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TECHNICAL REPORT

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INVESTIGATION OF MATERIALS AND SYSTEMS FOR PROTECTION AGAINST FLASHBLINDNESS EFFECTS OF NUCLEAR DETONATIONS

(PHASE 1)

by

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FOREWORD

This final report covers one year of research on a number of triphenylmethane and polymethine dyes and their photochromic characteristics. The research was undertaken to determine the feasibility of using such compounds for protection against retinal burn and flashblindness hazards arising from nuclear detonations.

The work was conducted by Polacoat, Inc., under Contract No. DA 19-129-AMC-112(N) and directed by Mr. John F. Dreyer and Mr. Robert W. Harries. Specific research phases were conducted by Mr. John Dreyer, Jr. (physical testing), Mr. Jerry Krekeler (application development), and Mr. Otto Maltenieks (synthesis). Cooperative research was conducted by Dr. H. Zimmer and Messrs. R. Bray, G. Chaney, J. Fookes, and L. Henzi.

The contract was initiated under Project No. 7X79-10-003 and administered under the direction of the Materials Research Division of the Clothing and Organic Materials Laboratory of the U. S. Army Natick Laboratories, with Mr. David Feldman as Project Officer and Dr. William E. C. Yelland as Alternate Project Officer.

This report was prepared by Dr. Richard Macnair and Mr. David Feldman, Materials Research Division, Clothing and Organic Materials Laboratory, U. S. Army Natick Laboratories, from three quarterly reports and a draft copy of an annual report submitted by Polacoat, Inc., supplemented by their own laboratory investigations.

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ABSTRACT

The initial phase of a research effort to develop an ophthalmic protective device for use against flashblindness resulting from nuclear detonations is outlined. Efforts to develop a sensitive and relatively transparent photothermosensitive material, which can be prepared as a thin film and can become a filter having high optical density upon exposure to intense electromagnetic radiation, are described.

Several materials were prepared which possessed satisfactory spectral absorption characteristics and were suitable for application to nuclear flashblindness protection. Their absorption peaks were broad, located in the visible, and were relatively close to the peak of the eye sensitivity curve. The synthesized compounds were members of the triphenylmethane, azo, and polymethine dye classes. The formulation of these materials as photochromic thin film filters produced systems which became colored in less than 40 nanoseconds and reached an optical density of 3.8 in 100 microseconds, measured at the wavelength of the absorption maxima. The films prepared had an initial transmittance of 70-80 percent.

A variety of plastic substrates for both photo- and thermosensitive systems were evaluated. The more suitable substrates, polyester films, were studied in greater detail.

It was established that temperatures from -50° to +95°C had no appreciable effect on the functionality of the photothermosensitive materials as measured by the radiant energy transmitted during activation.

The problem of storage stability of the photothermosensitive materials at -65°F to +125°F for periods of at least 6 months was not solved. However, the problem may be circumvented if necessary. The feasibility of a two-component system which combines the two components and activates the system just prior to use was established.

An attempt was made to obtain an understanding of the basic mechanisms involved in the photo-process for a variety of systems. Electron donor-acceptor concepts appear to fit the theory and the experimental facts.

I. INTRODUCTION

Previous efforts produced self-attenuating materials and systems which were capable of attaining neutral optical densities greater than 4, and which demonstrated initial reaction response times less than 50 microseconds. This program was a continuation of these studies.

To provide maximum flashblindness protection, it is necessary to have a photosensitive material or system which is not rendered insensitive to light by an increase in temperature. In addition, it may be desirable to have a system which could utilize the rise in temperature induced by the absorption of visible and infrared light to cause further development of the protective opacity in the filter material. Some photosensitive systems previously developed possess this property. However, because of the cumulative darkening of these systems, they cannot be stored longer than a few days or weeks before they become permanently opaque and nonphotochromic. Accordingly, efforts were directed toward the preparation and investigation of materials and systems which would be capable of:

1. Achieving an optical density of 3.5 or greater in the visible and near infrared wavelengths,

2. Retaining storage stability at temperatures of -65°F to +125°F for periods of at least 6 months,

3. Operating in field conditions and all climatic areas from -65°F to +115°F,

4. Being incorporated into a suitable film or resin polymer without undesirable optical properties, i.e., air bubbles, striations, uneven transmittance, wavy images, or loss of activity, as well as being,

5. Nonflammable, with the highest possible softening point. Resistance to an input of 30 calories per square centimeter for one (1) second is desired.

In addition, research efforts were directed toward obtaining an understanding of the basic mechanisms involved in the photochromic process.

II. DISCUSSION

A. IRREVERSIBLE SYSTEMS

The addition of a free radical source, such as chloroform, bromoform, carbon tetrabromide or β-tetrachloro-1-keto-naphthalene, to the leuco (colorless) form of a photochromic salt-isomerism type dye results in a system capable of an irreversible or "one-way" photo-induced color reaction. Both irreversible and reversible systems were considered for use in a flashblindness protection device. The advantages and disadvantages of the irreversible system compared to the reversible system are:

1. Advantages

a. Greater densities in thin cells or coatings can be achieved. An optical density of four can be obtained throughout the visible spectrum in liquid cells 4 mils thick and in semi-rigid coatings approximately 1 mil thick.

b. The optical density increases with temperature.

c. A broader activating wavelength range can be achieved. The better irreversible systems have activating wavelength regions which extend up to 450 mμ while the reversible systems of triphenylmethane and polymethine-type dyes, respectively, have an upper limit of approximately 330 and 380 mμ. A broader range could be a disadvantage, if the activation spectrum extended too far into the visible.

2. Disadvantages

a. The initial speed of response of the irreversible system is slower. The purely irreversible system is activated primarily by the photodecomposition of the free radical source. The products in turn attack the leuco dye to give the colored species. In comparison, a direct photo-activation of the leuco compound occurs in some reversible or photochromic systems.

b. The irreversible system has poor storage stability. The free radical generator of the irreversible system, while primarily a photo-activated material, is also thermally activated and has a small but significant free radical equilibrium at all but very low temperatures. This equilibrium severely restricts the practical utility of such a system since the color formation is cumulative.

Both disadvantages mentioned above have been circumvented to a large degree in the liquid system and to some extent in the rigid or semi-rigid formulations. The thermal instability is caused mainly by the combination of free radicals and leuco dye. Progress has been made in overcoming this instability in the liquid systems by storing the two components separately. These components, one containing the free radical generator and the other the leuco dye, are mixed just prior to use. This technique was also demonstrated as feasible in a semi-rigid system.

The problem of inadequate response speed can be minimized to a large extent in the liquid formulation by making a mixed irreversible-reversible system. This type of system consists partially of materials which would give a reversible system if no free radical generator were present. The gain in response is caused predominantly by the reversible portion of the formulation. In the semi-rigid or rigid formulations, application of this principle is still limited by the difficulties encountered in preparing reversible systems.

B. REVERSIBLE SYSTEMS (PHOTOCHROMIC)

The technical advantages and disadvantages of the reversible system are essentially the reverse of those discussed above for the irreversible system. However, there are two additional advantages.

1. In a flashblindness protection device a reversible system would provide continuous protection against repetitive exposures without replacement or resupply problems in the field.

2. A large number of photochromic dyes suitable for irreversible systems can be used in reversible systems as well. Improved formulations and techniques have shown photochromic response in many dyes which were previously considered non-photochromic. This behavior is typical of triphenylmethane, thiazine, azine, xanthene and mono-azo dyes.

Recently, attention has been paid to photochromic dyes other than triphenylmethanes and polymethines with two objectives in mind:

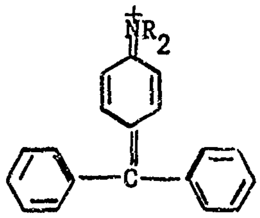
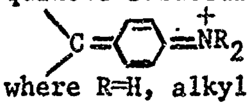
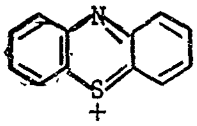
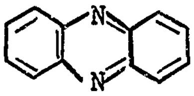
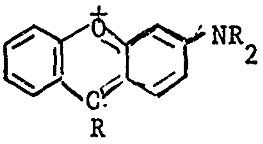
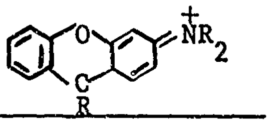
a. To expand present knowledge of photochromism in relation to structural differences of the dyes.

b. To obtain information on the interaction of these different types of dyes with various other compounds used in the formulations.

These studies have yielded considerable information regarding possible photochromic mechanisms. The information acquired has resulted in a better understanding of the interrelationship between various classes of dyes of different structure, their photochromic reactions, and their optimum photochromic environment. These new data should facilitate future investigations. Table I shows the structural characteristics of the major classes of dyes which were considered.

TABLE I

CLASSES OF DYESTUFFS INVESTIGATED FOR PHOTOCHROMISM

CLASS	STRUCTURE	REMARKS
Triphenylmethane		Chromophore is a resonance system including the quinoid structure:  where R=H, alkyl, or aryl. The system requires the presence of at least one auxochrome, usually in a para position.
Thiazine		Chromophore of this class is the thiazine ring which forms the central ring of the condensed ring system. The outer rings of the system may be either benzene (shown) or naphthalene nuclei.
Azine		Chromophore of this class is the pyrazine ring which joins two benzene rings to form the chromogenic molecule shown.
Xanthene		Chromophore is the resonance hybrid formed by the structure at left and that below; R=H, alkyl, or aryl. 

III. BACKGROUND AND THEORY

A. TRIPHENYLMETHANE AND POLYMETHINE SYSTEMS

1. Photochromic Mechanism

In 1921, Lifschitz and Joffe$^{(1)}$ proposed a mechanism for the fading-in-the-dark (dark reaction) of the illuminated leucocyanides of triphenylmethanes. Basing their conclusions on conductivity measurements of the photolyzed and unphotolyzed solutions, Lifschitz and Joffe represented the reaction as:

$$\left[(CH_3)_2NC_6H_4\right]_2\left[C_6H_5\right]\ C\text{—}CN \quad \underset{\text{dark}}{\overset{\text{u.v.}}{\rightleftarrows}}$$

Colorless - Nonactivated

$$\left[\left[(CH_3)_2NC_6H_4\right]_2\left[C_6H_5\right]\ CCN\right]^* \quad \underset{\text{dark}}{\overset{\text{u.v.}}{\rightleftarrows}}$$

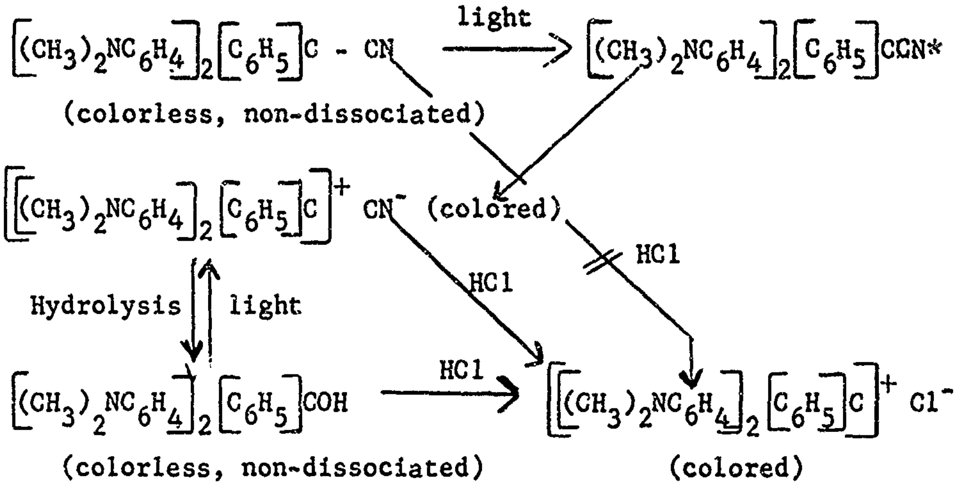
Activated State - Intermediate

$$\left[C\ :\ \left[(CH_3)_2NC_6H_4\right]_2\left[C_6H_5\right]\right]^+ \quad + \quad CN^-$$

Colored

They assumed that solvolysis of the colored compound was of secondary importance.

Harris, Kaminsky and Simard$^{(2)}$ found the above mechanism to be inadequate. They observed the rate of fading of the Malachite Green leucocyanide photocompound in absolute ethyl alcohol (99.9 percent), in alcohol (95 percent) and in photolyzed alcoholic solutions to which known quantities of potassium cyanide, potassium hydroxide and hydrochloric acid had been added immediately before or after photolysis. They found that the addition of water to the 95 percent alcohol solutions increased the rate of fading. Potassium hydroxide and potassium cyanide similarly accelerated the fading. No back reaction was observed if the hydrochloric acid was added. The addition of hydrochloric acid to the solution while the dark reaction was proceeding restored the color completely, but only 95-97 percent restoration was observed if the water content was greater than 20 percent. No coloration appeared if hydrochloric acid was added to an unexposed leucocyanide solution. This, they said, indicated that the product of the dark reaction in ethyl alcohol (95 percent) was not the original leucocyanide and therefore the mechanism of Lifschitz and Joffe was incorrect. They proposed the following mechanism for the photolysis of Malachite Green leucocyanide and for the dark reaction:



The final product of the dark reaction in the absence of hydrochloric acid was assumed to be the colorless carbinol, not the original leucocyanide.

Holmes(3) examined the absorption spectra of the products of the dark reaction of Malachite Green leucocyanide and compared them with those of the leucocyanide, the carbinol, and the ethyl ether. He found that if a very small amount of KOH, or KCN, or water was added to alcoholic solutions of the leucocyanide before irradiation, the dark reaction product was a mixture of the carbinol and the ether, with the carbinol present in larger amounts. In contrast, when dry alcohol alone was used as the solvent, the proportion of the ether was larger. On the other hand, when any of the above solutions were saturated with hydrogen cyanide gas, either before or after irradiation, the leucocyanide was the sole product.

Hence, any adequate mechanism* must be capable of explaining the formation of all three of the above mentioned products; namely, the leucocyanide, the carbinol and the ether. Therefore, Holmes proposed the following mechanism* which was able to account for the formation of the various dark reaction products according to the principles of mass action. Reactions r_1, r_2, and r_3 are all caused by the absorption of photons with frequencies in the ultraviolet or near visible region, whereas reactions r_4, r_5, and r_6 are all spontaneous reverse dark reactions.

Germann and Gibson(4), however, claim that no leucocarbinol is formed. If the leucocarbinol were the end product of the dark reaction, they point out that the absorption curve should shift from that of the pure leucocyanide to that of the leucocarbinol, as the photolyzed forms change to the faded solutions. The amount of shift would depend upon the time of irradiation(5). Such shifts were not observed. Their experiments indicated that the end product of the dark reaction of the photolysis of Malachite Green leucocyanide in ethyl alcohol containing some water has the following properties:

a. It is colorless, but has a peak in its absorption curve in the neighborhood of 3600 A.

b. It is formed more easily as the amount of water increases, but it is unstable in as much as 15 percent water.

c. It is not as stable as the leucocyanide, being decomposed by dilute hydrochloric acid or excess water to produce the colored ion of Malachite Green.

d. When irradiated with ultraviolet light, it produces the colored ion of Malachite Green.

e. Although derived from the Malachite Green ion and easily reproducing this same ion, its absorption curve shows it to have a structure essentially different from the leucocyanide and the leucocarbinol.

These properties would indicate that the end product of the dark reaction must be the result of some reaction between the solvent and the Malachite Green ion. In analogy with the mechanism proposed by Villiger and Kopetschin(6), this end product may be the ether form. However, Germann and Gibson(4) believe that such a compound should be more stable than the substances observed.

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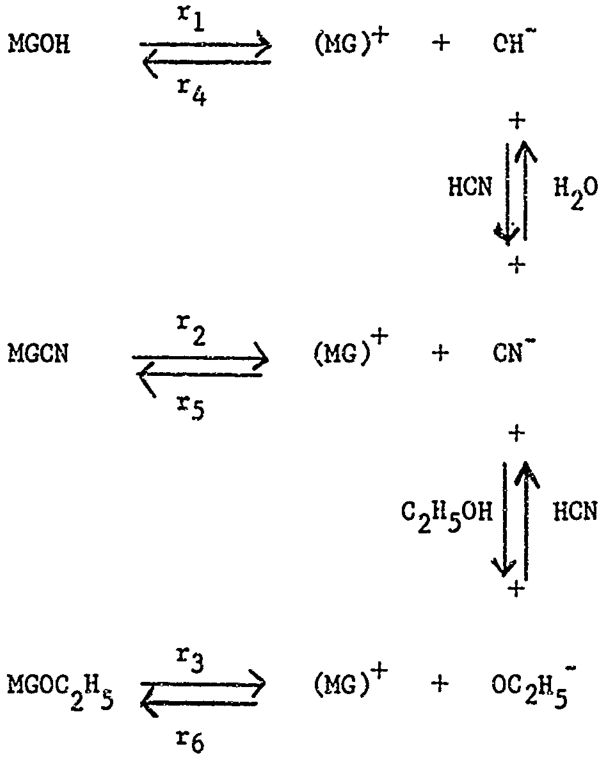
* See page 9



(MG = Malachite Green)

Lewis et. al.(7,8) claim that in triphenylmethane dyes, the solvent, especially if it is a substance like water, may combine with the colored dye molecule to produce a number of definite structures, each of which has its own absorption. These "compounds", they claim, are ordinarily the result of a hydrogen bond(9) between solvent and the nitrogen-containing group of the dye. It is their belief that all pronounced changes in color, when passing from one solvent to another, are due to such definite solvates, except in the single type of substance exemplified by p-nitroaniline. The colored solute may also combine with itself to form polymers which also have their own characteristic absorption.

