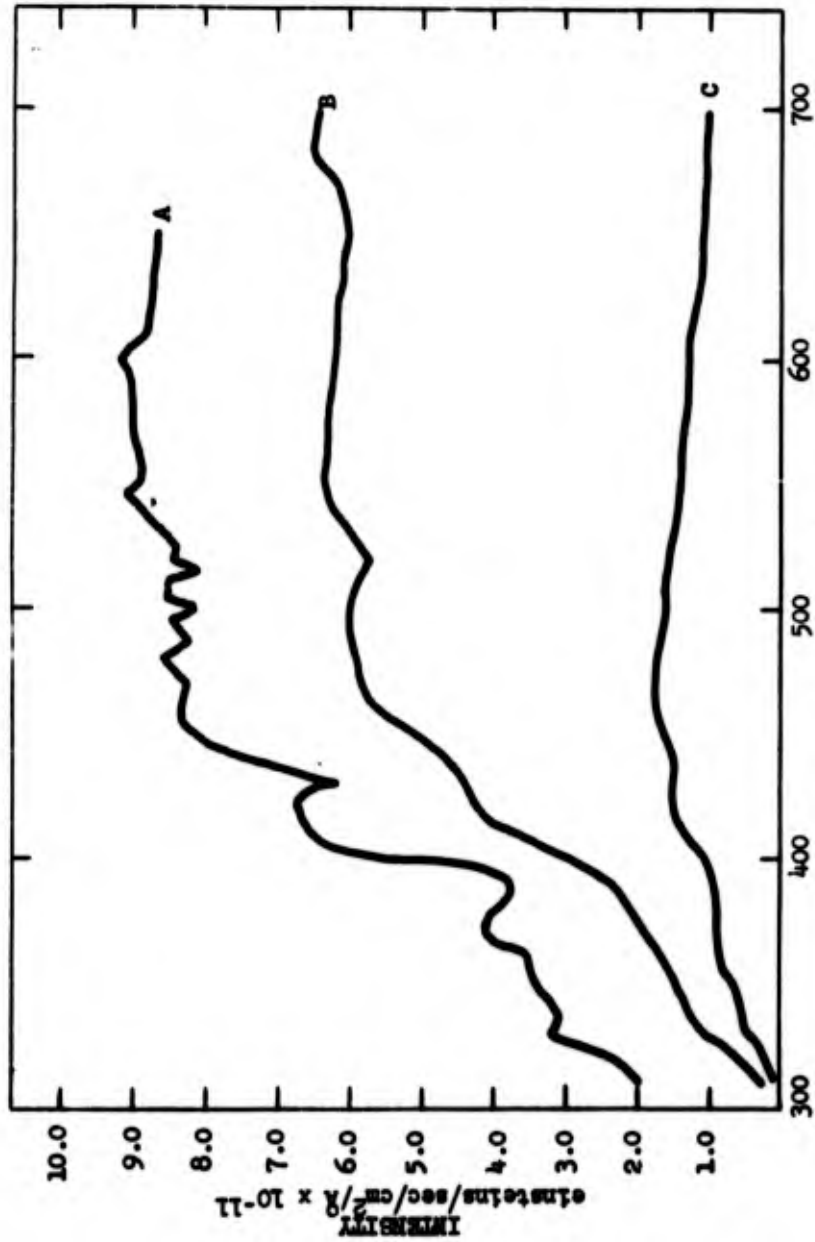
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APPENDIX

(FIGURES)

Note: For all spectral curves, the wavelength
abscissa is from 320 to 740 $m\mu$.



WAVELENGTH, MILLIMICRONS

Figure 1. Sunlight Intensity Distributions.

- A - Full solar radiation, (air mass = 0).
- B - Full sunlight, (skylight and direct sunlight) (solar noon in July).
- C - Skylight (solar noon in July).

Data For Figure 1
(in einsteins/sec/cm²/A° times 10⁻¹¹)

<u>λ (μ)</u>	<u>Solar Radiation</u>	<u>Direct Sunlight</u>	<u>Skylight</u>	<u>Full Sunlight</u>
305			0.062	
310	1.97	0.125	0.122	0.247
315	2.09	0.230	0.212	0.412
320	2.27	0.349	0.232	0.581
325	2.80	0.474	0.430	0.904
330	3.20	0.596	0.531	1.127
335	3.14	0.652	0.570	1.222
340	3.16	0.717	0.608	1.325
345	3.34	0.760	0.634	1.394
350	3.42	0.810	0.660	1.470
355	3.47	0.855	0.682	1.537
360	3.49	0.950	0.740	1.690
365	3.96	1.040	0.800	1.840
370	4.12	1.15	0.860	2.010
375	4.14	1.18	0.863	2.043
380	3.94	1.205	0.872	2.077
385	3.73	1.239	0.878	2.117
390	3.72	1.390	0.950	2.340
395	3.93	1.590	1.03	2.620
400	5.14	1.792	1.103	2.895
405	6.36		1.262	
410	6.65	2.33	1.432	3.762
415	6.66			
420	6.73	2.65	1.565	4.215
425	6.71			

Data for Fig. 1 (Continued)

<u>λ (mμ)</u>	<u>Solar Radiation</u>	<u>Direct Sunlight</u>	<u>Skylight</u>	<u>Full Sunlight</u>
430	6.14	2.905	1.53	4.435
435	6.62			
440	7.43	3.13	1.478	4.608
445	7.92			
450		3.41	1.631	5.041
455	8.36			
460		3.78	1.798	5.668
465	8.30			
470	8.32	4.03	1.793	5.796
480	8.64	4.18	1.738	5.918
485	8.23			
490		4.31	1.695	6.005
495	8.56			
500	8.15	4.38	1.612	5.992
510	8.52	4.32	1.567	5.887
515	8.08			
520	8.45	4.27	1.462	5.732
525	8.40			
530	8.66	4.56	1.438	5.998
540	8.86	4.84	1.428	6.268
545	9.11			
550		4.91	1.418	6.328
552	8.96			
560	8.89	4.91	1.365	6.266
570	8.95	5.00	1.317	6.317
575	9.00			

Data for Fig. 1 (Continued)

<u>λ (mμ)</u>	<u>Solar Radiation</u>	<u>Direct Sunlight</u>	<u>Skylight</u>	<u>Full Sunlight</u>
580	9.01	4.98	1.281	6.261
585	8.98			
590		5.02	1.223	6.243
598	9.10			
600	9.13	5.04	1.182	6.186
610	8.75	4.98	1.142	6.122
620		5.03	1.140	6.170
630	8.72	5.00	1.128	6.128
640		4.96	1.092	6.052
650	8.63	4.98	1.055	6.035
660		5.00	1.028	6.028
670		5.14	1.042	6.182
680		5.46	1.034	6.494
690		5.47	1.028	6.498
700		5.41	0.982	6.442

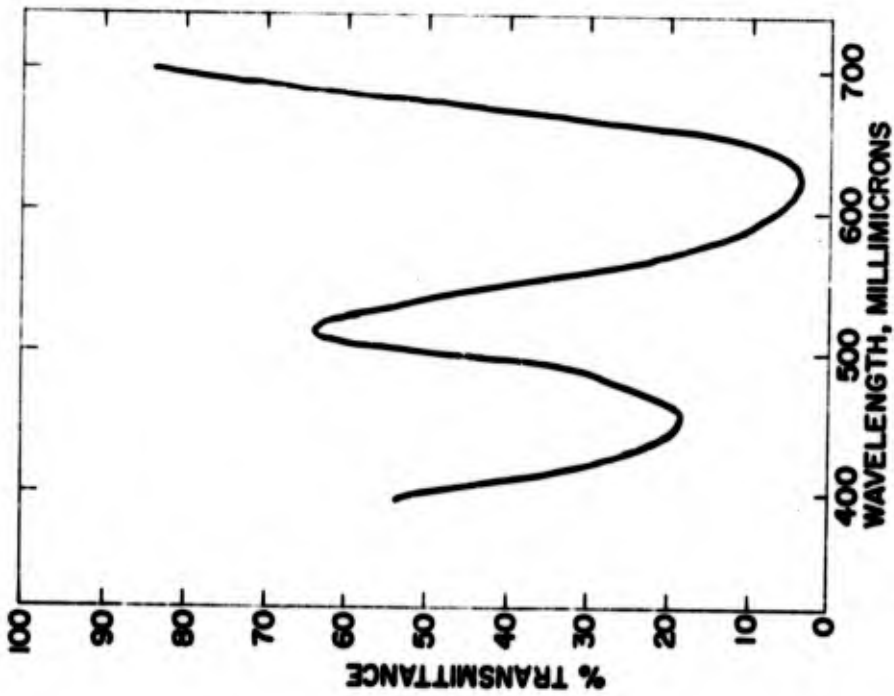


Figure 2. Spectral curve of dithizone, (II) in benzene, 0.01 gm./l., 1 cm. cell.

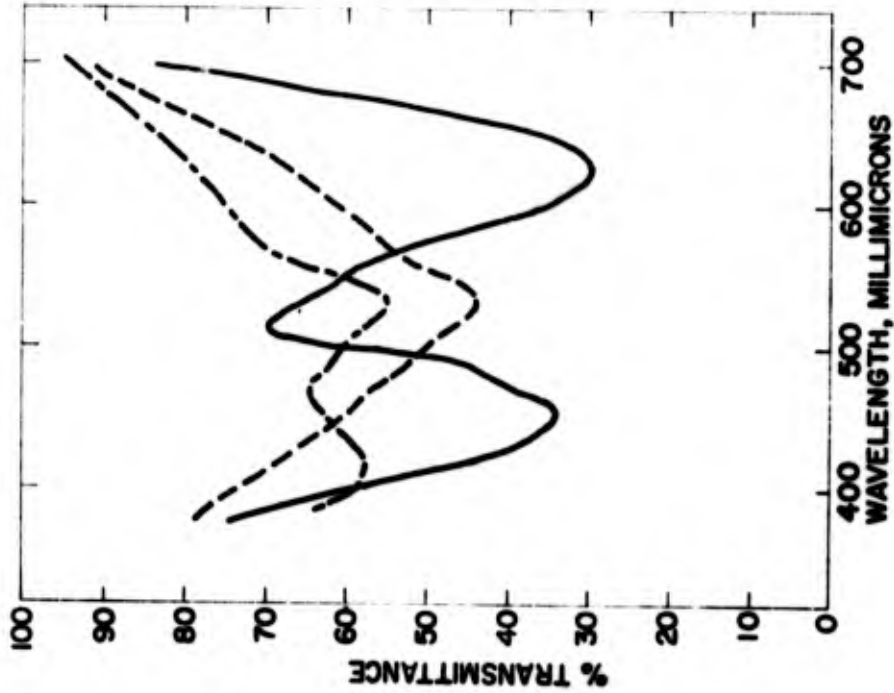


Figure 3. Spectral curves of dithizone (II) in hexane, at approximately 1°C.

— unirradiated
- - - irradiated (initial)
- · - · - irradiated (prolonged)

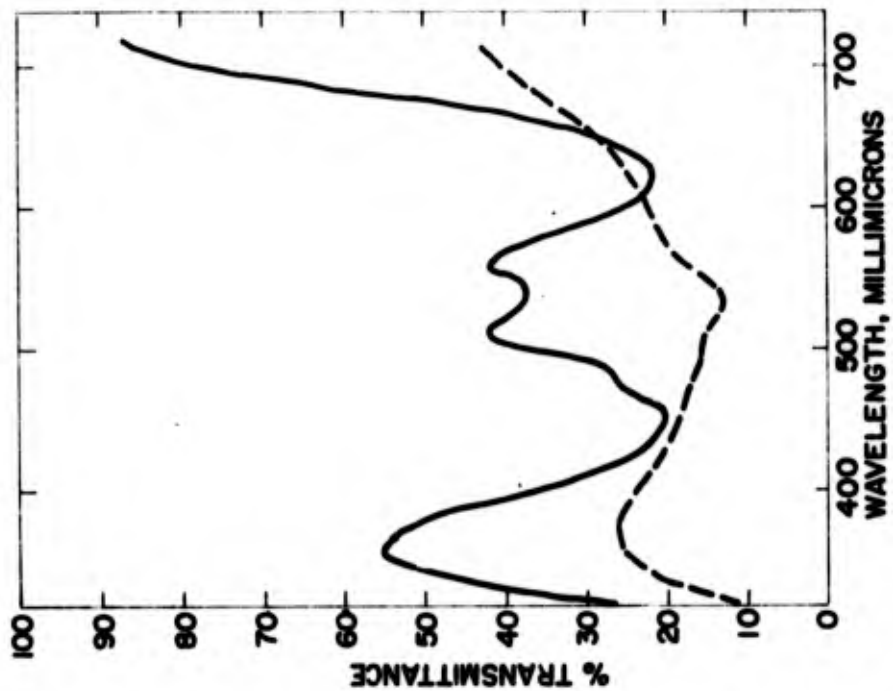


Figure 5. Spectral curves of dithizone (II), in hexane, sealed cell, at approximately 1°C.

— unirradiated
- - - irradiated

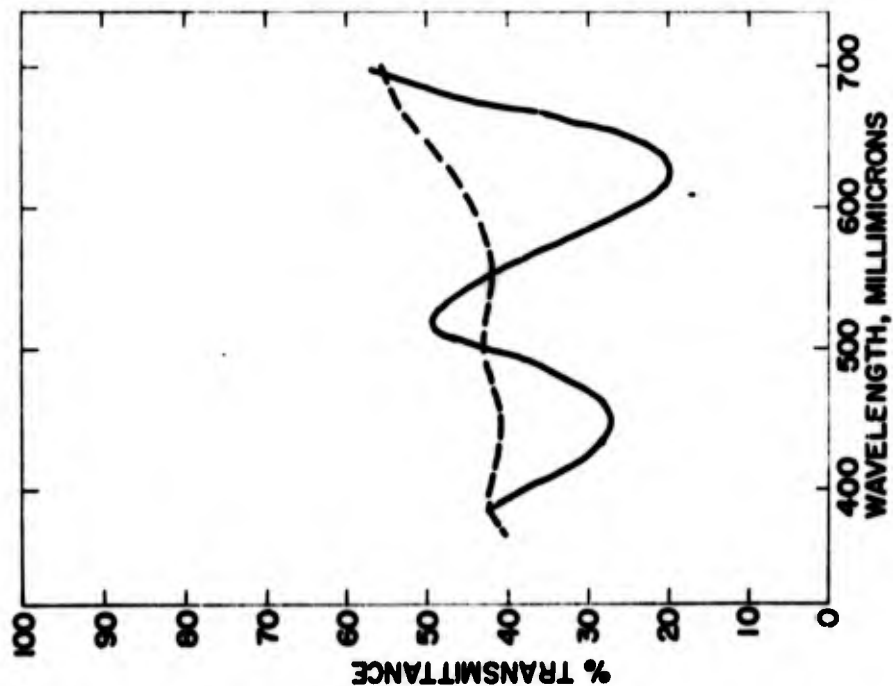


Figure 4. Spectral curves of dithizone (II), in polystyrene film, at approximately 1°C.

— unirradiated
- - - irradiated

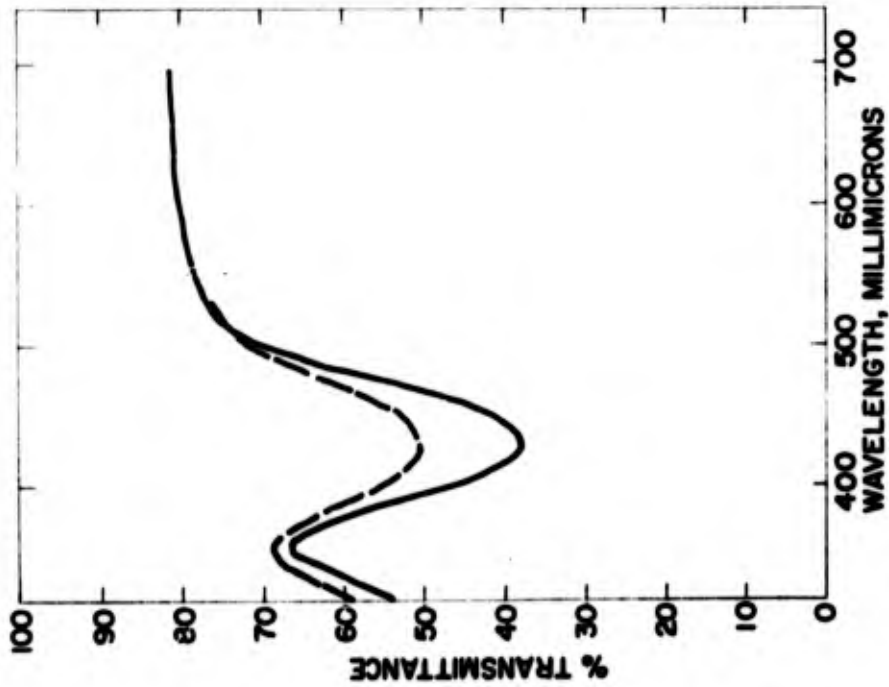


Figure 6. Spectral curves of dithizone (II) in polystyrene film at approximately 1°C. Sample aged; (exposed to sunlight plus room lights); for two months.