The belief that solvents affect the dye was further corroborated by Cigen(10) when he described seven species of the ortho-hydroxy derivative of Malachite Green in aqueous solutions. These different species resulted from either dissociation or hydration and were demonstrated to be dependent upon the proton concentration of the system. In this work, Cigen gives the reaction rate constant for eight reactions and it is of particular note that the reaction rate from one species to another can vary by a factor of 103.

2. Photochemical Dissociation Mechanism

Numerous studies of photochemical dissociation mechanisms have been made in rigid solvents and at low temperatures(8,11,12). This rigidity enables the worker to study isolated molecules. At the low concentrations used by most workers (10^{-4} M or less), the individual molecules are over 100 A apart on the average so that, when the solution is cooled to rigidity, no appreciable diffusion can occur and, therefore, no bimolecular reactions. Except in cases where the solute is polymerized before the state of rigidity is attained (polymethine dyes), only the dye molecule and the group of solvent molecules in its immediate neighborhood can participate in the photochemical process or in the reactions which occur after illumination. This restriction of all processes in the rigid solvent to the zone of a single molecule limits the number of possible structures that may be assigned to the photochemical products.

Lewis and Lipkin(13) found three types of photochemical reactions. The first was photodissociation or molecular splitting into uncharged radicals. For example, when a solution of triphenylmethyl radical in EPA (5 parts of ether, 5 parts of isopentane, and 2 parts of alcohol by volume) was cooled to about -50°C, it was completely converted into hexaphenylethane. On irradiation with ultraviolet light, the cold solution showed the sharp absorption band of triphenylmethyl.

The second type was the ejection of an electron by the illuminated molecule. The authors called this photo-oxidation. Leuco Malachite Green, leuco Crystal Violet and Michler's hydride were found to undergo photo-oxidation in rigid solvents.

When a molecule such as the leuco dye (DH), that exists as a dimer $(DH)_2$ at low temperatures in a rigid solvent, is illuminated, prominent bands in the infrared attributable to D^+, D, and DH^+ are formed. On standing, the DH^+ band disappears while the D^+ and D bands increase by about 50 percent.

Compounds like biphenylamine and tri-p-tolylamine gave the same products on chemical oxidation at room temperature and photo-oxidation at liquid air temperature.

Lewis and Lipkin speculated that the ejected electron probably becomes attached to a solvent molecule or to a group of molecules, or even to a unique point in the solvent determined by the rigid structure. The electron must lie in an energy potential hole which is deep enough that the large electrostatic field of the ion is unable to dislodge it. The color formed persists at liquid air temperatures for several days, but disappears at only slightly higher temperature. Presumably, when this occurs, the electron has returned to the ion.

When the ion of Wurster's Blue was produced in a solvent containing dissolved air, a slight blue color remained after warming. This might be due to the permanent capture of electrons by the oxygen molecules.

The third type of photochemical reaction described by Lewis and Lipkin was photo-ionization which can be observed under ordinary conditions in such substances as the leucocyanides of Crystal Violet and Malachite Green[2]. These positive ions behave as secondary acids(14,15).

In summation, the three (3) mechanisms investigated were:

1. Photodissociation to form two uncharged radicals, i.e., free radicals.

2. Photo-oxidation in which an electron is ejected.

3. Photo-ionization in which two oppositely charged particles result.

3. Fatigue Mechanisms

In this category are all other irreversible reactions which take place during or after the photochromic cycle. It is known that salt-isomerism type photochromic materials break down under prolonged irradiation with ultraviolet light. Sporer(16) claimed that this breakdown occurred with a quantum efficiency of 3 percent for Crystal Violet leuco hydroxide systems.

Iwamoto(15) reported that leuco bases were obtained as photodecomposition products from Malachite Green and Crystal Violet when they were exposed in the solid state to sunlight in sealed tubes and that ketones were obtained when exposure was made in the presence of air. Henriques(17) demonstrated the formation of Fuchsin and Doebner's Violet by a demethylation process from Crystal Violet and Malachite Green, respectively, when exposed in aqueous solution to ultraviolet and visible light. The process was found to be fast with ultraviolet and slow with visible light. Ackerman(18) concluded that the fading of Methyl Violet and Alkali Blue colors involved both oxidation and reduction, without isolating any products.

Desai(19) demonstrated that when triphenylmethane dyes, particularly Brilliant Green and Malachite Green are exposed to sunlight, either in the solid form or in solution, they are oxidized, partially reduced and dealkylated, yielding a series of products. With Crystal Violet the oxidation process is less prominent, and with Rosaniline it is extremely slow. Using chemical and photometric methods, Desai showed that Brilliant Green and Malachite Green, either in powder form or in solution, yield leuco bases and p-diethyl- or p-dimethylaminobenzophenone, respectively. A small amount of an amine was also detected. The presence of a third absorption band at a wavelength of 2012 millimicrons could not be explained. With Crystal Violet, reduction is favored in the powder form, whereas oxidation and dealkylation are favored in solution. Thermal, as well as photochemical oxidation of Brilliant Green with hydrogen peroxide yielded p-diethylaminobenzophenone. Desai offered explanations for the reactions of the different triphenylmethane dyes, one of which explanations was based on the charge distribution. The positive charge in Brilliant Green and Malachite Green is not equally distributed over the dye molecule because one phenyl nucleus is unsubstituted. In contrast, Crystal Violet and Rosaniline have symmetrical substitution and correspondingly equal charge distribution among the phenyl rings. This means that there should be a greater resonance stabilization in the latter pair of compounds than there is in the former pair. Thus, resonance stabilization of the positive charge may explain the relative stability to oxidation of these two pair of dyes.

The dark reaction, that is, the transformation of the colored form back to the colorless form in the dark of salt-isomerism type photochromic-reversible systems either suffers fatigue or is prevented when halogenated solvents are added to the systems. The result is an irreversible, cumulative increase in optical density. One explanation for this irreversibility is the photolytic decomposition of the halogen solvent during which free radicals are formed. These radicals can prevent the reverse reaction of any of the three photochemical dissociation mechanisms previously discussed.

If photodissociation of the leuco hydroxide to free radicals occurs, the free radicals generated from the halogenated solvent would interact with those generated from the dye.

If photo-oxidation is the initial response, the electron ejected has preferential position in the electron-deficient halogenated solvent free radical.

If photo-ionization is the initial response, it is possible for an electron-deficient free radical from the halogenated solvent to pull an electron from the negative ion produced by the dissociation. This would create a new free radical species, thus creating a free-radical chain reaction. Experimental observations verify that an apparent chain reaction or "coasting" occurs in these halogenated solvent irreversible photosensitive systems, during which additional color is developed after the activating light source has been removed.

A logical question arises when considering reversible versus irreversible systems. Is there any advantage of one system over the other? A generalized curve (Figure 1) illustrates the relationship between the irreversible and reversible systems when both systems are irradiated by a constant intensity source and have the same molar absorption coefficient and quantum efficiency.

In the reversible system an equilibrium optical density is reached which is quantitatively dependent on the amount of incident activating energy. The optical density limit is theoretically dependent only on the solubility of the material and the molar absorption coefficient of the colored species. According to the curve, the irreversible system has an apparent advantage in absorbing more energy than the reversible one. This advantage was demonstrated experimentally by using low intensity activating energy sources. When using fast discharge electronic flash tubes ($<200\ \mu$ sec.), this effect was not demonstrable. Evidently, the speed of the back reaction for the reversible systems is sufficiently slow that a reduced energy absorption effect is not noticeable during short exposures to light.

4. Sensitization Methods

Efforts to increase sensitivity to light in both reversible and irreversible photochromic systems may be accomplished either by the judicious placement of substituent groups in the salt-isomerism molecule or by establishing optimum environmental conditions for a photochromic reaction. The latter method is performed by studying

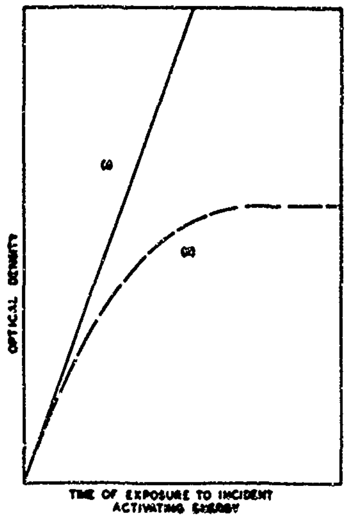


Figure 1. Generalized Plot of Optical Density Versus Time of Exposure to Incident Activating Energy for: 1) an Irreversible Photosensitive System; 2) a Reversible Photochromic System

the effects of solvents, additives, temperature and other physical means on the photochromic reaction.

5. Salt-Isomerism Mechanisms

There seems to be agreement in the literature that the color obtained by ultraviolet irradiation of leuco triarylmethane dyes is a result of the resonance among the possible quinoid structures of the dye cation. Thus the characteristic dye color is due to the formation of a resonating and positively charged dye species. However, there has been some difference of opinion as to how this ionized dye species is formed by ultraviolet irradiation of a leuco solution. Experimentally, it has been observed that irradiation of the pure solid or crystalline leuco compound by ultraviolet light results in no observable color formation. This indicates that the solvent plays a definite role in the phenomenon of photochromism.

Actually, different solvents affect the color formation and reversal to the colorless form of the dye to varying degrees. The alcohols appear to be the better solvents for obtaining a good (that is, deeply colored) photochromic reaction with many of the dyes considered in this research.

A primary requirement for a photochromic response is that the leuco dye must be soluble to some extent in the medium solution. This, of necessity, involves an association or binding of some sort between the solvent and the solute molecules. Lewis and Galvin(20) have postulated that the colored dye molecule might combine with the solvent to produce complexes or aggregate molecules. This is highly probable since solvation of solute molecules to form associated species has long been acknowledged.

These associations result from attractive forces between ions and neutral atoms or molecules, which are much weaker than ionic or covalent bonds. These interactions may be considered as one of the four broad categories:

a. dipole-dipole

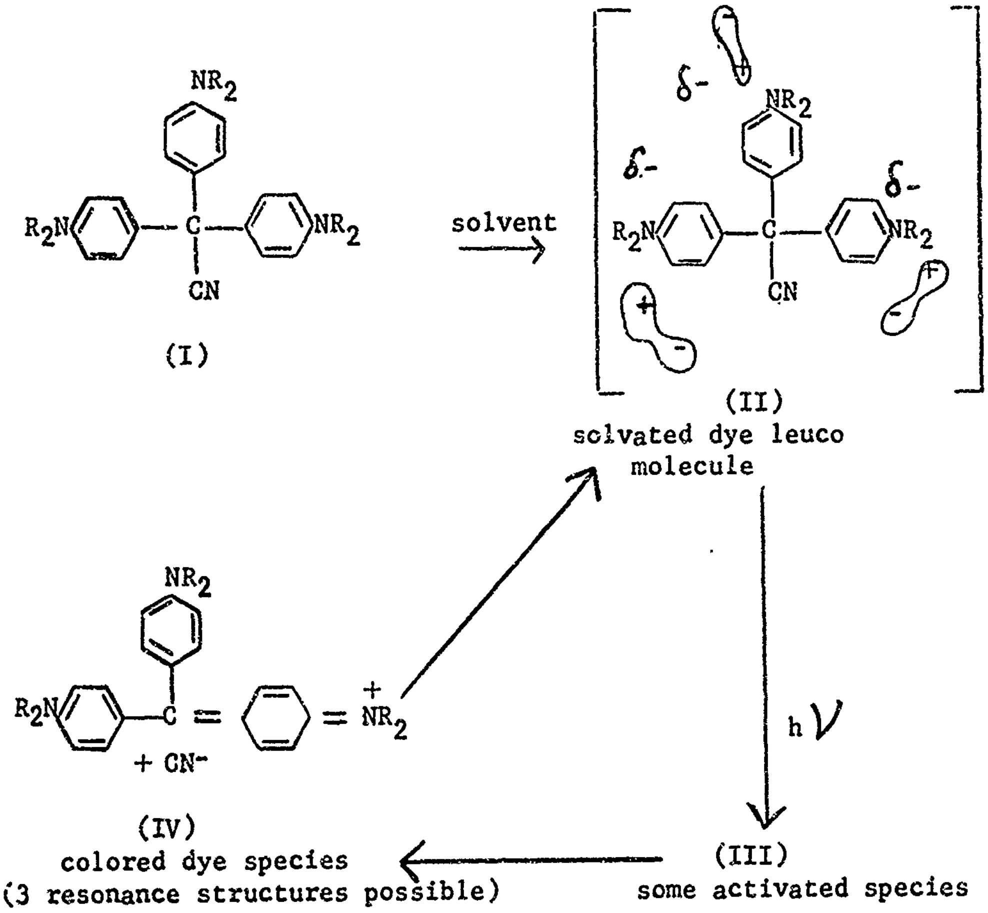
b. dipole-induced dipole

c. ion-dipole

d. ion-induced dipole

The solvents which have been found to support photochromic response are capable of exhibiting the dipole-induced dipole type of association with the leuco dye. These solvents are polar molecules; i.e., they possess a separation of electrostatic charge due to differences in electronegativities of the atoms. It is postulated that a dipole is induced in the leuco dye after solvation of the dye molecule and that this ultimately results in the formation of a colored species when the molecule is irradiated with near ultraviolet light. A possible mechanism for this is shown below where (I) represents any triarylmethane leuco dye.

The addition of the solvent to the leuco dye results in the formation of a solvated species. Since an unshared pair of electrons exists on the amino nitrogens which are necessarily negative in character, the positive end of the polar solvent molecule may be attracted to them. There may be more than one



solvent molecule per dye molecule. Upon irradiation with ultraviolet light some intermediate is formed, consisting of an activated species from which the cyanide group splits off.

The characteristic color of the dye is produced by the resulting quinoid chromophore structure (IV). After removal of the light, the colored form reverses to a colorless solvated species.

Solvation by an alcohol would result from hydrogen bonding between the alcohol and the amino nitrogen. The short-chain alcohols support photochromism better than the long chain alcohols. Diols containing five carbon atoms or less also support photochromism.

The Lewis acid or base nature of the solvent, that is, its ability to either gain or lose electrons, is another factor which affects the photochromic response mechanism. Many solvents (e.g., tetranitromethane, dimethyl sulfite, and dimethyl sulfate) produce the characteristic color of the dye immediately upon contact with the leuco compound. The solvent can therefore be thought of as being reduced and the leuco dye as being oxidized (losing an electron), thus producing the colored cationic species.

It has also been observed that oxygen, absorbed from the atmosphere by the leuco dye solution, enhanced its photochromic response. The oxygen molecules may act as part of a solvent bridge connecting the cyanide to the amino nitrogen. Oxygen is known to be an electron acceptor and alters the redox potential.

It is doubtful that, under the conditions used in this investigation, the photochromic response of the triarylmethane dyes proceeds by a free radical mechanism. It has long been known that triphenylcarbinol $[(C_6H_5)_3COH]$, which may be considered as the simplest leuco triarylmethane, forms very stable carbonium ions (+), carbanions (-), and the triphenylmethyl free radical. However, Sporer(16) has found through ESR (electron spin resonance) that the only detectable free radicals in such compounds were due to minor breakdown products. Therefore, ionization of the dye has been assumed to be the major step in the mechanism of color formation.

Additives have also been found which significantly enhance the amount of color formed in reversible systems. It is inferred that the additive shifts the equilibrium to the right by either solvating or otherwise weakly binding the anion, thereby diminishing the normal recombination rate of the anion with dye cation.

In conclusion, the postulated mechanism of the salt-isomerism photochromic phenomena is as follows:

a. The leuco dye is solvated and exists in dipole-induced association with the solvent.