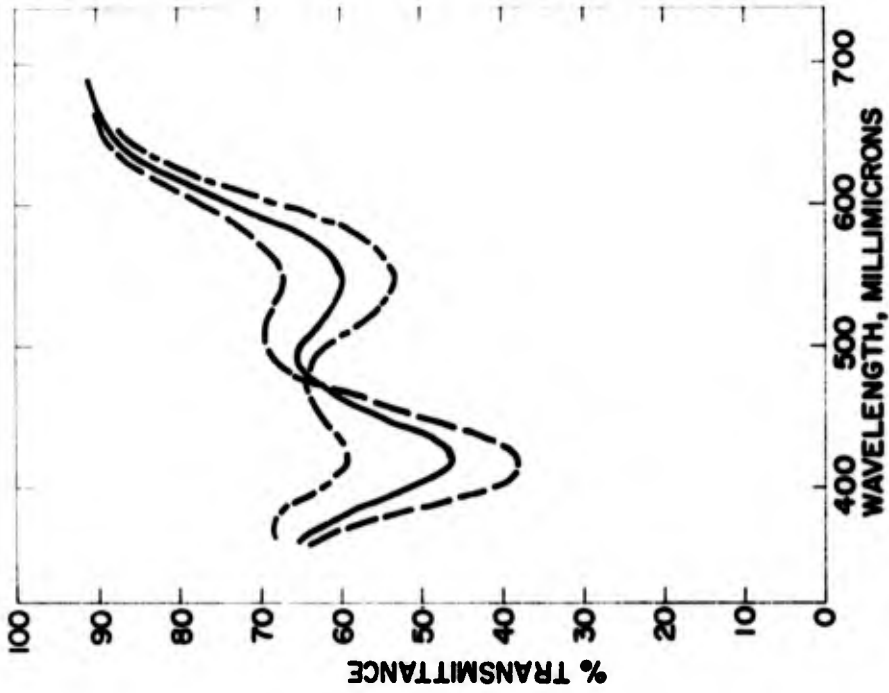


Figure 7. Spectral curves of the S-methyl analog of dithizone, (III), in cellulose acetate, 0.1% wt., cast film.

- unirradiated (24 hours in dark)
- - - after irradiation with 420 mμ light
- · - after irradiation with 540 mμ light

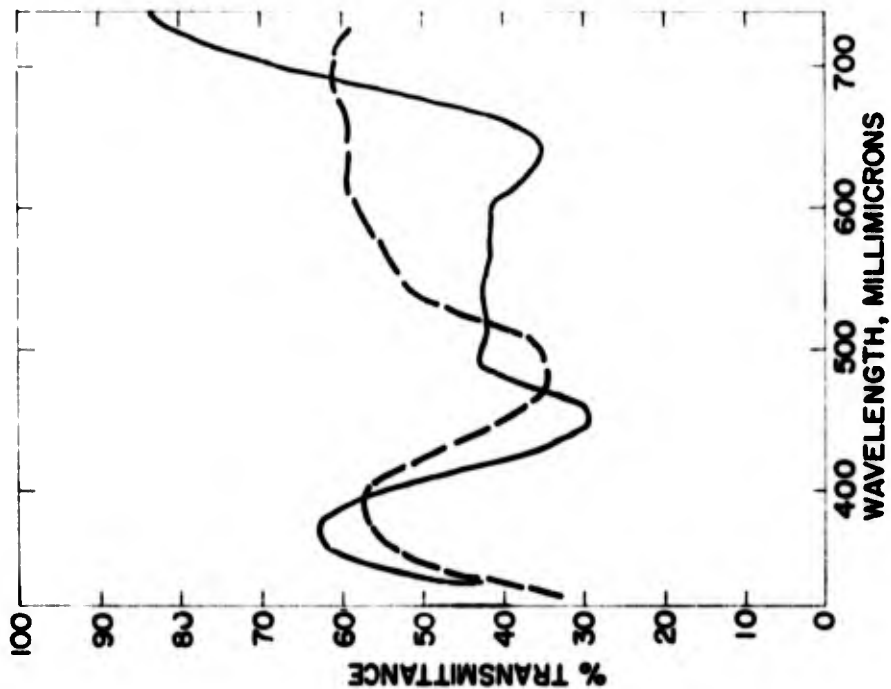


Figure 9. Spectral curves of palladium bisdithizonate in cellulose acetate at approximately 1°C.

— unirradiated
- - - irradiated

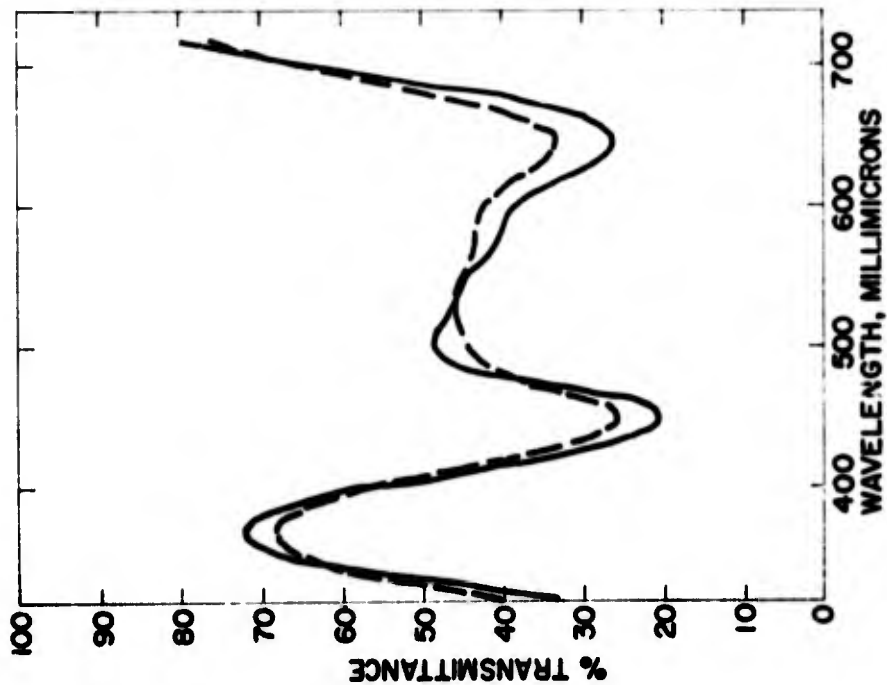


Figure 8. Spectral curves of palladium bisdithizonate in tetrahydrofuran, 0.01 gm./l., 1.0 cm. cell.

— unirradiated
- - - irradiated

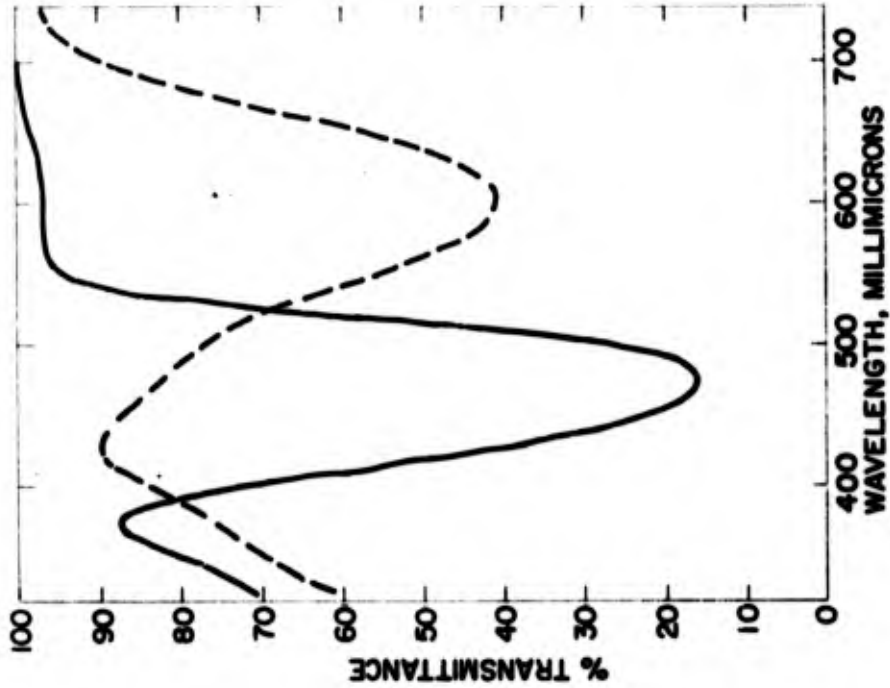


Figure 11. Spectral curves of methylmercury dithizonate in benzene, 6.67×10^{-3} gm./l., 1.0 cm. cell.

— unirradiated
- - - irradiated

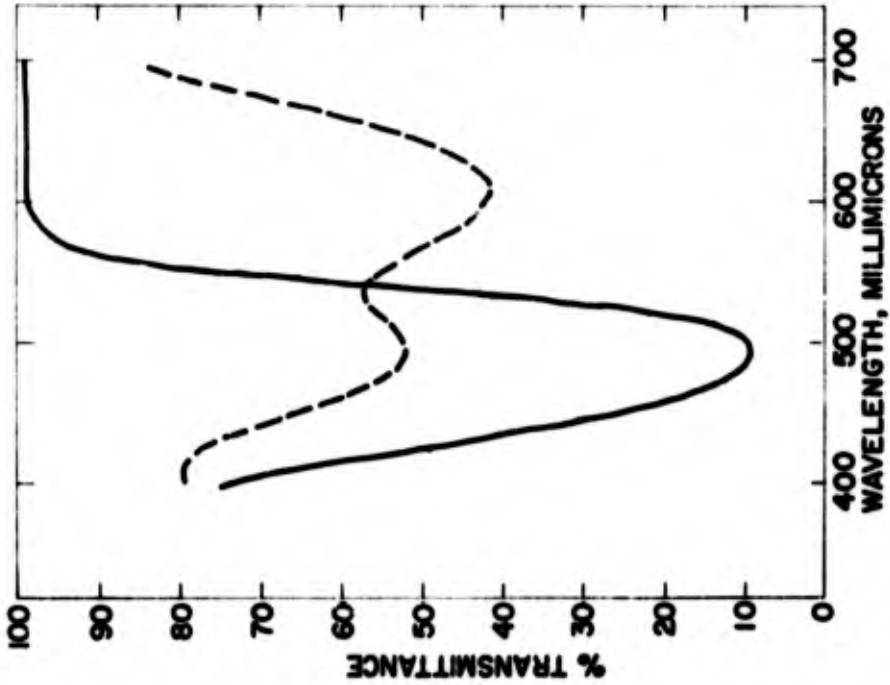


Figure 10. Spectral curves of mercury bisdithizonate in benzene, 1.11 x 10⁻² gm./l., 1.0 cm. cell.

— unirradiated
- - - irradiated

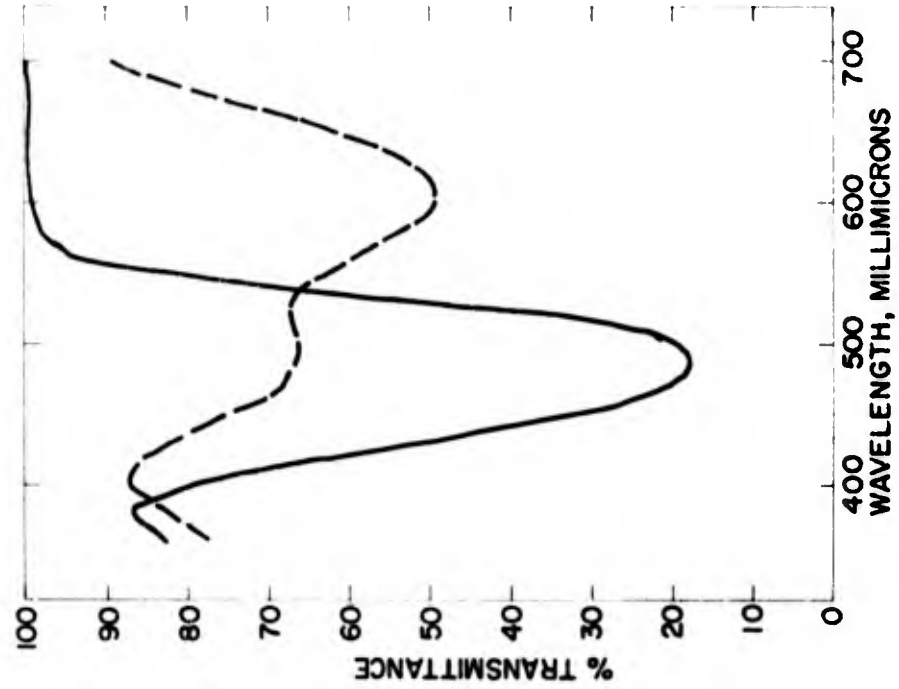


Figure 13. Spectral curves of mercury bis-dithizonate in "dry" benzene, (stored over Linde 3A molecular sieves), 8.23×10^{-3} gm./l., 1.0 cm. cell.

———— unirradiated
----- irradiated

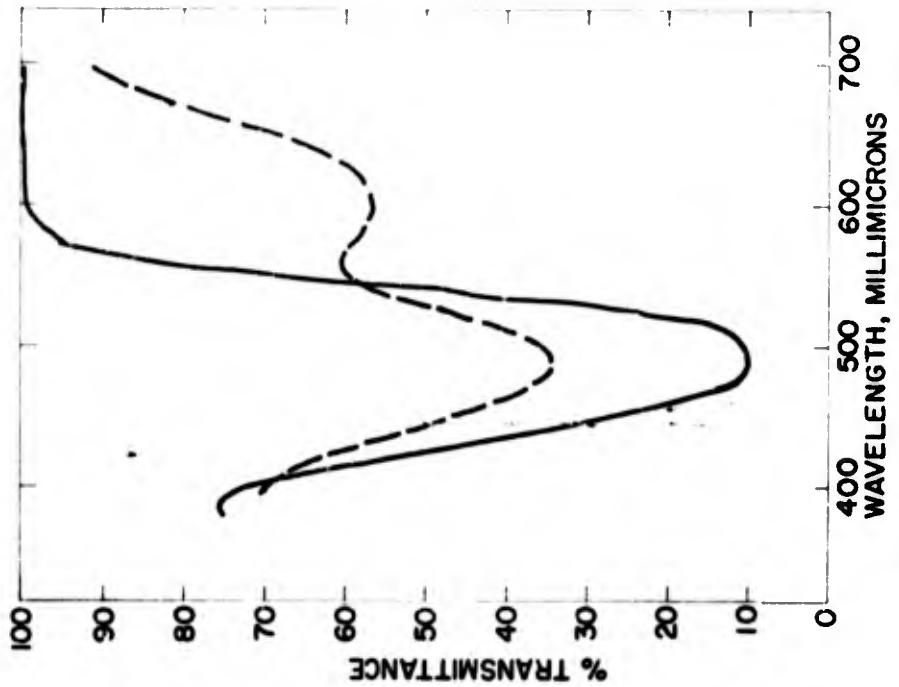


Figure 12. Spectral curves of mercury bisdithizonate in "wet" benzene (water added), 1.11×10^{-2} gm./l., 1.0 cm. cell.