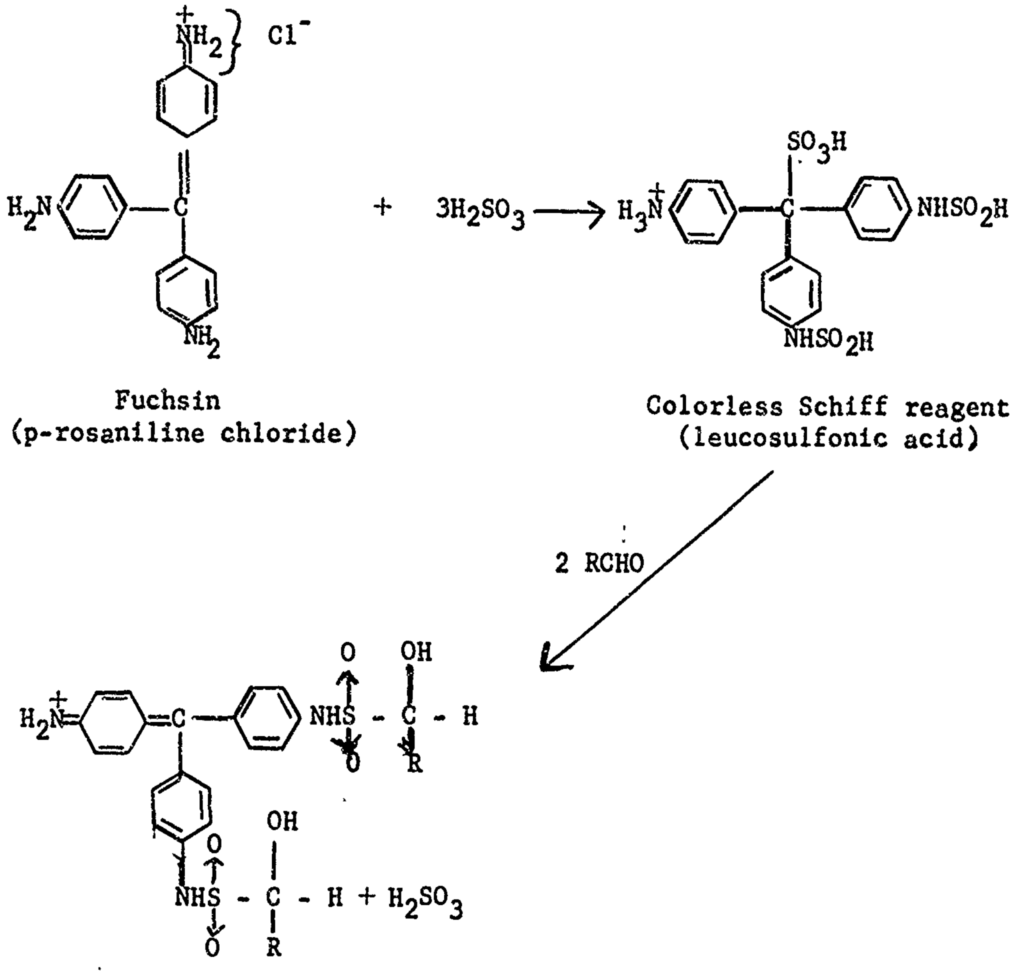
b. The excitation of the leuco form with ultraviolet light causes an electron density shift along a dipole bridge from the amino nitrogen to the bleach anion.

c. The bond between the bleach moiety and the central carbon atom is broken and gives a charged structure, thus giving a colored dye cation.

d. Removal of the exciting source allows the reverse reaction to proceed, giving the solvated leuco form.

6. Bleaching Mechanisms

The mechanism of the dye-water-bisulfite bleaching systems has been indicated by the known reactions for the fuchsin-aldehyde test. This test is described in most organic text books, specifically in Shriner, Fuson and Curtiss(21). The equations below illustrate the chemical steps in the test where, first, the leuco reagent is formed by addition of H_2SO_3, and second, the reaction with an aldehyde produces a colored species.



Fuchsin
(p-rosaniline chloride)

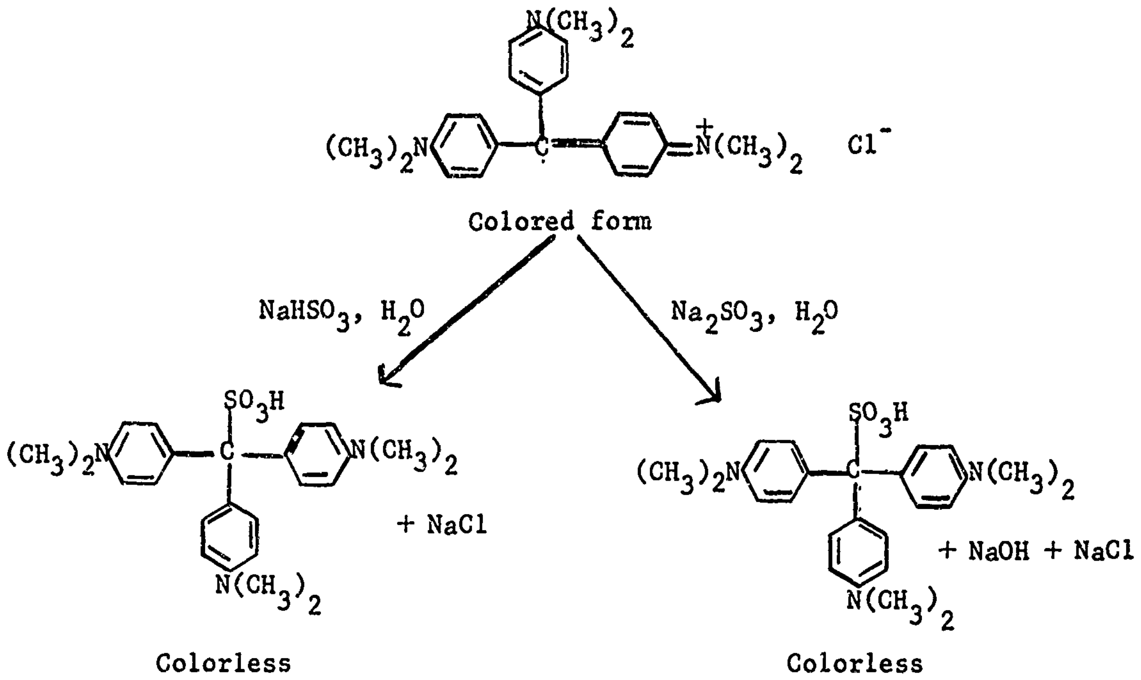
Colorless Schiff reagent
(leucosulfonic acid)

Colored

Instead of sulfurous acid, sodium bisulfite can be used in the preparation of the aldehyde reagent(22). Sodium sulfite also serves as an effective bleaching agent for many dyes, whereas sodium sulfate does not. This implies that the sulfite ion in which sulfur has an oxidation state of +4, is required for the bleaching effect.

Eight aqueous solutions of triphenylmethane dyes were bleached with $NaHSO_3$ and treated with benzaldehyde. All seemed to react like fuchsin in the formation of the leuco forms and in the reaction toward aldehydes. Dyes with substituted amino groups reacted as well as those without. Therefore, the principal requirement for a photochromic leucosulfonic acid is apparently the presence of bisulfite ion on the central carbon.

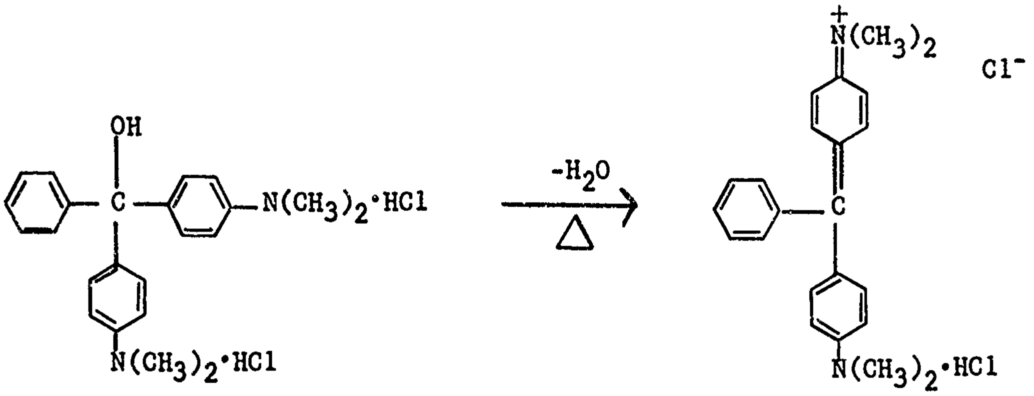
The balanced equations for the bleaching of aqueous Crystal Violet (PC 1016) with both $NaHSO_3$ and Na_2SO_3 are given below and illustrate the proposed mechanism.



As a rule, the naphthalene derivatives of the triarylmethane dyes have been found incapable of bleaching with $NaHSO_3$. Steric hindrance at the central carbon atom is probably a primary reason. No photochromic response has been observed thus far for any dye bleached with $NaHSO_3$ other than triphenylmethanes. Therefore, the bisulfite action seems to be restricted to the triphenylmethane dyes. Ultraviolet irradiation apparently breaks the carbon-to-sulfur bond giving rise to the colored dye species and HSO_3^-.

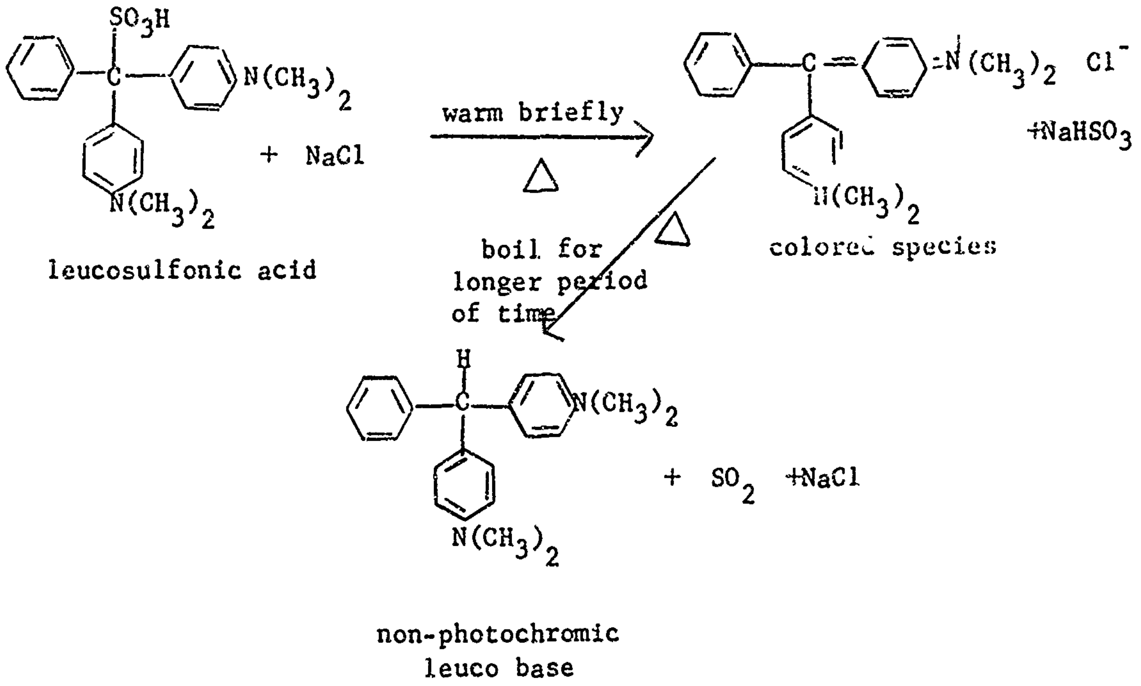
7. Thermochromic Mechanism

Holleman(23) states that Malachite Green carbinol dissolved in acids is converted to the colored form upon warming.



Many triphenylmethane dyesexhibit thermochromism when bleached with $NaHSO_3$. Experiments have shown that this process occurs by elimination of SO_2 with the subsequent formation of the non-thermochromic (and non-photochromic) leuco base. In open vessels the SO_2 escapes causing fatigue of thermochromism.

If the vessel containing the dye solution is closed and heated, thus preventing loss of SO_2, the dye solution will still exhibit thermochromism (and photochromism) but will not fatigue as soon as a solution in an open vessel.



Heating the solutions in open vessels for a brief time only results in formation of the colored species which will reverse to the leuco upon standing due to the excess of bisulfite.

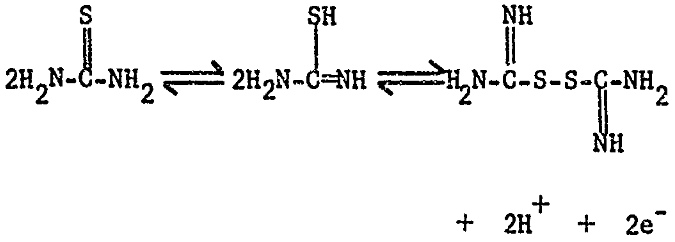
B. THIAZINE SYSTEMS

Rabinowich and Epstein and other authors(24) have reported that thiazine dyes do not obey Beer's law in most solvents and that in water the spectra are concentration-dependent. These dyes also were reported as being planar in structure. The authors stated, furthermore, that photo-bleaching of thiazines requires high concentrations of the reducing agent. Our experiments have verified this. The photo recovery of the dye from its leuco form by ultraviolet light occurs by the loss of an electron from the excited leuco dye, followed immediately by the loss of a proton to give the colored dye species. This is a redox reaction.

Angelescu and Cornea(25) proposed a mechanism for the thiazine-thiourea type system. They stated that the amount of the dye decreases with repeated decolorizations and recolorations and that an excess of thiourea favors the decolorization reaction. Based on this and our experimental data, the following mechanism illustrated with Methylene Blue is proposed:

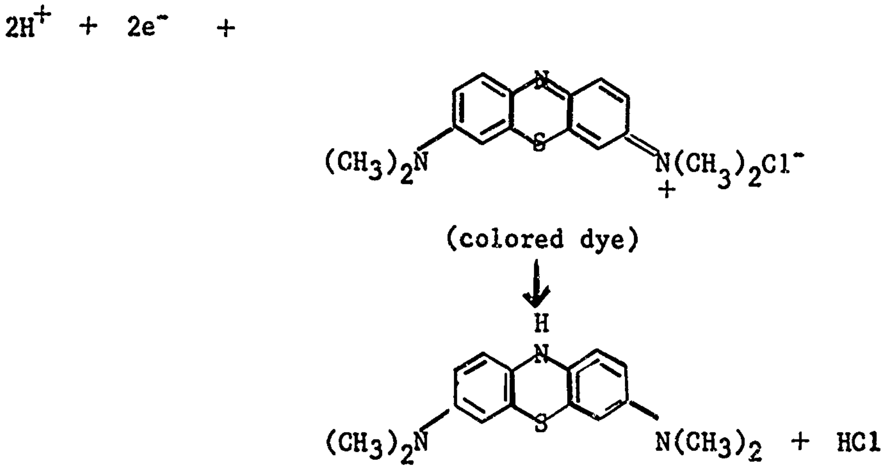
The Bleaching Reaction:

(1)



$$2H_2N-\overset{S}{\overset{\|}{C}}-NH_2 \rightleftharpoons 2H_2N-\overset{SH}{\overset{|}{C}}=NH \rightleftharpoons H_2N-\overset{NH}{\overset{\|}{C}}-S-S-\underset{NH}{\underset{\|}{C}}-NH_2 + 2H^+ + 2e^-$$

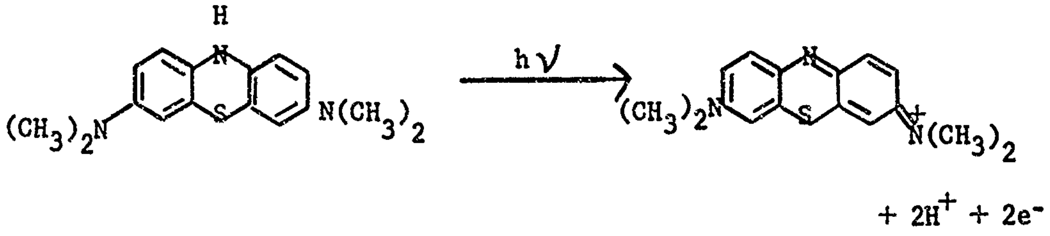
(2)



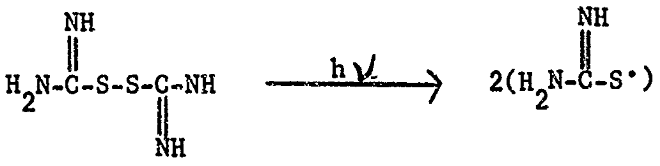
(colored dye)

(coloress leuco)

The Color Formation Reaction:



Breakdown Reaction:



$$H_2N-\overset{\overset{\displaystyle NH}{\|}}{C}-S-S-\underset{\underset{\displaystyle NH}{\|}}{C}-NH \xrightarrow{h\nu} 2(H_2N-\overset{\overset{\displaystyle NH}{\|}}{C}-S\cdot)$$

This is a reactive free radical capable of permanently reacting with dye to give a non-photosensitive leuco form.

IV. SYNTHESIS PROGRAM

A. PHOTOSENSITIVE BUT NON-PHOTOCHROMIC DYES*

Eight dyes were synthesized. (See Appendix A for general synthesis procedure.) The structures are shown in Table II. The objective was to obtain dyes having the following characteristics:

1. Increased photochemical sensitivity.

2. Activating wavelength band close to the visible wavelengths.

3. The capability of exhibiting a neutral color such as black or grey.

Unfortunately, increased photosensitivity and an activation wavelength closer to the visible wavelengths were not obtained. However, a major shift of the visible absorption peak was obtained for PP 1085, PP 2114, and PP 2133 which was attributed to the naphthol ring in the first, and to the azo groups in the second and third compounds.