———— unirradiated
----- irradiated

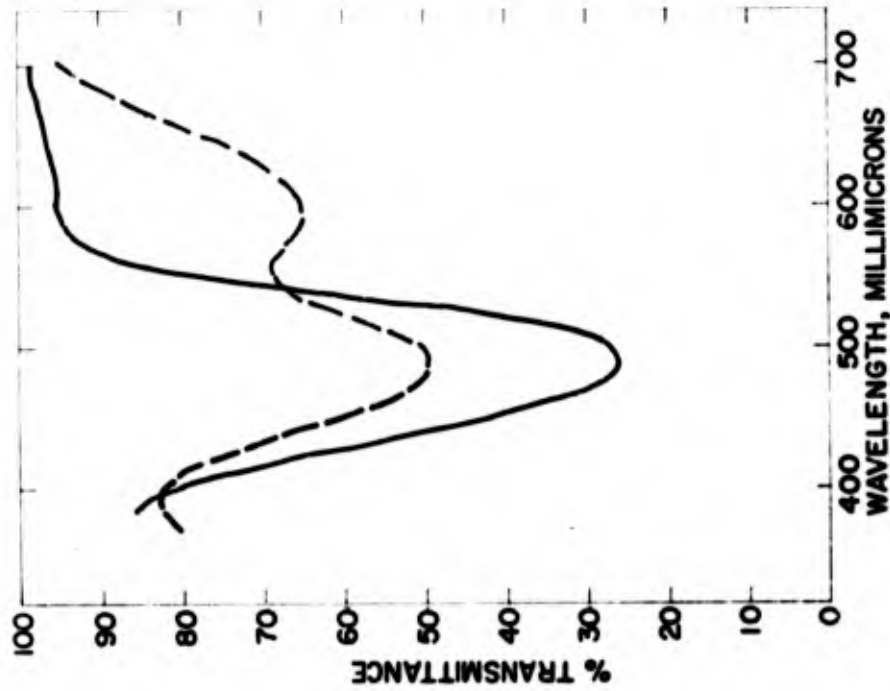


Figure 15. Spectral curves of mercury bis-dithizonate in cellulose acetate, 0.1%/wt., cast film, immersed in water.

— unirradiated
- - - irradiated

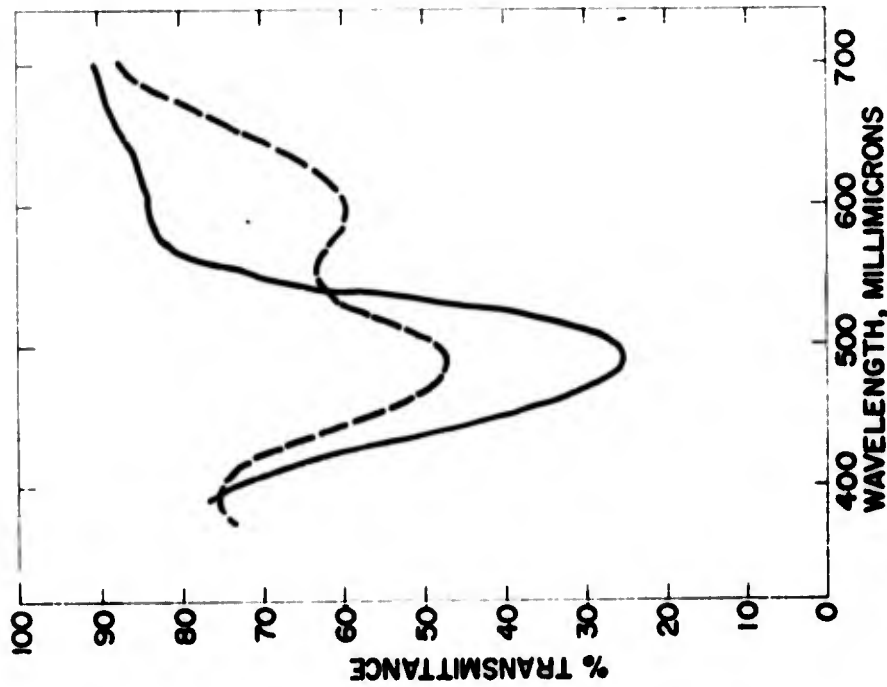


Figure 14. Spectral curves of mercury bisdithizonate in cellulose acetate, 0.1%/wt., cast film, equilibrated at room relative humidity.

— unirradiated
- - - irradiated

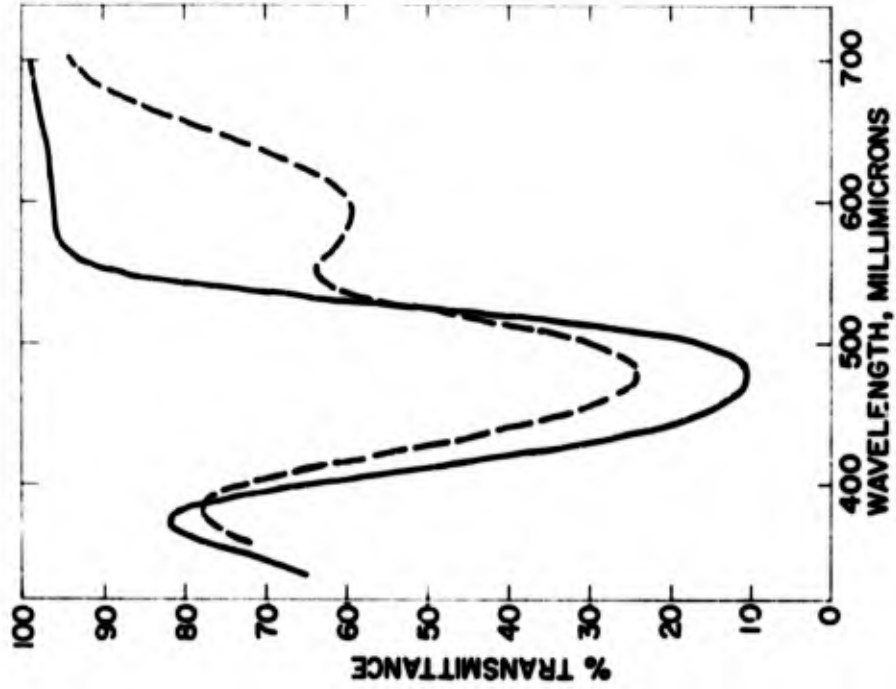


Figure 17. Spectral curves of methylmercury dithizonate in cellulose acetate, 0.1%/wt., cast film, immersed in water.

— unirradiated
- - - irradiated

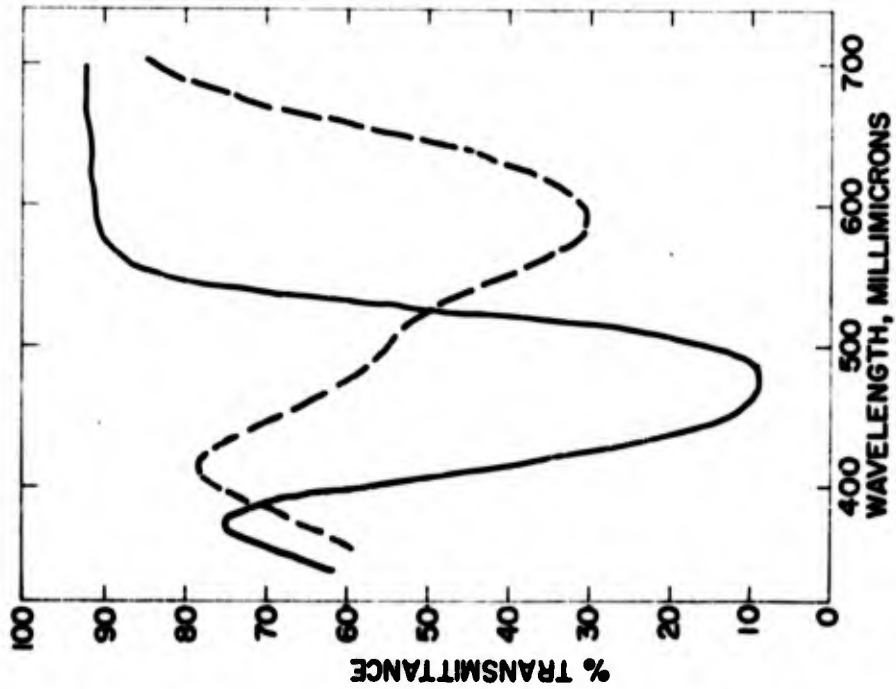


Figure 16. Spectral curves of methylmercury dithizonate in cellulose acetate, 0.1%/wt., cast film, equilibrated at room relative humidity.

— unirradiated
- - - irradiated

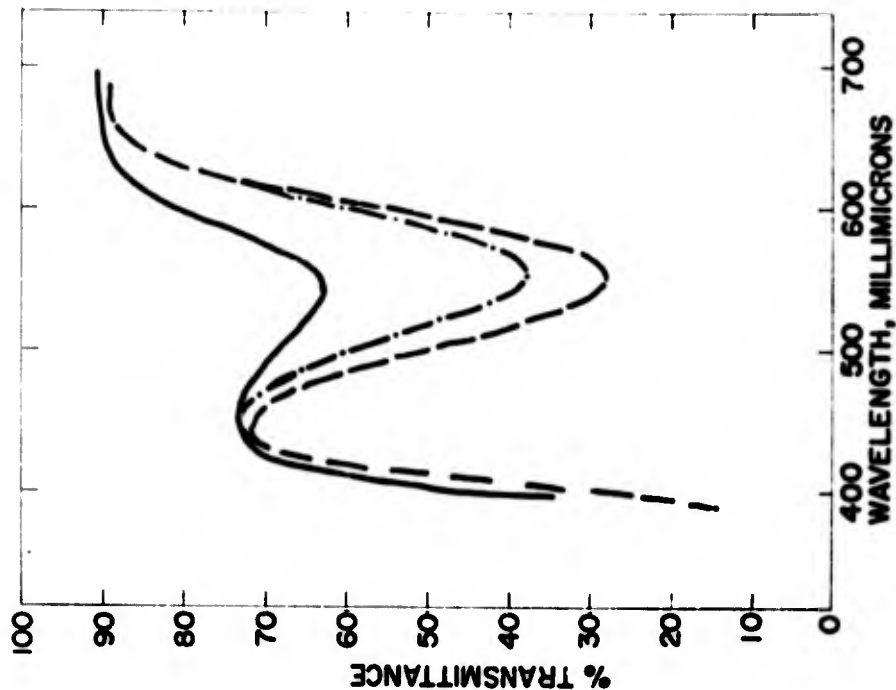
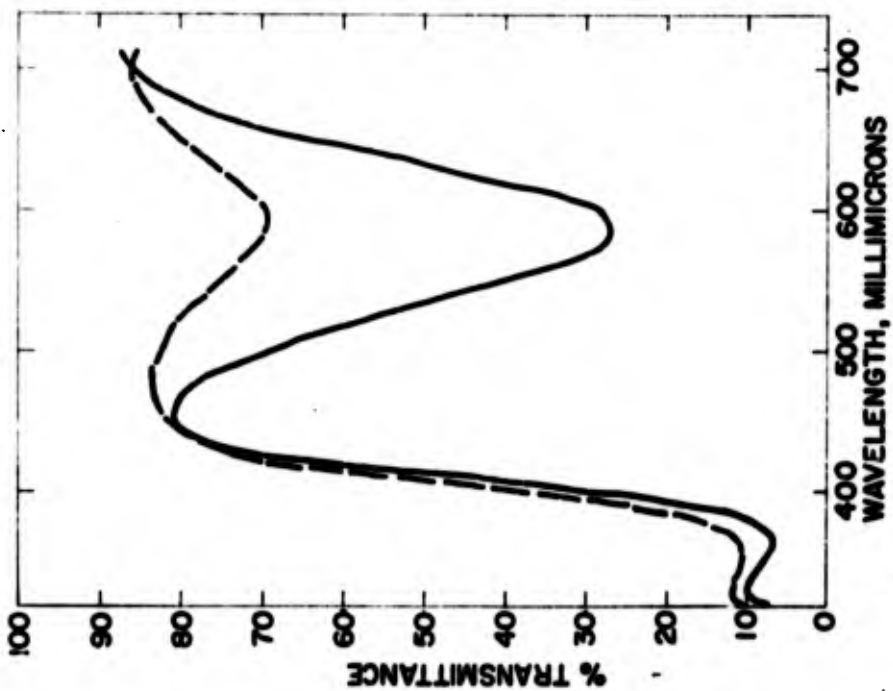


Figure 18. Spectral curves of 6'-chloro-8'-nitrobenzospiropyran, (VIb), in cellulose acetate, 3.0%/wt., dipped microscope slide.

Figure 19. Spectral curves of 6'-nitrobenzospiropyran, (VIa), in cellulose acetate, 3.0%/wt., dipped microscope slide.

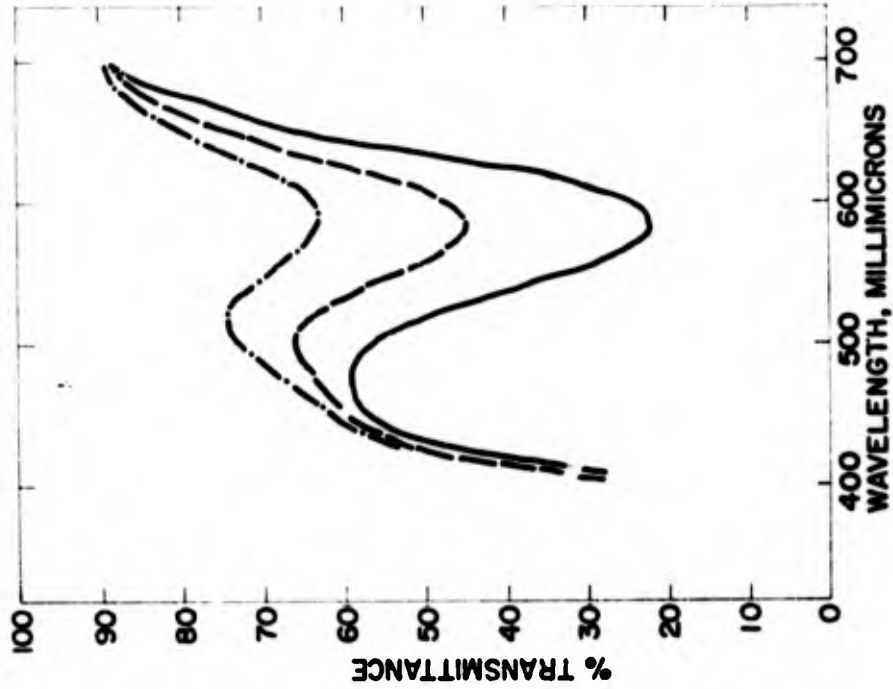


Figure 21. Spectral curves of 6'-chloro-8'-nitrobenzospiropyran, (VIb), in cellulose acetate, 3.0%/wt., dipped microscope slide.

— unirradiated
- · - · - irradiated with full sunlight
- - - irradiated with skylight

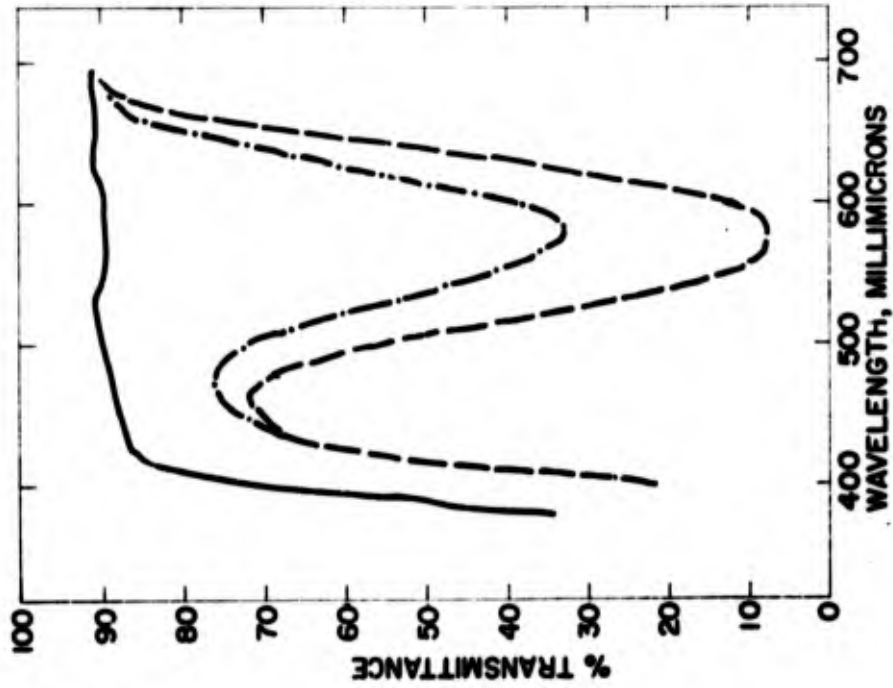


Figure 20. Spectral curves of 6'-nitrobenzospiropyran, (VIa), in polymethylmethacrylate, 3.0%/wt., dipped microscope slide.