Also, dyes PP 1086, PP 1116, and PP 2133 in irreversible systems produced a color which was almost a neutral black to the eye.

B. PHOTOCHROMIC DYES

1. Objectives

The primary objective of this phase of the synthesis program was to obtain polymethine dyes which possessed the following properties:

a. Increased photochromic sensitivity with the activating wavelength band close to the visible wavelengths.

b. High resistance of the activated state to deterioration caused by elevated temperatures and prolonged activating radiation.

c. A single broad major absorption peak centered at about 553 mμ.

d. Rapid reversibility from colored to colorless state upon the discontinuation of the activating radiation.

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*Photosensitive but non-photochromic dyes in this context are dyes which change color irreversibly under the influence of light.

In an effort to obtain dyes with these properties, variations were made in the structure of dye cations previously synthesized. Rigorous rules for predicting the resulting characteristics caused by structure changes are nonexistent, although some generalizations can be made concerning the absorption effects of chromophores and auxophores. These generalizations were applied in the choice of compounds to be synthesized.

2. Compounds Synthesized

During this contract 52 new photochromic dyes were synthesized. Of these, the dyes shown in Table III were of particular interest. The methods used to synthesize these dyes are presented in Appendix A.

3. General Properties

The most significant result was the synthesis of the photochromic dye, PP 2120, which possessed a relatively broad absorption peak, close to 550 mμ. Preliminary evaluation of the dye indicated relatively good sensitivity for the photochromic response. Since the molecular structure of this compound is quite different from previously considered compounds, a potentially large number of compounds must be considered in future efforts toward improved photochromic materials.

As expected, no appreciable change in the general range of activating wavelengths was noted for the dyes synthesized. Dyes PP 2109, PP 2110, and PP 2112 have rather wide absorption bands at their maxima. The broadening of the absorption peaks may be attributed to the fluorine atom in the dyes PP 2109 and PP 2112 and to the amino group in PP 2110.

TABLE II

NON-PHOTOCHROMIC BUT PHOTOSENSITIVE DYES

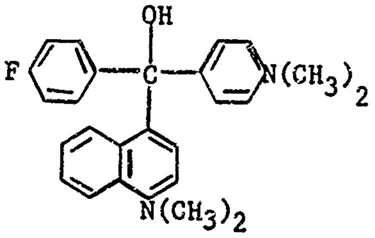
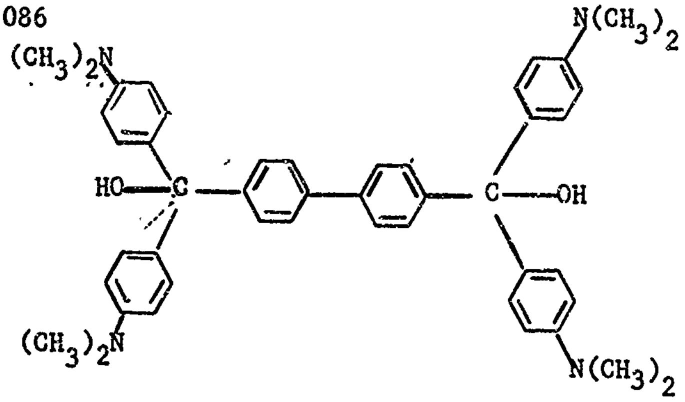
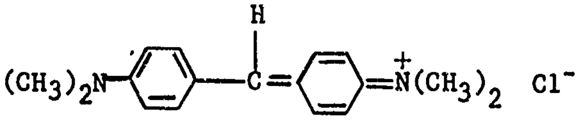
Dye Number	Structure	λ max (mμ)
PP 1085		600-618
PP 1086		570-590
PP 1115		610

TABLE II (Cont'd)

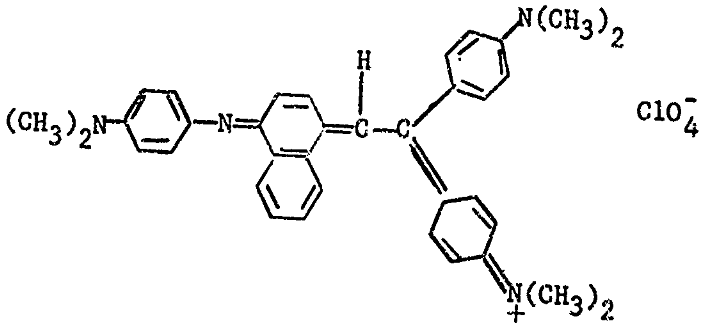
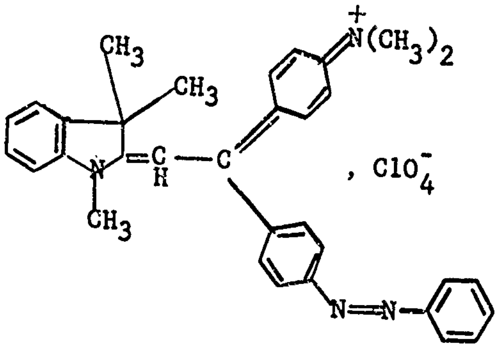
Dye Number	Structure	λ max (mμ)
PP 1116	 ClO_4^-	590-610
PP 2113	 , ClO_4^-	600

TABLE II (Cont'd)

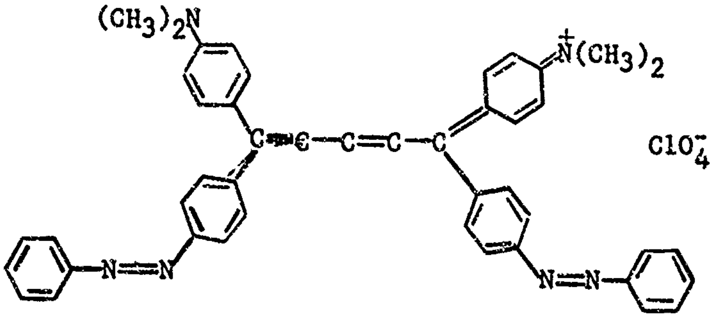
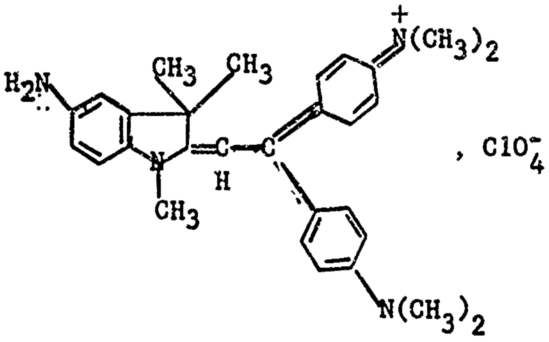
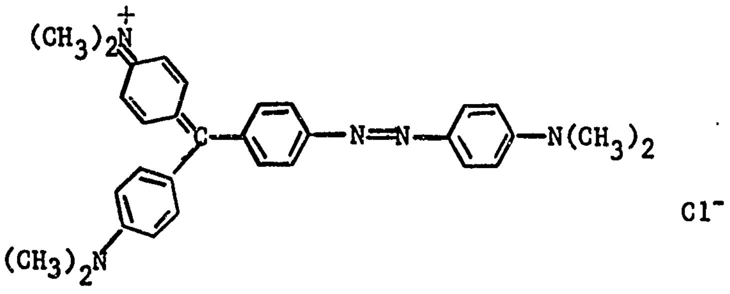
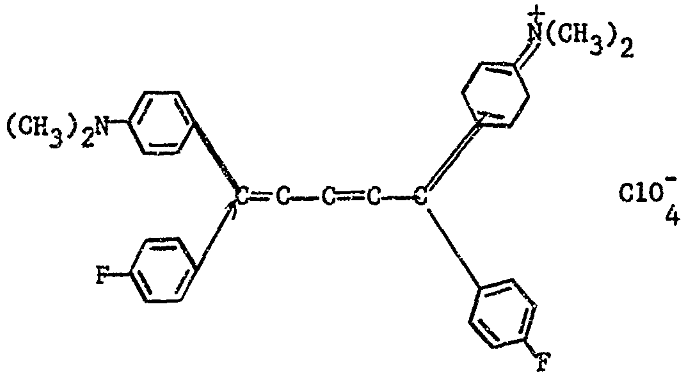
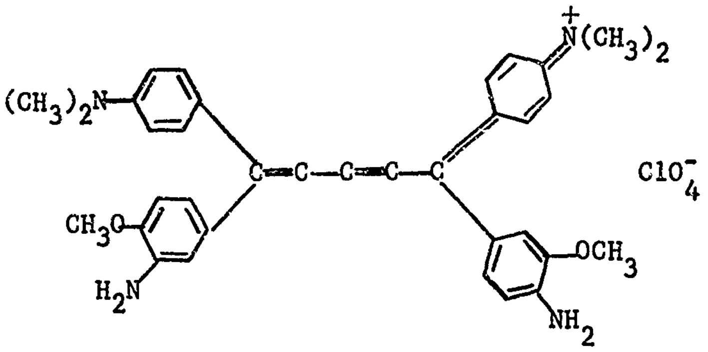
Dye Number	Structure	λ max (mμ)
PP 2114		950
PP 2115		555
PP 2133		400 & 630

TABLE III

PHOTOCHROMIC DYES*

Dye Number	Molecular Structure	λ max (mμ)
PP 2109C		412, 550, 870
PP 2110		570-850

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*These dyes were also useable as photosensitive but non-photochromic dyes in formulations which prevented the usual reversible color formation from taking place.

TABLE III (Cont'd)

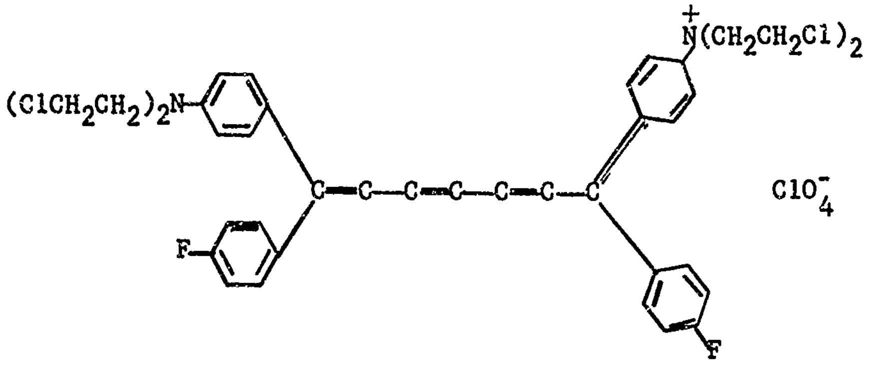
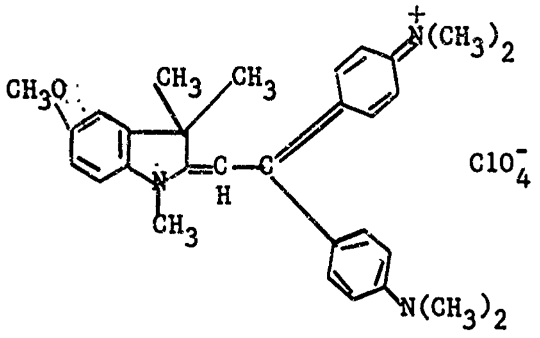
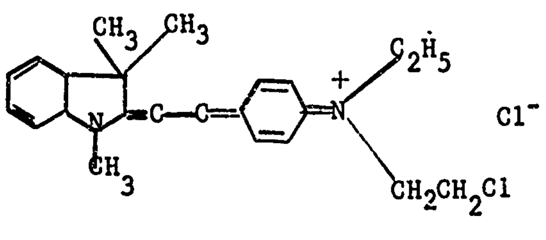
Dye Number	Molecular Structure	λ max (mμ)
PP 2112		550-875
PP 2119		520
PP 2120		540

TABLE III (Cont'd)

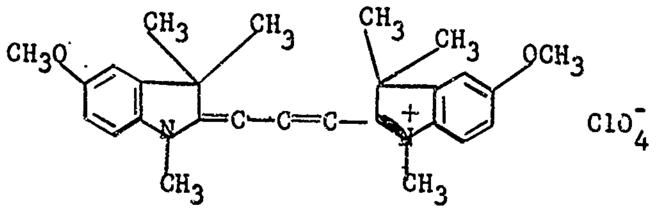
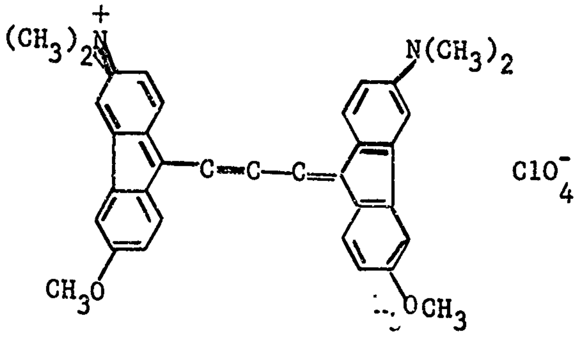
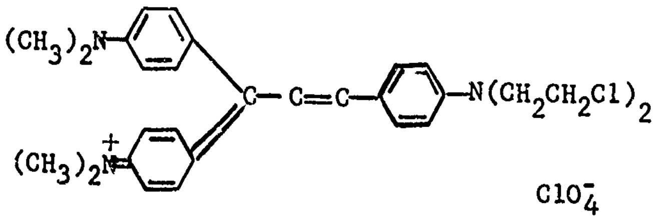
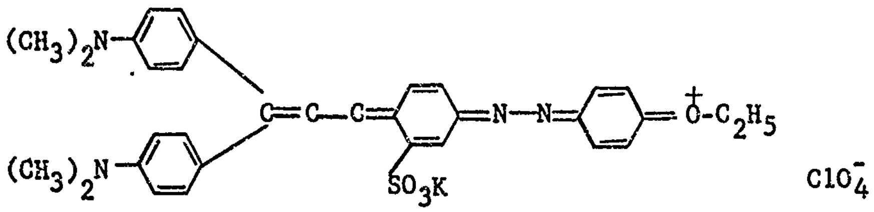
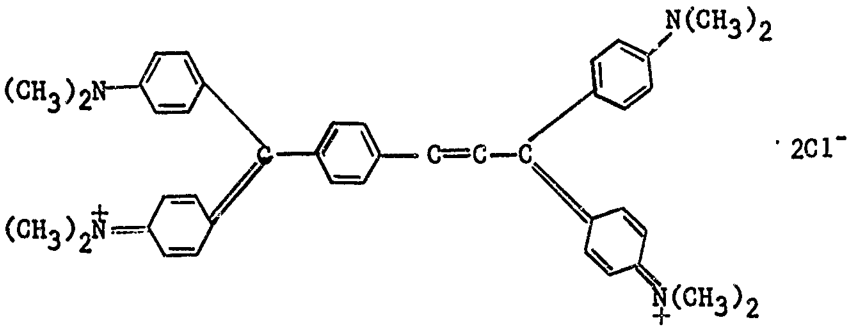
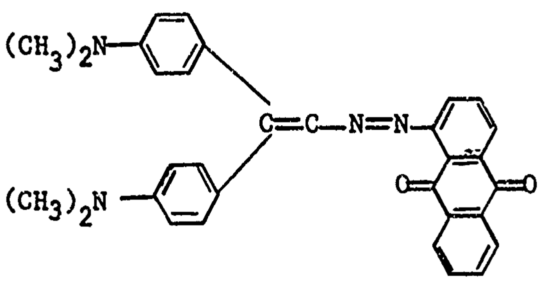
Dye Number	Molecular Structure	λ max (mμ)
PP 2121		569
PP 2128		815
PP 2130		680

TABLE III (Cont'd)

Dye Number	Molecular Structure	λmax (mμ)
PP 2131		630
PP 2134		620
PP 2136		580-600

V. FORMULATIONS

A. NON-PHOTOCHROMIC OR "ONE WAY" SYSTEMS

All samples were prepared as semi-rigid laminated films by the following technique. First, a coating lacquer was formulated containing:

6.5 wt % Leuco Dye
3.3 wt % Free Radical Generator
1.7 wt % Plasticizer (2,2-Dimethyl-1,3-butanediol)
13.0 wt % Acryloid B-44 Resin
75.5 wt % Toluene

The lacquer was then flow-coated onto 5 mil Mylar, Type D film. The finished samples were prepared by pressure-laminating two pieces of the coated film together.

The sensitivity of irreversible formulations is influenced predominantly by the choice of the leuco dye and the free radical generator. An extensive search for better free radical generators was made. The compound β-tetrachloro-1-ketonaphthalene (β-TC-1-KN), a halogenated semi-quinone, showed very good photosensitivity but indicated poor thermal stability. β-TC-1-KN is of special interest because it is also photochromic. This gives rise to a possible double color system which is not limited by an indirect free radical activation.

Studies of these semi-rigid formulations were made by measuring relative sensitivities in an irradiation test. The results of the better formulations are shown in Table IV.

The relative sensitivity was recorded as the time required for the standard S-PP 2017 formulation to reach an optical density (O.D.) of 2.0 (as recorded by a Densichron photometer) divided by the time required for the formulation in question to reach an O.D. of 2.0. The irradiating source was a G.E. 275-watt sunlamp, type RS. The sample film was placed 10 cm from the bulb surface.

The activating wavelength of pure β-TC-1-KN was determined as a function of wavelength (Figure 2).

The initial results indicated that more work should be done with this compound and that variations of the compound should be of interest.

TABLE IV

RELATIVE PHOTOSENSITIVITES OF SOME IRREVERSIBLE FORMULATIONS

Formulation Number	Leuco Dye	Radical Generator System	Relative Photo-Sensitivity	Remarks
S-PP 2017	PP 2017 leuco OH	1/1 CHI_3/CBr_4	1.0	Did not attain a density of 2.0
S-PP 2056	PP 2056 leuco OH	1/1 CHI_3/CBr_4	1.0	
120-B	PP 1016 leuco CN	1/1 CHI_3/CBr_4	—	"
513-A	PP 2017 leuco OH	β-TC-1-KN	2.0	—
514-A	PP 2056 leuco OH	β-TC-1-KN	2.5	—
514-B	PP 1016 leuco OH	β-TC-1-KN	—	Very Thermally Unstable

An alternate route for utilizing the benefits of a free radical system, without encountering heat and storage instability, has been investigated. This approach consists of storing the free radical generator and the leuco dye out of direct contact with each other. The system is activated by combining these components just prior to use. The low rate of thermal or dark reaction, which presents a major problem upon prolonged storage with present systems, would then be of only minor consequence, although it might limit the useful life of the proposed system.

While the mechanical methods of accomplishing this approach have been briefly examined, its feasibility has been demonstrated with the "pod" system as shown in Figure 3.

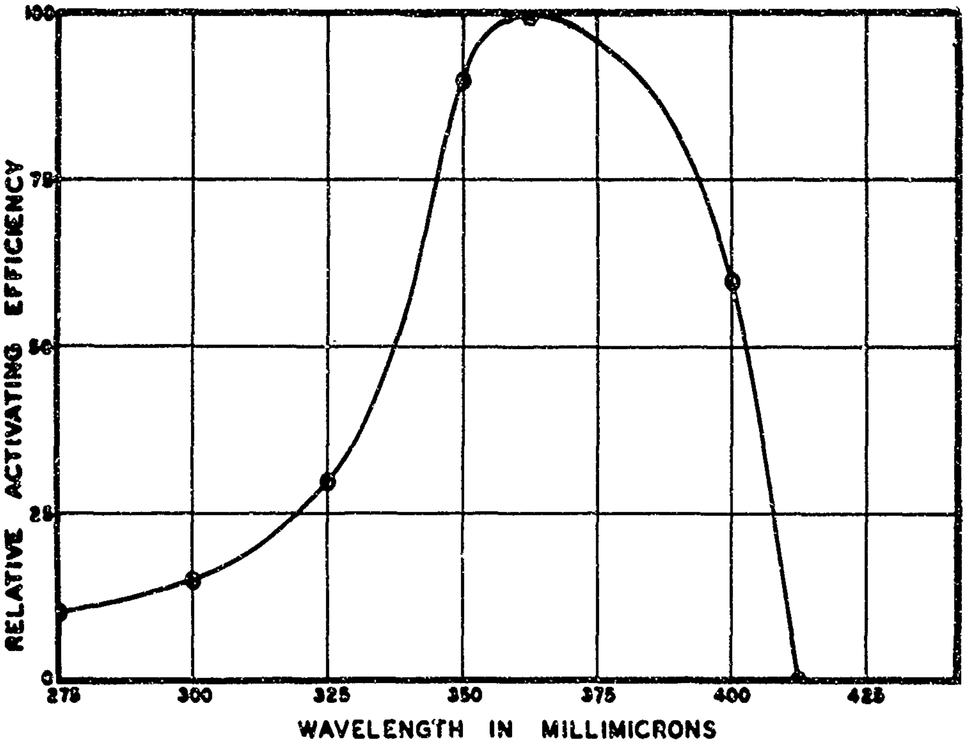


Figure 2. Normalized Activation Spectrum of β-Tetrachloro-1-Keto Naphthalene as a Function of Wavelength.

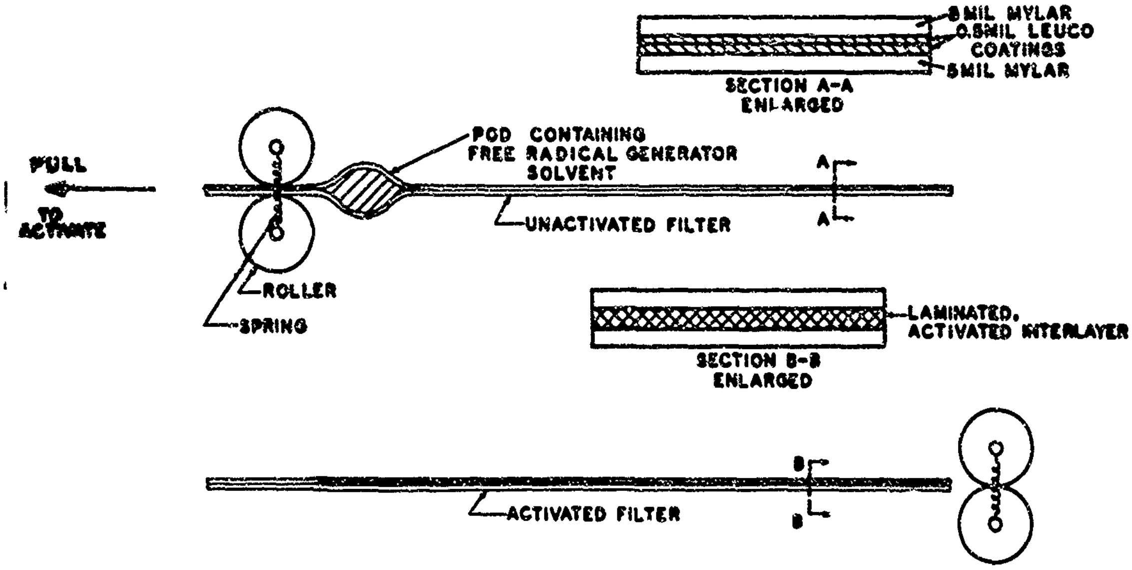


Figure 3. Pod System Used in Laboratory Feasibility Study

The systems consisted of a pod (small plastic bag) between two films in contact with each other. The pod was at one end of the system and contained the free radical generator. The films were each coated on the contact surface with leuco dye. To activate the system, the end containing the pod was pulled between pressure rollers. This ruptured the pod and forced its contents between the films. Continuation of the "laminate" through the rolls distributed the free radical generator over the leuco dye coatings.

Laboratory tests have shown that this technique is capable of producing material as sensitive as present premixed materials. The optical properties, however, do not meet the standards of present materials but should be greatly improved by further development. This technique will be used as an alternate if the present method yields negative results.

B. PHOTOCHROMIC SYSTEMS

1. General

Although we have accumulated a large amount of data on the triphenylmethane dyes, many questions still remain unanswered. For instance, among the dyes showing photochromism, can a common species be found in the mechanism to facilitate further investigation of still other dye classes? What types of solvents and additives result in the best system for a particular dye class and why? And how can these be selected on the basis of the dye's chemical structure?

Studies of photochromic dyes, including triphenylmethanes, thiazines, azines and others, were made in solution using several solvents with numerous additives. The effects of solvent on the optical density change obtained in response to the activating UV light were determined as well as the effects of additives. The latter were used in an attempt to enhance the back reaction without retarding the forward reaction. The dyes were studied in solution because they do not exhibit photochromism in the solid state.

2. Triphenylmethane Dyes

a. New Formulations

Photochromism has been noticed not only in aqueous formulations of dyes which were formerly considered as being nonphotochromic but also in dyes which did not exhibit the expected amount of photochromic response in previous solvent formulations. Specific examples are PC 1104 (CI 42100) and PC 1106 (CI 42095) as shown in Table V which contains information on the more promising new formulations. All tests performed were qualitative. The data on the previous organic solvent formulations are included for comparison with the aqueous systems. An additive in the sense used here is the reagent which "bleaches" the dye to the leuco form. The column designated "Effect of UV" is based on visual observation and gives the extent to which the formulation exhibits photochromism. All systems were reversible, some faster than others. Listed under "Comments" are the color of the dye solution after exposure, the major absorption peaks of a 2 x 10^{-5} M solution in a particular solvent, and other pertinent facts.

Table V also indicates that some photochromic systems with aqueous solvents performed as well or better than those systems using dimethyl sulfoxide (DMSO) or "Methyl Cellosolve". The latter two organic solvents were previously considered best suited for photochromic systems.

b. UV Absorption Characteristics

Typical spectra which were obtained for photochromic dyes are illustrated by the curves in Figure 4. Shown here are the absorption characteristics of a 2 x 10^{-5} M solution of PC 1090 (CI 42590) in methyl cellosolve under three conditions. The activating curve is Curve 1. Curve 2 is that of the "bleached" dye and Curve 3 is that of the irradiated leuco dye solution.

The absorption peaks of compounds shift somewhat from solvent to solvent and examples of this are shown in Table VI for three triphenylmethanes. Such variations in absorption spectra are to be expected due to the solvation and association characteristics of the various solvents.

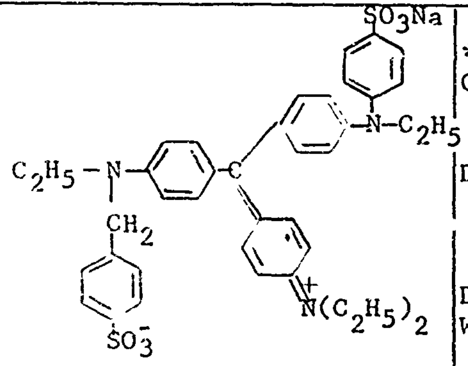
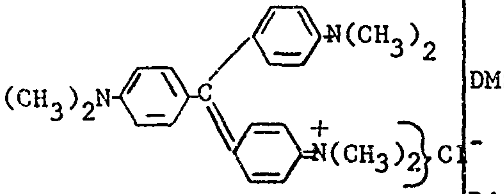
c. Back Reaction Studies

Many dyes have been "bleached" with inorganic reagents such as Na_3PO_4, $Na_4P_2O_7 \cdot 10H_2O$, $Na_2B_4O_7$, Na_2HPO_4, Na_2SO_3 and $NaHSO_3$. The best of these with regard to speed of bleaching and overall effect on photochromic response have been found to be Na_2SO_3 and $NaHSO_3$. Considerable exploratory work has been done with the latter. Most of the dyes bleach easily with $NaHSO_3$ but an excess is required.

Table VII shows the effects of other reagents and compounds (called additives) which were evaluated as possible bleaching agents for a typical triphenylmethane dye. These compounds are both inorganic and organic. Table VIII shows the structures of the organic

TABLE V

PHOTOCHROMIC FORMULATIONS OF REPRESENTATIVE
TRIPHENYLMETHANE DYES

Identification Number*	Structure	Solvent **	Additive	Effect of U.V.	Comments
PC 1011R (CI 42650)		**Methyl Cellosolve	KCN in MeOH	Slight photo-chromism	Light violet.
		DMSO	KCN in MeOH	Good photo-chromism	Light violet. Major absorption peak 595 mμ.
		Distilled Water	$NaHSO_3$	Good photo-chromism	Dark violet.
PC 1016 (CI 42555)		**Methyl Cellosolve	KCN in MeOH	Good photo-chromism	Violet.
		DMSO	KCN in MeOH	Good photo-chromism	Violet.
		Distilled Water	$NaHSO_3$	Good photo-chromism	Violet. Thermochromic

*The identification numbers are Polacoat numbers and Colour Index numbers. The structures of the dyes were obtained from the Colour Index, Volume 3.

**Methyl Cellosolve is a trade name for ethylene glycol monomethyl ether. DMSO refers to Dimethyl Sulfoxide.

TABLE V (Cont'd)

PHOTOCHROMIC FORMULATIONS OF REPRESENTATIVE TRIPHENYLMETHANE DYES

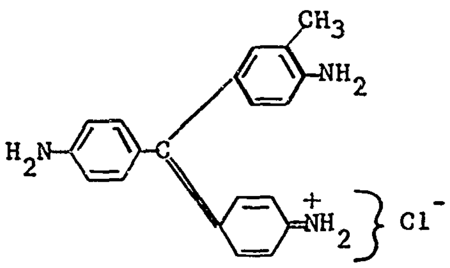
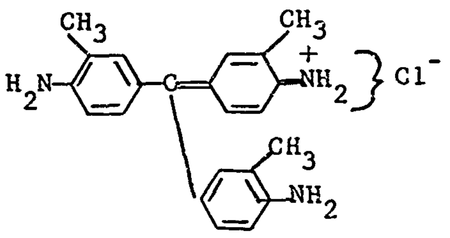
Identification Number	Structure	Solvent	Additive	Effect of U.V.	Comments
PC 1023R (CI 42510)		Methyl Cellosolve	KCN in MeOH	Fair photochromism	Light red.
		DMSO	KCN in MeOH	Good photochromism	Red. Major absorption peak 558 mμ.
		Distilled Water	$NaHSO_3$	Good photochromism	Positive thermochromism
PC 1024R (CI 42520)		Methyl Cellosolve	KCN in MeOH	Good photochromism	Red.
		DMSO	KCN in MeOH	Good photochromism	Red. Major absorption peaks 290, 580 mμ.
		Distilled Water	$NaHSO_3$	Good photochromism	Red. Thermochromic

TABLE V (Cont'd)

PHOTOCHROMIC FORMULATIONS OF REPRESENTATIVE TRIPHENYLMETHANE DYES

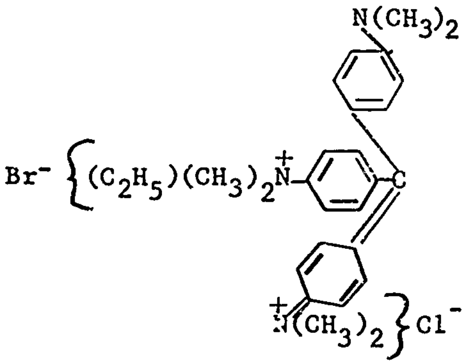
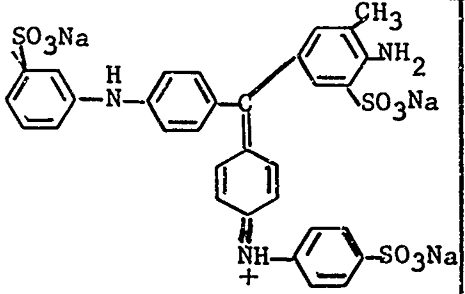
Identification Number	Structure	Solvent	Additive	Effect of U.V.	Comments
PC 1090 (CI 42590)		Methyl Cellosolve	KCN in MeOH	Good photo-chromism	Violet. Major absorption peaks 635, 422 and 310 mμ.
		DMSO	KCN in MeOH	Good photo-chromism	Bright green. Major absorption peaks 625, 426 and 315 mμ.
		Distilled Water	$NaHSO_3$	Good photo-chromism	Can bleach either violet or colorless depending upon amount of bleach added. Thermochromic
PC 1091 (CI 42755)		Methyl Cellosolve	KCN in MeOH	Good photo-chromism	Red. Major absorption peaks 300 and 600 mμ.
		DMSO	KCN in MeOH	Good photo-chromism	Pink.
		Distilled Water	$NaHSO_3$	Good photo-chromism	Blue. Thermochromic

TABLE V (Cont'd)

PHOTOCHROMIC FORMULATIONS OF REPRESENTATIVE TRIPHENYLMETHANE DYES

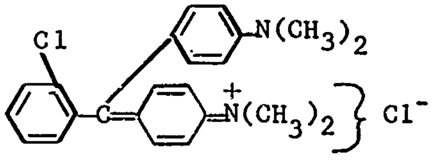
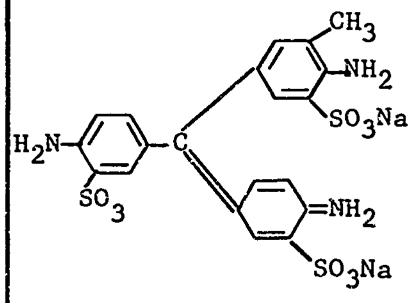
Identification Number	Structure	Solvent	Additive	Effect of U.V.	Comments
PC 1092 (CI 42025)		Methyl Cellosolve	KCN in MeOH	Good photochromism	Green.
		DMSO	KCN in MeOH	Good photochromism	Green. Major absorption peaks 635, 420 and 308 mµ.
		Distilled Water	$NaHSO_3$	Good photochromism	Green.
PC 1093 (CI 42685)		Methyl Cellosolve	KCN in MeOH	Fair photochromism	Pink
		DMSO	KCN in MeOH	Good photochromism	Light red. Major absorption peaks 550 and 290 mµ.
		Distilled Water	$NaHSO_3$	Good photochromism	Red. Thermochromic.