— unirradiated
- · - · - irradiated with full sunlight
- - - irradiated with skylight

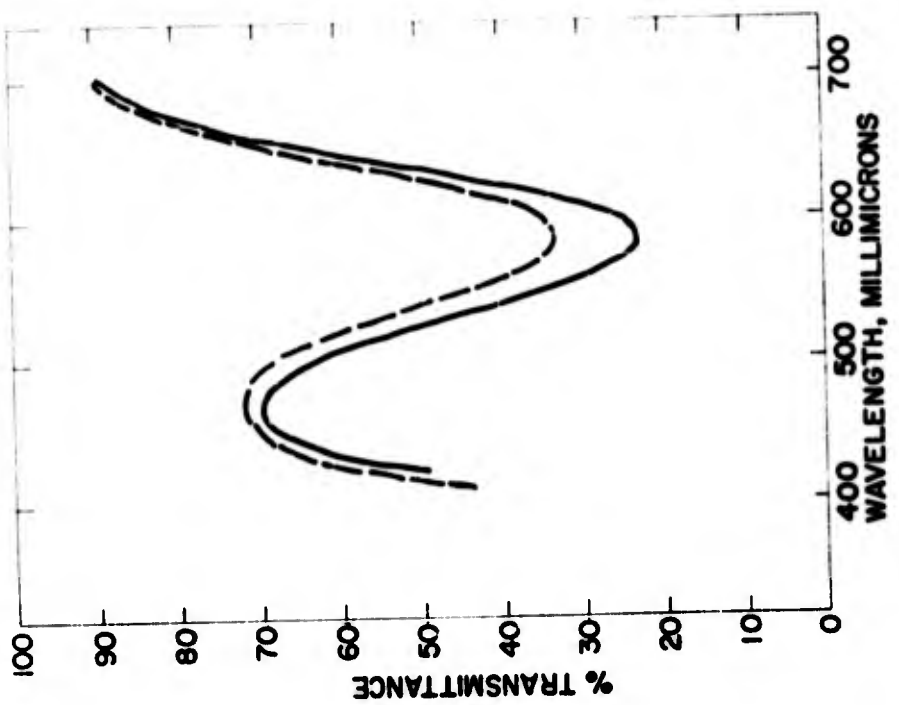


Figure 23. Spectral curves of 6'-chloro-8'-nitrobenzospiropyran, (XVII); in cellulose acetate, 3.0%/wt., dipped microscope slide.

— at approximately 35°C
--- at approximately 65°C

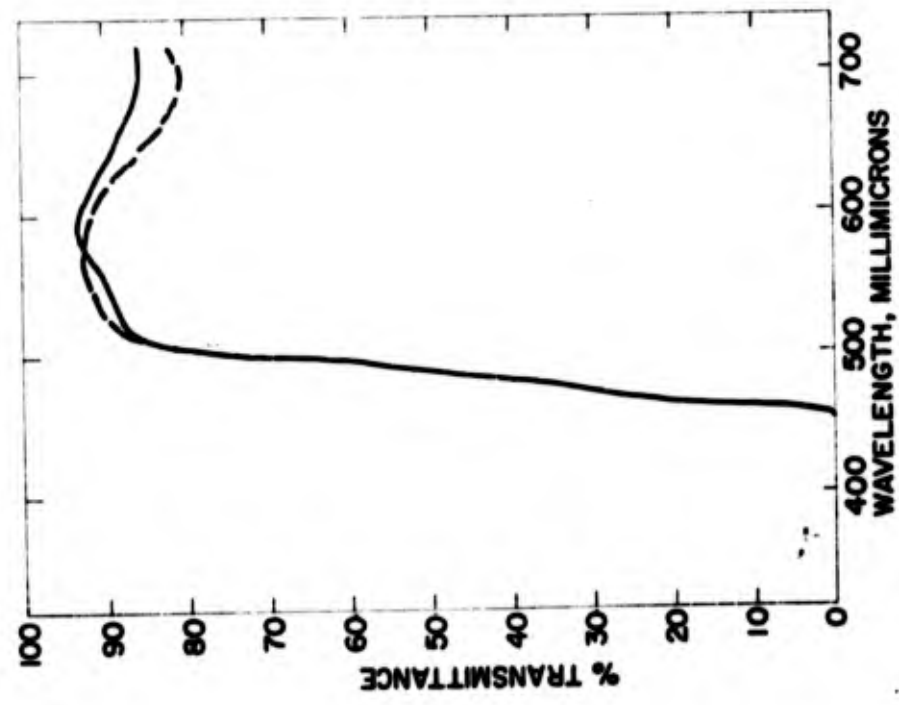


Figure 22. Spectral curves of 10,10'-bisanthrene; (XIV); in dimethylformamide, approximately 1.0 gm./l., 1.0 cm. cell.

— at room temperature
--- at approximately 60°C.

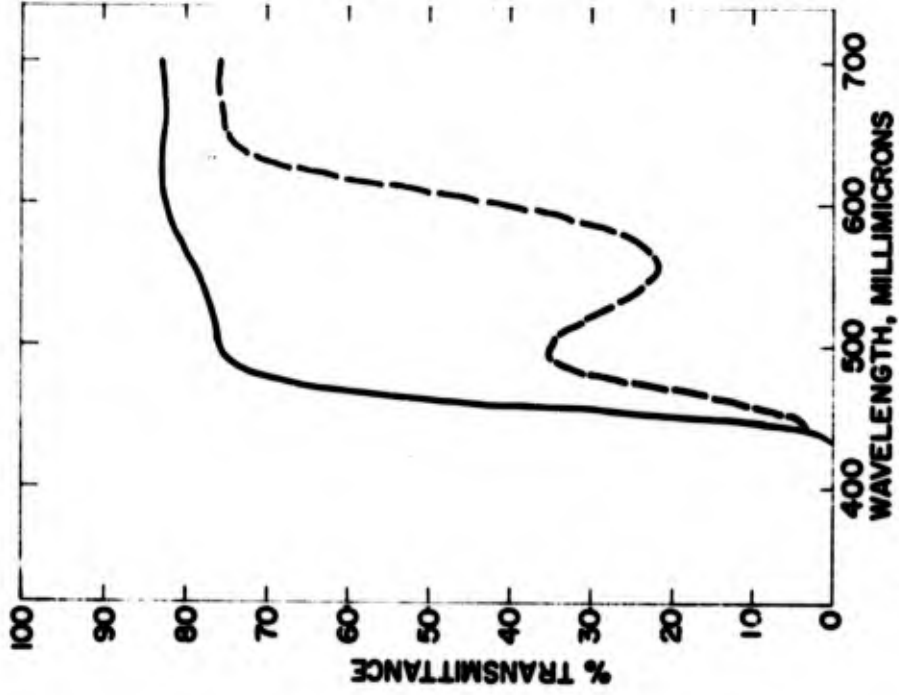


Figure 25. Spectral curves of merocyanine dyes, (XVIII), in polyvinylpyrrolidone, tipped microscope slide.

— at room temperature and humidity
- - - at approximately 60°C

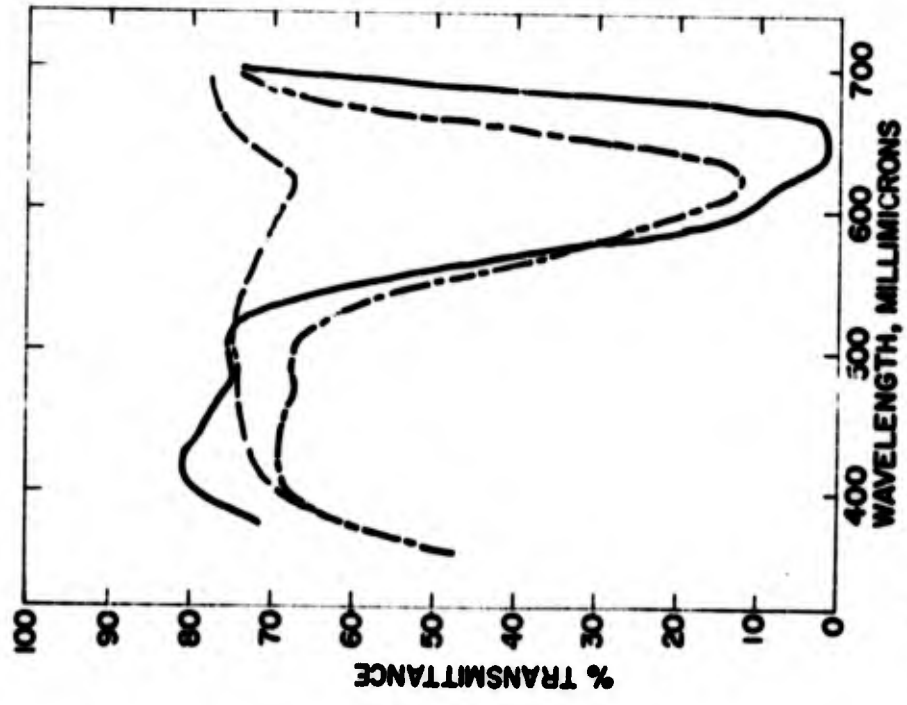


Figure 24. Spectral curves of methylene blue in polyvinyl alcohol, cast film.