TABLE V (Cont'd)

PHOTOCHROMIC FORMULATIONS OF REPRESENTATIVE TRIPHENYLMETHANE DYES

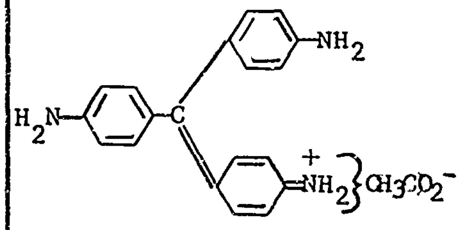
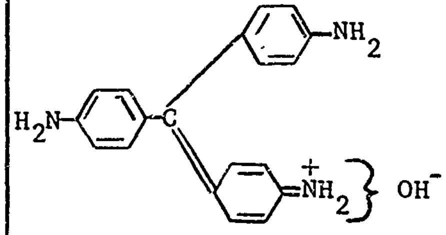
Identification Number	Structure	Solvent	Additive	Effect of U.V.	Comments
PC 1094 (CI 42500)		Methyl Cellosolve	KCN in MeOH	Fair photochromism	Light red.
		DMSO	KCN in MeOH	Good photochromism	Light red. Major absorption peaks 550 and 294 mμ.
		Distilled Water	$NaHSO_3$	Good photochromism	Red.
PC 1095 (CI 42500)		Methyl Cellosolve	KCN in MeOH	Poor photochromism	Light orange.
		DMSO	KCN in MeOH	Poor photochromism	Light orange. Major absorption peak 560 mμ.
		Distilled Water	$NaHSO_3$	Good photochromism	Dye is very slightly soluble.

TABLE V (Cont'd)

PHOTOCHROMIC FORMULATIONS OF REPRESENTATIVE
TRIPHENYLMETHANE DYES

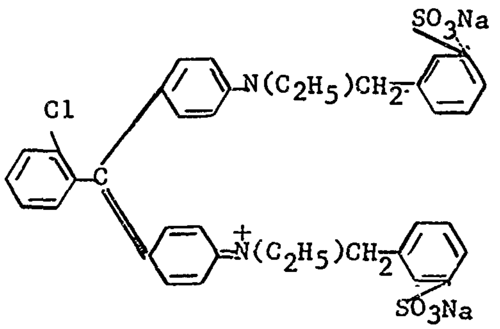
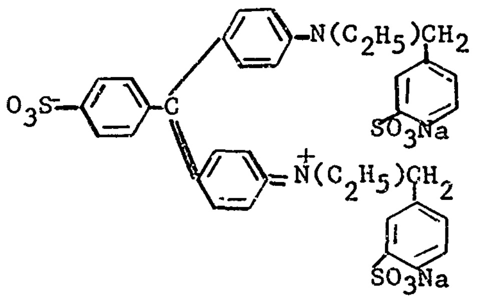
Identification Number	Structure	Solvent	Additive	Effect of U.V.	Comments
PC 1104 (CI 42100)		Methyl Cellosolve	KCN in MeOH	Poor photo-chromism	Light green.
		DMSO	KCN in MeOH	Poor photo-chromism	Light green.
		Distilled Water	$NaHSO_3$	Good photo-chromism	Green.
PC 1106 (CI 42095)		Methyl Cellosolve	KCN in MeOH	No photo-chromism	
		DMSO	KCN in MeOH	No photo-chromism	
		Distilled Water	$NaHSO_3$	Good photo-chromism	Green.

TABLE V (Cont'd)

PHOTOCHROMIC FORMULATIONS OF REPRESENTATIVE TRIPHENYLMETHANE DYES

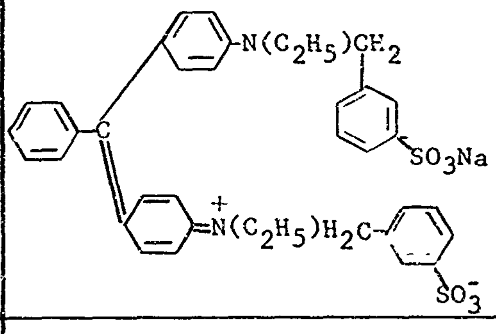
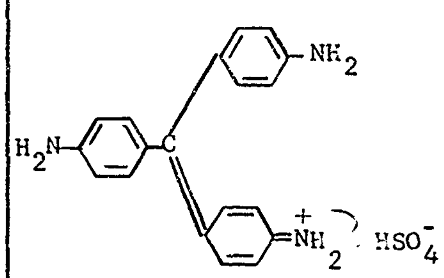
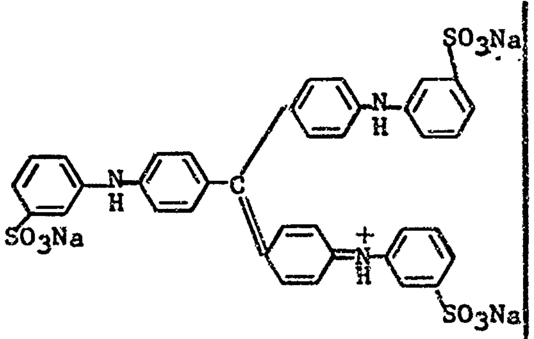
Identification Number	Structure	Solvent	Additive	Effect of U.V.	Comments
PC 1113 (CI 42085)		Methyl Cellosolve	KCN in MeOH	Fair photo-chromism	Light green.
		DMSO	KCN in MeOH	Good photo-chromism	Green. Major absorption peaks 635 and 430 mμ.
		Distilled Water	$NaHSO_3$	Good photo-chromism	Green.
PC 1115 (CI 42500)		Methyl Cellosolve	KCN in MeOH	Fair photo-chromism	Light red.
		DMSO	KCN in MeOH	Good photo-chromism	Red. Major absorption peaks 550 and 293 mμ.
		Distilled Water	$NaHSO_3$	Good photo-chromism	Red.

TABLE V (Cont'd)

PHOTOCHROMIC FORMULATIONS OF REPRESENTATIVE TRIPHENYLMETHANE DYES

Identification Number	Structure	Solvent	Additive	Effect of U.V.	Comments
PC 1117 (CI 42780)		Methyl Cellosolve	KCN in MeOH	No photochromism	
		DMSO	KCN in MeOH	Fair photochromism	Light red-violet Major absorption peaks 592 and 310 mμ.
		Distilled Water	$NaHSO_3$	No photochromism	

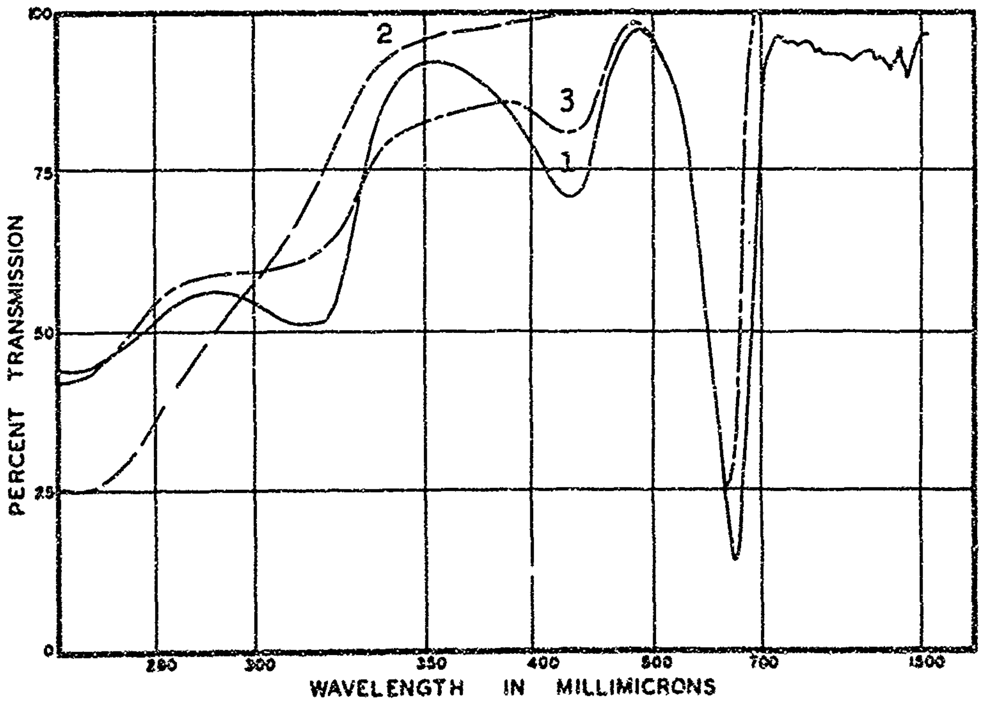


Figure 4. Spectral Absorption Characteristics of a 2 x 10^{-5} M Solution of PC 1090 (CI 42590) in Methyl "Cellosolve". [1) - 2 x 10^{-5} M Dye Solution; 2) - "Bleached" Dye Solution; 3) - "Bleached" Solution Exposed to UV Light.]

additives evaluated (not all of which are considered in Table VII). Certain additives cause easy reduction of the dye to the colorless leuco form while some require light. Some formulations exhibited photochromism in acidic media. Many of the additives (e.g., $SnSO_4$) are known to participate in oxidation-reduction reactions. This could account for the formation of some leuco species. An organic reagent like benzaldehyde may be oxidized in the presence of light and air to benzoic acid and thus cause reduction of the dye. Still other reagents (e.g., benzophenone) affect the formation of the leuco and colored forms in ways for which no mechanisms can now be postulated.

TABLE 11

MAJOR ABSORPTION PEAKS OF SELECTED TRIPHENYLMETHANE DYES IN VARIOUS SOLVENTS

Dye	Solvent	Peaks*
PC 1016 (CI 42555)	Methyl Cellosolve	622, 320 mμ
	Distilled Water	580, 302 mμ
PC 1023R (CI 42510)	Methyl Cellosolve	500-600, 290 mμ
	Distilled Water	580, 302 mμ
PC 1090 (CI 42590)	Methyl Cellosolve	635 422, 310 mμ
	Distilled Water	617 418, 311 mμ

*Data obtained with a Beckman DK-2 Spectrophotometer

TABLE VII

EFFECTS OF SELECTED ADDITIVES ON THE PHOTOCHROMIC RESPONSES OF METHYL GREEN (PC 1090; CI 42590) IN WATER AND METHYL CELLOSOLVE

Additive	Effect in Water	Effect in Methyl Cellosolve
$SnSO_4$	Color fades upon standing. System bleaches in dark with no subsequent photosensitivity.	Color fades upon standing. System bleaches in dark with no subsequent photosensitivity.
Zn powder	Color fades upon standing. System bleaches in dark with no subsequent photosensitivity.	Color fades upon standing. System bleaches in dark with no subsequent photosensitivity.
$Ce(HSO_4)_4$	Color fades upon standing. System bleaches in dark with no subsequent photosensitivity.	Color forms upon flashing. System bleaches in dark with subsequent photo-induced color reaction.
Allylthiourea	- -	Color fades upon standing. System bleaches in dark with no subsequent photosensitivity.
Ascorbic Acid	- -	Color fades upon standing. System bleaches in dark with no subsequent photosensitivity.
Benzophenone	- -	Color disappears upon flashing. No dark reaction.
Benzoin	- -	Color fades upon standing, disappears upon flashing. System bleaches in dark with no subsequent photosensitivity.
Benzaldehyde	- -	Color disappears upon flashing. No dark reaction but gives a photo-induced bleaching

TABLE VII (Cont'd)

EFFECTS OF SELECTED ADDITIVES ON THE PHOTOCHROMIC RESPONSES OF METHYL GREEN (PC 1090; CI 42590) IN WATER AND METHYL CELLOSOLVE

Additive	Effect in Water	Effect in Methyl Cellosolve
$KMnO_4$	- - - - - - - - - - - - - - - - - -	Color forms upon flashing. System bleaches in dark with subsequent photo-induced color reaction.
$K_2Cr_2O_7$	- - - - - - - - - - - - - - - - - -	Color forms upon flashing. System bleaches in dark with subsequent photo-induced color reaction.
Thiourea + HCl	Color disappears upon standing. System bleaches in dark with no subsequent photosensitivity.	Color disappears upon flashing. No dark reaction but gives a photo-induced bleaching.
Benzidine + HCl	Color disappears upon standing. System bleaches in dark with no subsequent photosensitivity.	Color disappears upon flashing. No dark reaction but gives a photo-induced bleaching.
Ascorbic Acid + HCl	Color disappears upon standing. System bleaches in dark with no subsequent photosensitivity.	- -
Allylthiourea + HCl	Color disappears upon standing, forms upon flashing. System bleaches in dark with subsequent photo-induced color reaction.	- -
Citric Acid + HCl	Color disappears upon standing. System bleaches in dark with no subsequent photosensitivity.	- -

TABLE VII (Cont'd)

EFFECTS OF SELECTED ADDITIVES ON THE PHOTOCHROMIC RESPONSES OF METHYL GREEN (PC 1090; CI 42590) IN WATER AND METHYL CELLOSOLVE

Additive	Effect in Water	Effect in Methyl Cellosolve
Benzophenone + HCl	Color disappears upon standing. System bleaches in dark with no subsequent photosensitivity.	- -
Cu_2Br_2 + HCl	Color disappears upon standing. System bleaches in dark with no subsequent photosensitivity.	- -
$Cu(NO_3^-)_3$ + HCl	Color disappears upon standing. System bleaches in dark with no subsequent photosensitivity.	- -
$CuCl_2$ + HCl	Color disappears upon standing. System bleaches in dark with no subsequent photosensitivity.	- -
Benzoin + HCl	Color forms upon flashing. System bleaches in dark with subsequent photo-induced color reaction.	- -
Benzaldehyde + HCl	Color forms upon flashing. System bleaches in dark with subsequent photo-induced color reaction.	- -

TABLE VIII

STRUCTURE OF ORGANIC ADDITIVES EVALUATED AS BLEACHING AGENTS

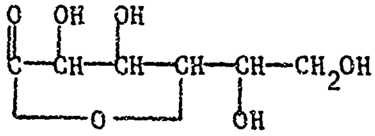
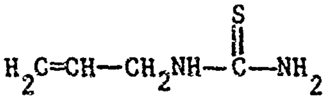
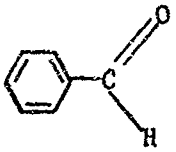
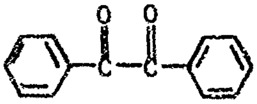
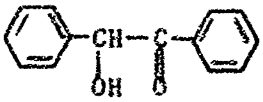
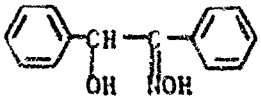
Additive	Structure
Ascorbic Acid	
Allylthiourea	 $H_2C{=}CH{-}CH_2NH{-}\overset{S}{\overset{\Vert}{C}}{-}NH_2$
Benzaldehyde	
Benzil	
Benzoin	
Benzoin-β-oxime	

TABLE VIII (Cont'd)

STRUCTURE OF ORGANIC ADDITIVES EVALUATED AS BLEACHING AGENTS

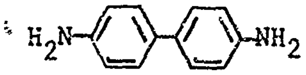
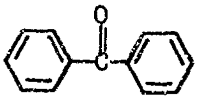
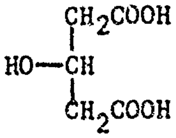
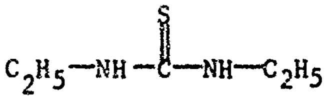
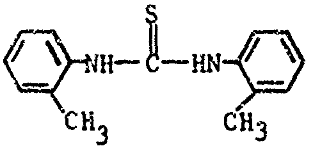
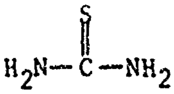
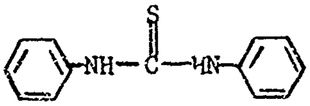
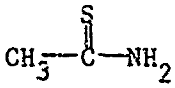
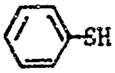
Additive	Structure
Benzidine	
Benzophenone	
Citric Acid	 $HO-CH(CH_2COOH)_2$
1,3-Diethylthiourea	 $C_2H_5-NH-C(=S)-NH-C_2H_5$
2,2'-Dimethylthiocarbanilide	
Thiourea	 $H_2N-C(=S)-NH_2$

TABLE VIII (Cont'd)

STRUCTURE OF ORGANIC ADDITIVES EVALUATED AS BLEACHING AGENTS

Additive	Structure
Thiocarbanilide	
Thioacetamide	 $CH_3-\overset{\overset{S}{\parallel}}{C}-NH_2$
Thiophene	
Thiophenol	
2,2'-Thiodiethanol	$HOCH_2CH_2SCH_2CH_2OH$
3,3'-Thiodipropionic acid	$HOOCCH_2CH_2SCH_2CH_2COOH$
Thiodiacetic acid	$HOOCCH_2SCH_2COOH$

[illegible] of Malachite Green
(PC 1090; CI 42590 [illegible]

It was found that Malachite Green [illegible] if the bisulfite adduct solution was [illegible] open vessel. Evidently, the evolution of [illegible] to form in place of the leucosulfonic acid. [illegible] repeated exposures to light gradually cause degradation [illegible] Green system and result in solutions which do not exhibit [illegible] a photochromic reaction as would a fresh sample. Two aqueous [illegible] fite solutions of PC 1090 were tested, one of which was previously exposed to a continuous ultraviolet source for 17 hours. The solutions were then exposed to repeated flashes from a Xenon flash tube. The solutions were allowed to decolorize between each successive flash. The transmission measurements were taken at 600 mμ which is very near the major absorption peak for the dye.

e. Negative Photochromism

Certain formulations, as shown in Table X, have resulted in negative photochromic response, that is, the dye color disappears upon irradiation with ultraviolet light. In some cases, the dye seems to be degraded and a non-photochromic species formed. In other cases, air oxidation may be the cause of the reversible response. These systems have not been studied thoroughly and were tested only to obtain the effect of thiourea on triphenylmethanes for comparison with concentrated HCl as a bleaching agent for thiazines.

f. Thermochromism

Some of the aqueous bisulfite solutions of triphenylmethane dyes exhibited both photochromic and thermochromic properties. Thermochromism is the phenomenon of a change in color caused by a change in temperature. Among the dyes showing this effect were PC 1090 (CI 42590), PC 1023 (CI 42510), and PC 1016 (CI 42555). Methyl Green (PC 1090) also exhibited thermochromism and photochromism in viscous aqueous methyl cellulose (types 400 and 1500 centipoise) solutions.