— unirradiated
- - - irradiated
- · - · - after recovery from first irradiation

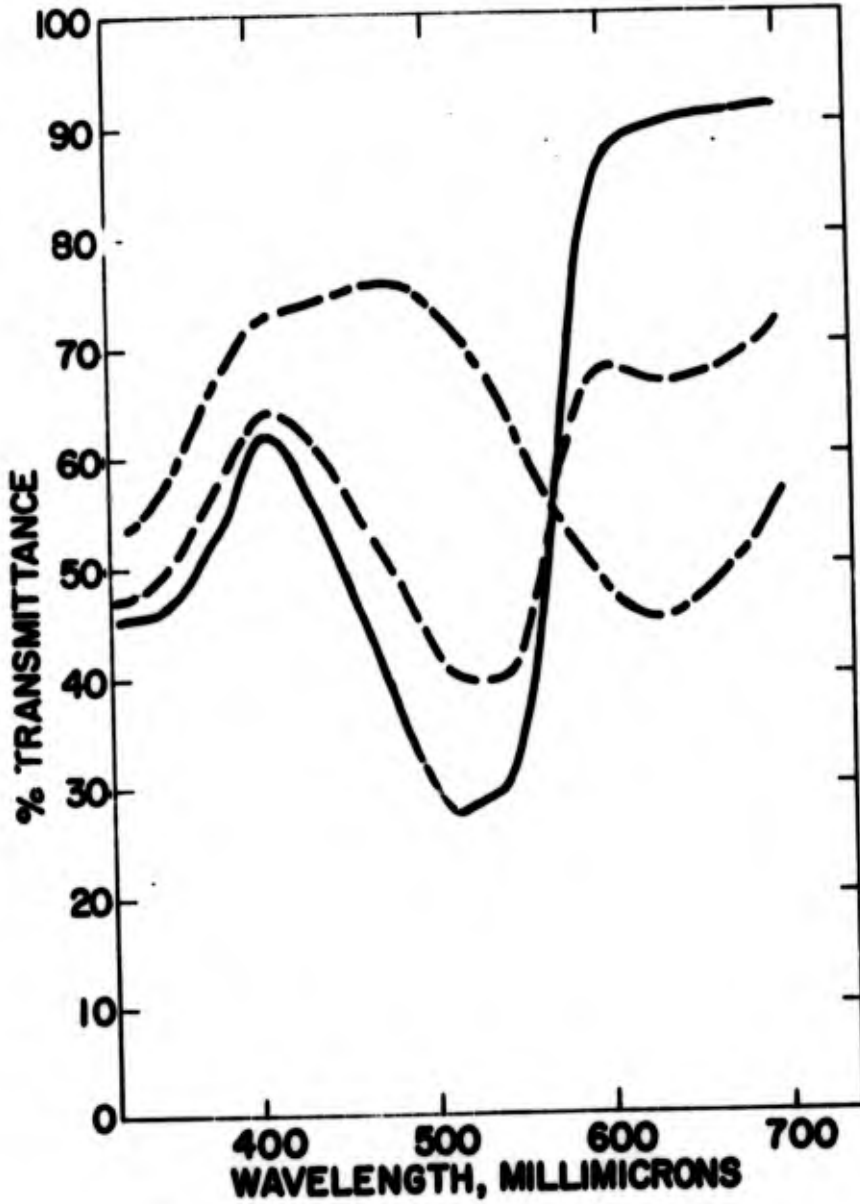


Figure 26. Spectral curves of benzopurpurine, (XX), dyed into cellophane film.

- equilibrated in distilled water
- - - equilibrated at pH 1.0
- · - · - equilibrated in strong acid (6N HCl)

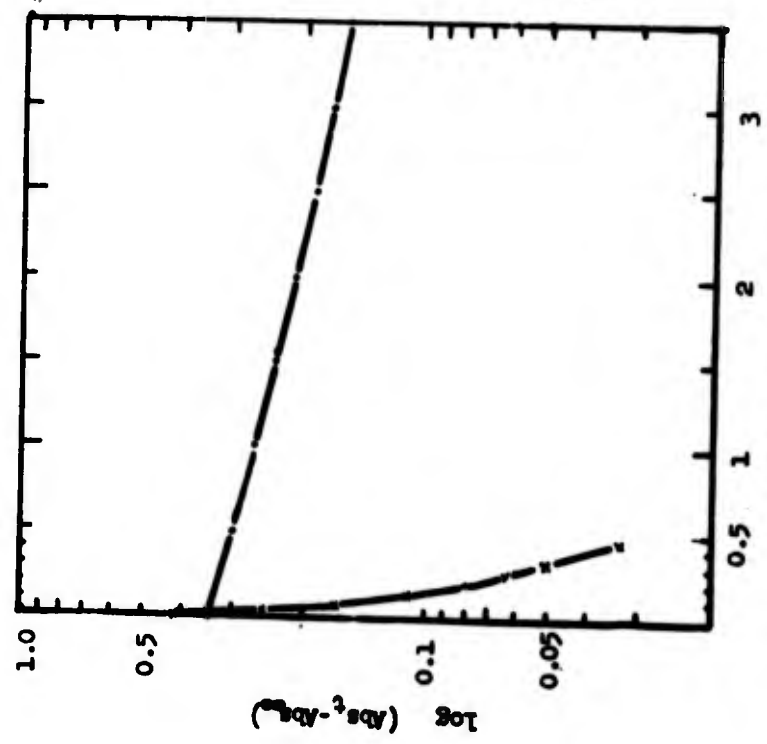


Figure 26. Kinetic plots for mercury bis-dithizonate in cellulose acetate. Change in absorbance at 600 μ vs. time.

- thermal return, (orange to blue); $t_{1/2} = 4$ sec.
- - - - - thermal return (blue to orange); $t_{1/2} = 92$ sec.

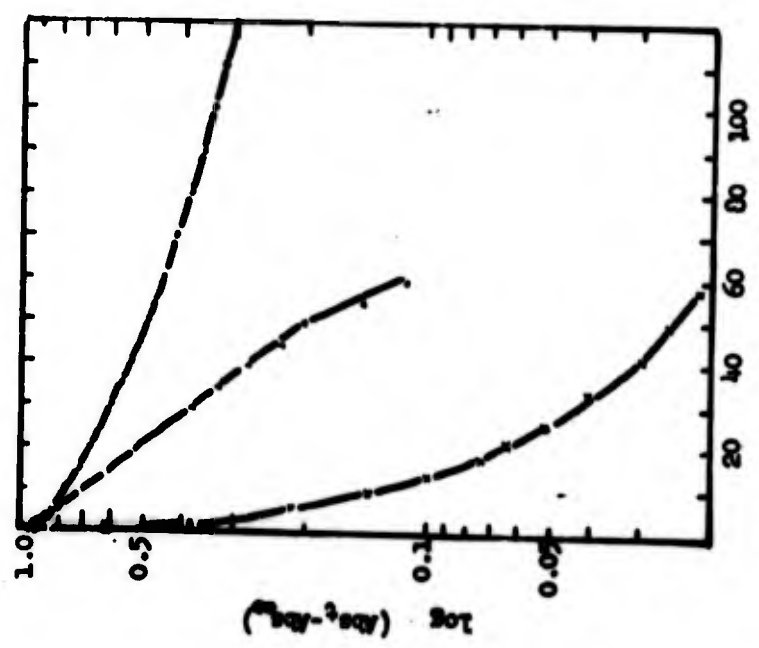


Figure 27. Kinetic plots for 6-nitrobenzopyrrophan, (VIa), in polymethylmethacrylate. Changes in absorbance at 590 μ vs. time.

- visibly activated photobleach; $t_{1/2} = 3$ sec.
- - - ultraviolet activated photo-color; $t_{1/2} = 23.5$ sec.
- · - · - thermal return, (time in minutes); $t_{1/2} = 57$ min.

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