TABLE IX

TRANSMISSION MEASUREMENTS AT 600 mμ OBTAINED AFTER REPEATED IRRADIATIONS OF TWO AQUEOUS BISULFITE SOLUTIONS OF PC 1090 (CI 42590)

Sample I*		Sample II**	
INITIAL TRANSMISSION (%)	TRANSMISSION AFTER EXPOSURE TO LIGHT	INITIAL TRANSMISSION (%)	TRANSMISSION AFTER EXPOSURE TO LIGHT
84	10	89	7
78	13	85	7
74	14	74	6
84	11	86	9
83	13	86	10
83	24	86	11
84	13	85	12
84	13	87	11
80	18	81	11
81	17	84	11
81	18	81	10
80	20	81	10
83	16	85	11
85	20	87	11
79	18	79	11
85	22	86	13
83	20	84	13

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*Irradiated for 17 hours by ultraviolet light before testing.
**Not irradiated before testing.

TABLE X

NEGATIVE PHOTOCHROMIC FORMULATIONS USING TRIPHENYLMETHANE DYES

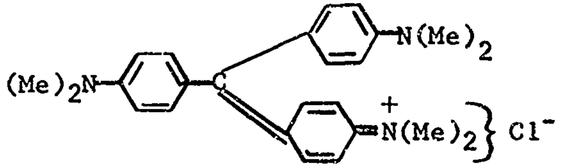
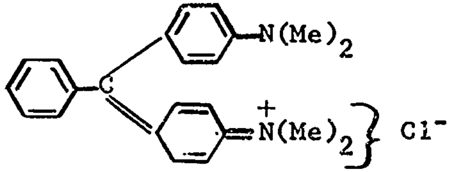
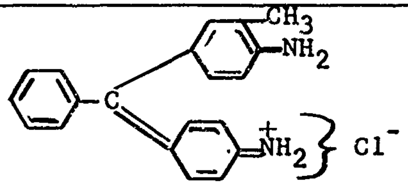
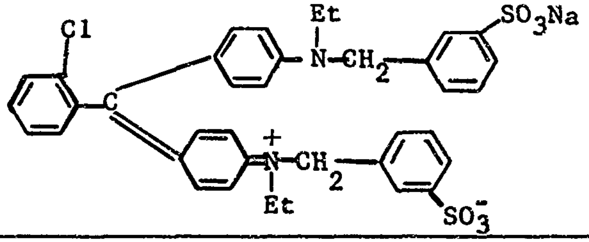
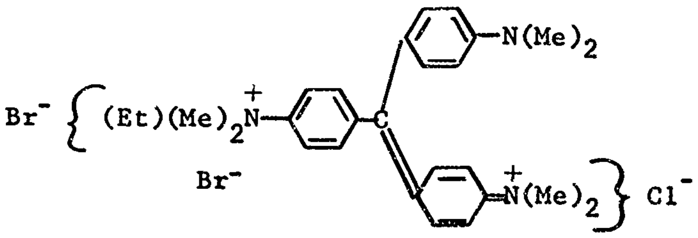
Identification Number	Structure	Solvent	Additive	Effect of U.V.
PC 1016 (CI 42555)		Methyl Cellosolve	Thiourea & Conc. HCl	Color disappears, returns upon removal of ultraviolet.
PC 1021 (CI 42000)		Methyl Cellosolve	Thiourea & Conc. HCl	Color disappears, returns upon removal of ultraviolet.
PC 1023R (CI 42510)		Methyl Cellosolve	Thiourea & Conc. HCl	Color disappears, returns upon removal of ultraviolet.
PC 1118 (CI 42100)			Allylthiourea, Benzoin, Benzaldehyde & Thiourea with Conc. HCl	Color disappears on standing and with ultraviolet.

TABLE X (Cont'd)

NEGATIVE PHOTOCHROMIC FORMULATIONS USING TRIPHENYLMETHANE DYES

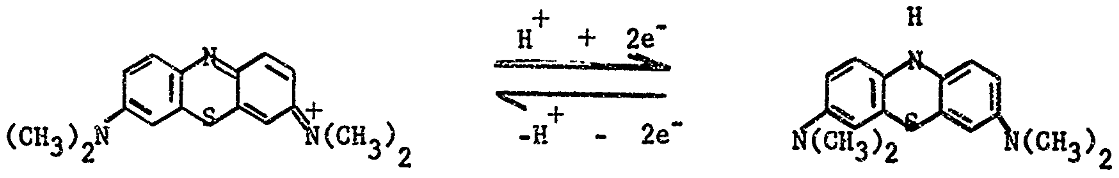
Identification Number	Structure	Solvent	Additive	Effect of U.V.
PC 1090 (CI 42590)		Methyl Cellosolve	Thiourea & Conc. HCl	Color disappears.
		"	Thiourea	No results.
		"	Allylthiourea	Color disappears.
		"	Benzoin	Color disappears or will gradually fade upon standing.
		"	Benzoin-β-Oxime	Color disappears.
		"	Benzil	Slight disappearance of color.
		"	Benzophenone	Color disappears.
		"	Benzidine	Color disappears.

3. Thiazine Dyes

a. Formulations

A considerable amount of work has been reported on the thiazine dyes, especially methods of reduction to the leuco forms. Oster(26) reported on the photo-reduction of these dyes upon exposure to light. The chemical reducing agents ascorbic acid and divalent iron were reported by Hardwick(27). Chelating agents such as ethylenediaminetetraacetic acid (EDTA), compounds such as reducing sugars and phenylhydrazine, and still other reducing agents both organic and inorganic have been used.

Table XI contains the formulations of several thiazine dyes which produce positive type photochromic solutions. In these formulations an excess of thiourea must be used and the pH must be less than one, usually about 0.7, for satisfactory formation of the leuco forms. The reduction is illustrated with Methylene Blue as follows:



Oxidized form
(Blue)

Leuco or Reduced Form
(Colorless)

Figure 5 illustrates the spectra obtained for an aqueous solution of Methylene Blue bleached with thiourea and hydrochloric acid. The major absorption peak of the dye is about 650 mμ. The activating wavelength for this formulation has been determined as approximately 360 mμ with the range extending from 320 to 385 mμ.

Table XII contains data on the color disappearance and the color formation (photochromic response) of two Methylene Blue solutions in the presence of various additives. In some cases, the reducing agents are capable of causing reduction of the dye on standing, resulting in the oxidation of the additive.

TABLE XI

PHOTOCHROMIC FORMULATIONS OF REPRESENTATIVE THIAZINE DYES

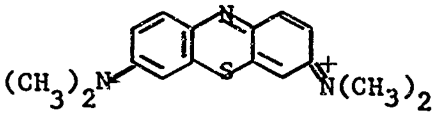
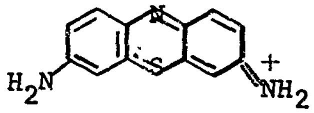
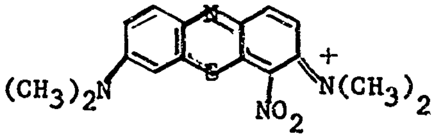
Identification Numbers	Structure	Solvent	Additive(s)	Effect of U.V.	Back Reaction	Comments
PC 4000 (CI 52015)	Methylene Blue 	Methyl Cellosolve	Thiourea Conc. HCl	Good photochromism	Positive	pH must be less than one (0.7). Also obtain photochromic systems in MeOH & EtOH. H_3PO_4 can be used instead of HCl.
		"	Ascorbic Acid Conc. HCl	Fair photochromism	Positive	- - - - - - -
		Distilled Water	Thiourea Conc. HCl	Good photochromism	Positive	Greater O.D. obtained if NaCl or other salt is added.
		"	Urea Conc. HCl	No photochromism	- - - - -	- - - - - - -
		"	Thiobenzanilide	Fair photochromism	- - - - -	- - - - - - - -

TABLE XI (cont'd)

PHOTOCHROMIC FORMULATIONS OF REPRESENTATIVE THIAZINE DYES

Identification Numbers	Structure	Solvent	Additive(s)	Effect of U.V.	Back Reaction	Comments
PC 4001 (CI 52000)	Thionine 	Methyl Cellosolve	Thiourea Conc. HCl	Good photo-chromism	Positive	pH less than one. The more alkaline the soln. (i.e., above pH 1) the greater the obtainable O.D. but the slower the back reaction.
PC 4002 (CI 52020)	Methylene Green 	Methyl Cellosolve	Thiourea Conc. HCl	Good photo-chromism	Positive	- - - - - - -

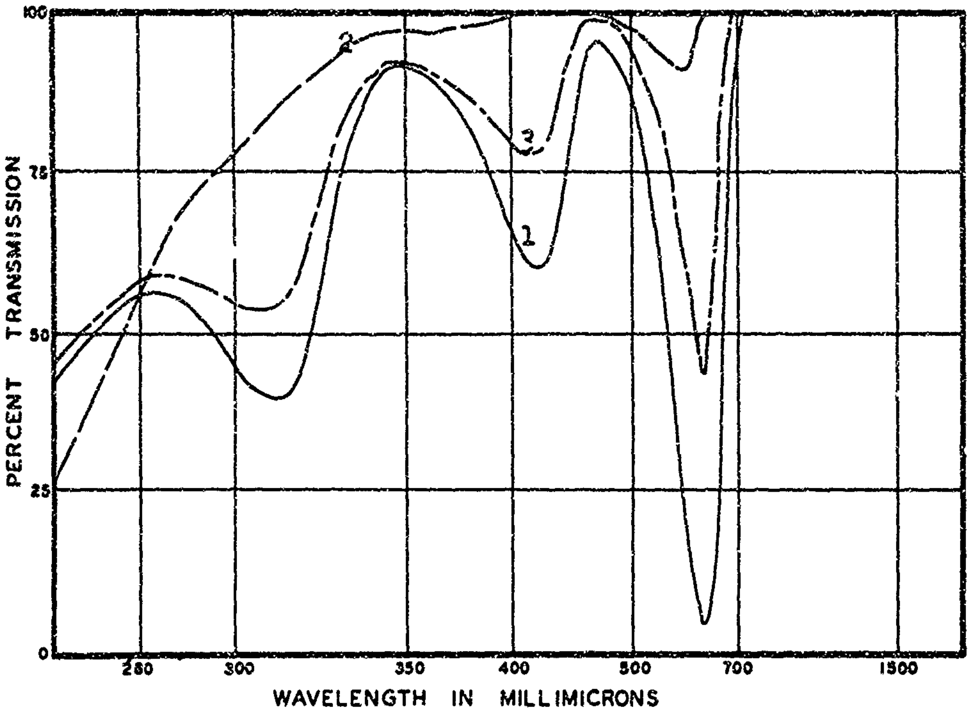


Figure 5. Spectral Absorption Characteristics of an Aqueous Solution of Methylene Blue Bleached with Thiourea and Hydrochloric Acid. [1) - Non-Irradiated Bleached Dye Solution. 2) - Dye Solution Exposed to U.V.]

TABLE XII

EFFECTS OF SELECTED ADDITIVES ON THE PHOTOCHROMIC RESPONSE OF METHYLENE BLUE IN WATER AND METHYL CELLOSOLVE

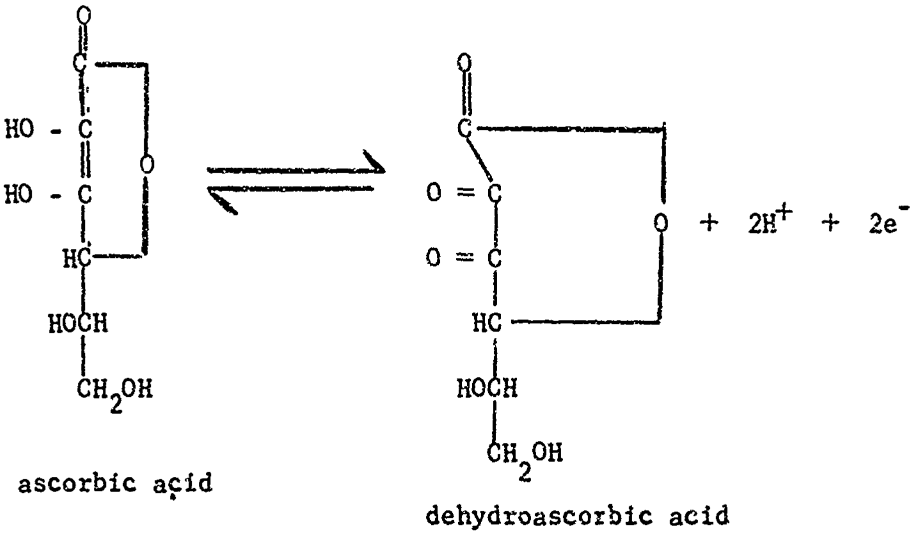
Additive	Effect in Water	Effect in Methyl Cellosolve
Ascorbic Acid	Color fades upon standing. System bleaches in dark with no subsequent photosensitivity.	Color fades upon standing. System bleaches in dark with no subsequent photosensitivity.
Allylthiourea	Color disappears upon flashing. No dark reaction.	Color disappears upon flashing. No dark reaction.
Benzaldehyde	Gives a two-phase system. Color disappears from aqueous layer upon flashing.	Color disappears upon flashing. No dark reaction.
$SnSO_4$	Color fades upon standing. System bleaches in dark with no subsequent photosensitivity.	- - - - - - - - - - - - - - - - - -
$Ce(HSO_4)_4$	Color fades upon standing. System bleaches in dark with no subsequent photosensitivity.	- - - - - - - - - - - - - - - - - -
Benzophenone	- - - - - - - - - - - - - - - - - -	Color disappears upon flashing. No dark reaction.
Benzoin	- - - - - - - - - - - - - - - - - -	Color disappears upon flashing. No dark reaction.
Cu_2Br_2 + HCl	Color disappears upon standing. System bleaches in dark with no subsequent photosensitivity.	Color disappears upon flashing. No dark reaction.

TABLE XII (Cont'd)

EFFECTS OF SELECTED ADDITIVES ON THE PHOTOCHROMIC RESPONSE OF METHYLENE BLUE IN WATER AND METHYL CELLOSOLVE

Additive	Effect in Water	Effect in Methyl Cellosolve
Thiourea + HCl	Color disappears upon standing, forms upon flashing. System bleaches in dark with subsequent photo-induced color reaction.	Color forms upon flashing. System bleaches in dark with subsequent photo-induced color reaction.
Zn + HCl	Color forms upon flashing, disappears upon standing. System bleaches in dark with subsequent photo-induced color reaction.	Color disappears upon standing. Color forms upon flashing. System bleaches in dark with subsequent photo-induced color reaction.
Allylthiourea + HCl	Color forms upon flashing. System bleaches in dark with subsequent photo-induced color reaction.	- - - - - - - - - - - - - - - - -
$SnSO_4$ + HCl	- - - - - - - - - - - - - - - - - -	Color disappears upon flashing. No. dark reaction..

The additive thus donates the protons or electrons which are necessary for the reduction of the dye. Ascorbic acid oxidizes as shown below, whereas stannous sulfate is oxidized to the tetravalent stannic form.



An acidified aqueous solution in contact with zinc metal causes reduction due to the formation of nascent hydrogen which readily combines with the dye to produce the reduced, or leuco, form. The mechanism of the thiourea reaction has not yet been determined.

Only a few of the reducing agents studied produced systems which exhibited good photochromism as shown in Table XII. The thiourea system produced a colloidal precipitate upon repeated exposures to ultraviolet light. The zinc system was readily oxidized by atmospheric oxygen to produce the colored form of the dye. The variation of responses of the systems in water and methyl cellosolve may be due to pH differences, solvating power, ionizing ability, or some other property of the solvent. In general, water has been favored over methyl cellosolve in the formulation of a good photochromic system due to the solubilities of the salts which have been used.

Acids such as phosphoric and picric have been added with thiourea to produce a photochromic response of Methylene Blue in aqueous media. Thioacetamide and 1,3-diethylthiourea can be used instead of thiourea to yield photochromic solutions. Other sulfur compounds which were tested and showed no photochromic response were: thiocarbanilide, thiophene, thiophenol, thiodiacetic acid, 2,2-thiodiethanol, 2,2'-dimethylthiocarbanilide, and 3,3-thiodipropionic acid.

b. Negative Photochromic Formulations

It is interesting also that several thiazines have been made to exhibit either positive or negative photochromism. Table XIII illustrates several formulations which exhibit a negative photochromic response in methyl cellosolve.

4. Azine Dyes

The azines were chosen as possible photochromic dyes because their basic structure is similar to the thiazines which are known to exhibit photochromism. Before the desired photochromic response could be obtained, the leuco forms had to be prepared as in the study of the thiazines. Initially, "bleaches" used successfully with other dyes were investigated.

Potassium cyanide, which is a very effective bleach for many triphenylmethanes, and an acidified aqueous thiourea solution, which was used effectively for the thiazines, were both found ineffective with the azine Neutral Red (PC 5000; CI 50040). However, powdered zinc in the presence of a small amount of hydrochloric acid effectively reduced the dye to the leuco form which was capable of exhibiting photochromism. The formation of the leuco compound is explained by the addition of a proton and the shift of 2 electrons as shown below. The proposed mechanism is similar to that proposed for the zinc reduction of the thiazines. The extent of reduction of Neutral Red with zinc can be controlled so that upon exposure to ultraviolet, the compound will show either an irreversible or a reversible color change. This has not been studied.

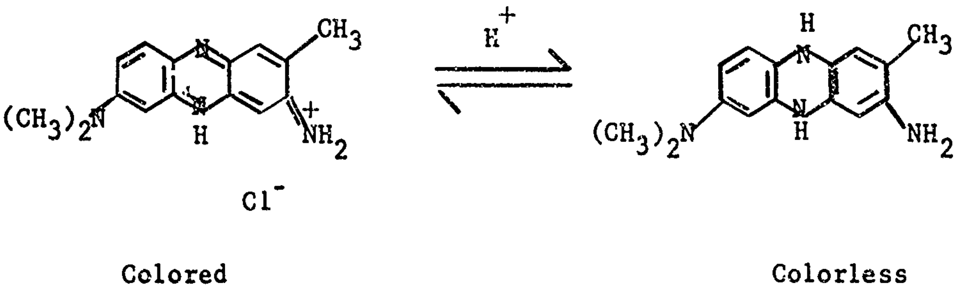
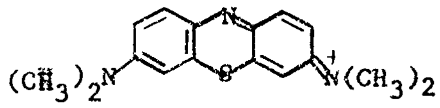
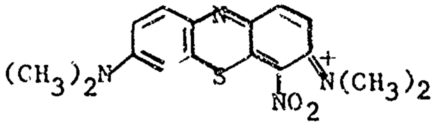
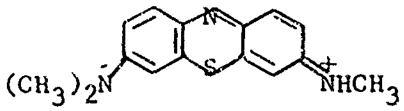
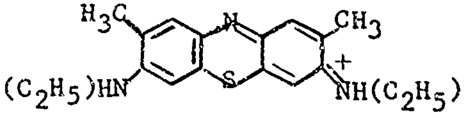
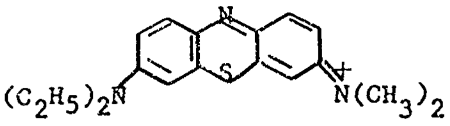


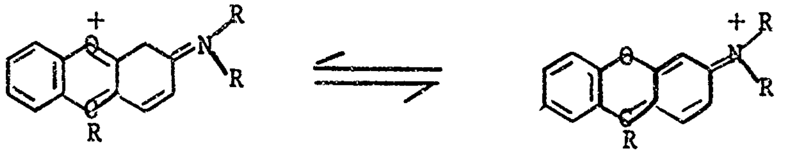
TABLE XIII

NEGATIVE PHOTOCHROMIC FORMULATIONS USING THIAZINE DYES

Identification	Structure	Additive
PC 4000 (CI 52015) Methylene Blue		Benzaldehyde Benzoin
PC 4002 (CI 52020) Methylene Green		Allylthiourea Benzaldehyde Benzoin
PC 4003 (CI 52010) Methylene Azure		Allylthiourea Benzaldehyde
PC 4004 (CI 52030) Basic Blue 24		Allylthiourea + Conc. HCl Benzaldehyde
PC 4005 (CI 52025) Basic Blue 25		Benzaldehyde

5. Xanthene Dyes

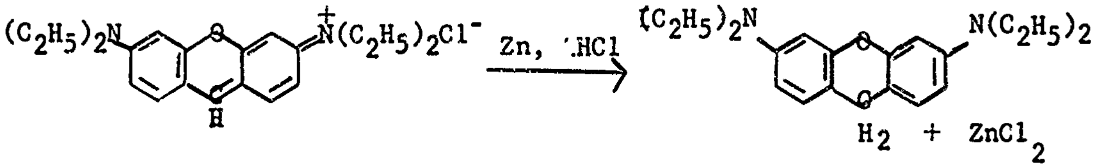
The xanthenes are structurally similar to the thiazines and azines, and several similarly exhibit photochromism in solution. The chromophore of the aminoxanthene dyes is the resonance hybrid shown below:



where R = H, alkyl, or aryl.

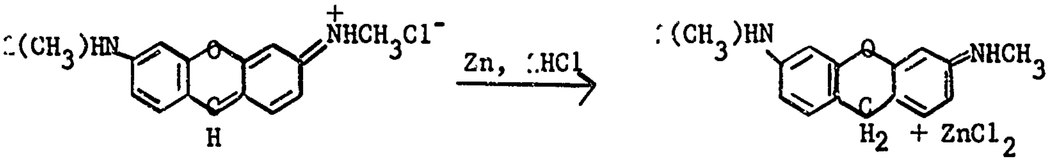
Pyronine B (PC 6000; CI 45010) and Acridine Red 3B (PC 6001; CI 45000) were reduced to leuco compounds with zinc dust in an acidified aqueous solution. The equations are shown below:

Pyronine B (PC 6000; CI 45010)



colored (red) colorless

Acridine Red (PC 6001; CI 45000)



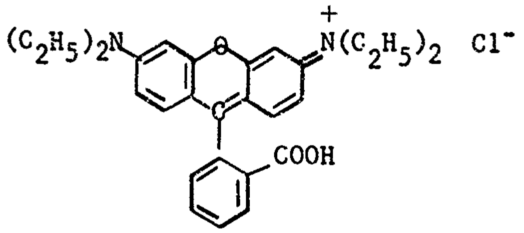
colored (red) colorless

These solutions were photochromic upon exposure to ultraviolet light. The reduction of the dye could be controlled to the extent that the back reaction was either quite rapid or so slow that an apparently irreversible response was obtained. The mechanism of reduction is similar to that for the thiazines and azines. It is proposed that nascent hydrogen attacks the dye molecule and is accompanied by the shift of two electrons, thus forming the leuco dye species.

The hydrogen could be bound in such a manner that light could easily effect its removal, thus giving rise to the colored species. Pyronine B exhibited good photochromism whereas Acridine Red 3B exhibited only fair photochromism.

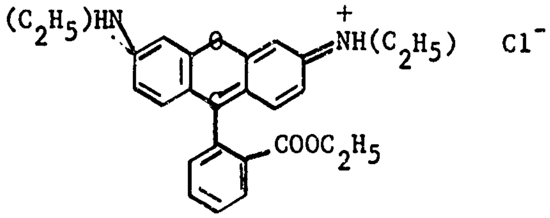
The proposed proton addition mechanism for the bleaching reaction is justified by the fact that the following dyes exhibited no photochromism.

Rhodamine B (PC 6002; CI 45170)



The substituted phenyl ring blocks the central carbon atom so that proton addition does not occur, thus indicating that this carbon is essential in the formation of a colorless species.

Basic Red 8, Ethyl Ester
(PC 6003; Ethyl Ester of CI 45150)

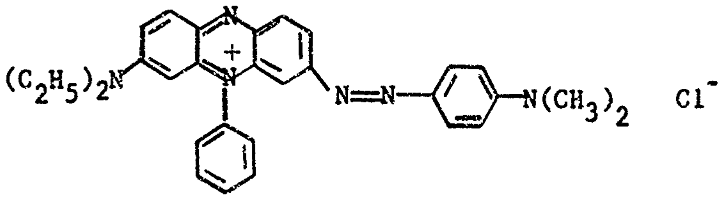


6. Multiple Chromophore Dyes

A specific example is Janus Green B (PC 7000; CI 11050) (shown below) which contains both an azine and an azo group. The green dye can be reduced with strong reducing agents, such as zinc and hydrochloric acid, to a light yellow species which turns red upon exposure to ultraviolet light. The red color fades and disappears while the original color reappears upon standing.

This dye, when reduced to the leuco form with zinc and hydrochloric acid, is sensitive to atmospheric oxygen (as are the thiazines) and slowly oxidizes from the yellow form back to the green form. The complex dyes have the desirable characteristic of a broad absorption over the visible range.

Janus Green B (PC 7000; CI 11050)



C. THERMOCHROMIC SYSTEMS

Aqueous leuco sulfonic acid systems show a positive thermochromic effect, that is, an increase in color formation with an increase in temperature. This effect is important in the development of salt-isomerism photochromic systems for flashblindness protection because it can augment the photochromic response. Most of the systems discussed previously show a negative thermochromic response which opposes the photochromic response and limits color formation if the temperature rises during exposure. Hence, the compounding procedure until now has been to optimize the photochromic response only. But since a system is available which shows thermochromic possibilities, the overall sensitivity, including both photo- and thermoactivation, should also be maximized.

VI. ENVIRONMENTAL EFFECTS

A. SOLVENTS

1. General Requirements for Support of Photochromism

The investigation of the salt-isomerism types of photochromic materials, both reversible and irreversible, was carried out by studying solutions because materials of this type show no photochromism in the solid state. In an attempt to understand the mechanism of the phenomena in solutions, a solvent study was made during which the following general requirements for a photochromism-supporting solvent were developed:

a. The solvent must be capable of dissolving both the leuco and the colored forms of the dye. (Generally, the solubility of a dye increases with the polarity of the solvent, while the solubility of its leuco form decreases.)

b. The solvent must be neutral with respect to the compound in question. (If the solvent is acidic, the leuco compound will react with the acidic group, giving the dye or colored form. This is the reverse of the bleaching reaction used in preparing the leuco form. If the solvent is basic, the photodissociation of the leuco dye is completely or very greatly retarded.)

c. The solvent must be transparent, or nearly so, to visible wavelengths (400 to 700 mμ) for optical visibility and to near ultraviolet wavelengths (275 to 400 mμ) so that the activating energy can reach the photochromic material.

2. Classification

In general, solvents can be divided into four classes as follows:

a. Aprotic (neither proton acceptors nor proton donors).

b. Protophilic (basic because they have a lone pair of electrons on one or more hetero atoms O, N, or S; ethers and dimethyl sulfoxide (DMSO) are typical examples).

c. Protogenic (slightly ionizable as the alcohols).

d. Miscellaneous (do not fit into any of the above classifications).

Table XIV shows some individual solvents listed according to the above classification. These solvents were used both in the evaluations of, and determination of the requirements for, the support of photochromism.

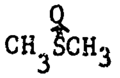
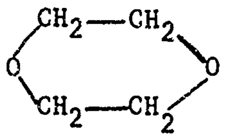
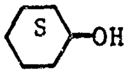
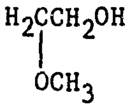
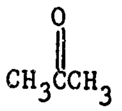
3. Evaluation for Support of Photochromism

Several types of solvents were evaluated and are shown with some of the results in Table XV. The hydroxyl-containing compounds, particularly the alcohols, gave the best support to photochromic response. The evaluations were carried out primarily with the triphenylmethane dye PP 1016 (Crystal Violet, CI 42555) and the polymethine dye PP 2038 in their leuco form but a few evaluations were made also with leuco form of PC 1021 (Malachite Green, CI 42000) and of the thiazine PC 4000 (Methylene Blue, CI 52015). Some of these evaluations are shown in Table XVI for individual solvents. Other evaluations with PP 1016 and PP 2038 dyes were made with the solvents listed in Table XIV. Methyl cellosolve supported the fastest color development and reversal time of the triphenylmethane dye. Methanol, butanol, dimethyl sulfoxide and methyl cellosolve supported the best response in the polymethine compound. Thus, the protogenic solvents and those solvents with relatively high dielectric constants appeared best but with some exceptions. Most alcohols provided a good medium for photochromism and the diols, 2,2-dimethyl-1,3-butanediol and 1,5-pentanediol, seemed to be better than some of the monofunctional alcohols. The monofunctional alcohol series extended from methanol to 2-octanol. The long chain alcohols did not function as well as the short chain members, perhaps because they were less polar.

Several four carbon alcohols were compared to get an indication of the effect of alcohol structure on the photochromic response of PP 1016 and PP 2038. Irradiation was carried out with an ultraviolet light for 30 seconds. The alcohols tested are listed below according to decreasing ability to support photochromism. The results show that, except for the diol, the solvents produced consistent and orderly responses relative to each other. Solvent geometry is therefore important. There was apparently no effect on the back reaction which was complete within minutes in all solvents.

TABLE XIV

SOLVENTS CLASSIFIED ACCORDING TO PROTON BEHAVIOR

Solvent Class	Solvent	Structural Formula	Dielectric Constant*
Aprotic	Benzene		2.27 @ 25°C
Protophilic	Dimethyl Sulfoxide	 $CH_3\overset{O}{S}CH_3$	46.5 @ 25°C
	Diethyl Ether	$CH_3CH_2OCH_2CH_3$	4.34 @ 20°C
	Dioxane (1,4)		2.20 @ 25°C
Protogenic	Methanol	CH_3OH	32.63 @ 25°C
	1-Butanol	$CH_3CH_2CH_2CH_2OH$	17.1 @ 25°C
	Cyclohexanol		15 @ 25°C
	Methyl Cellosolve	 $H_2\underset{\displaystyle OCH_3}{C}CH_2OH$	16 @ 30°C
Miscellaneous	Bromoform	$CHBr_3$	4.39 @ 20°C
	Chloroform	$CHCl_3$	4.80 @ 25°C
	Acetone	 $CH_3\overset{O}{\overset{\Vert}{C}}CH_3$	20.7 @ 25°C

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*N.B.S. Circular 514, "Table of Dielectric Constants of Pure Liquids," United States Printing Office, Washington, D. C., 1951.

TABLE XV

EVALUATION OF SOLVENT TYPES FOR SUPPORT OF PHOTOCHROMIC REACTIONS

Solvent or Solvent Type	Support of Photochromic Reaction	Remarks
Alcohols	Positive	Support the reaction to varying degrees.
Ether Alcohols	Positive	Support the reaction to varying degrees.
Polyglycols	Positive	Support the reaction to varying degrees.
Dimethyl Sulfoxide (DMSO)	Positive	Gives a good reaction with some materials and suggests other solvents.
Dimethyl Acetamide (DMA)-Water Mixture	Positive	Effective only in the 10-20% water concentration range.
Alkanes	Negative	- - - - - - - - - -
Benzene and its Alkyl Substituted Derivatives (i.e., toluene, etc.)	Negative	- - - - - - - - - -
Halide Substituted Alkanes	Negative	In general, these materials give some degree of irreversible reaction not necessarily photochemical in nature.
Nitroparaffins	Negative	- - - - - - - - - - -

TABLE XVI

EVALUATION OF SELECTED SOLVENTS FOR SUPPORT OF PHOTOCHROMISM

Solvent	Dye	Remarks
H_2O	PC 4000 (CI 52015) with thiourea and H_2SO_4	Gives good forward and reverse reactions.
H_2O	PC 1021 (CI 42000) with $NaHSO_3$	Gives good forward and reverse reactions. This dye is one of a number of triphenylmethane dyes which give good photochromic responses in this formulation.
Formamide	PC 4000 (CI 52015) with thiourea and H_2SO_4	Gives good forward and reverse reactions.
Dow Silicone Type Z6040	PP 1016 (CI 42555) Leuco CN	Gives fair forward and reverse reactions.
Dow Silicone Type Z6040	PP 2038 Leuco OH	Gives fair forward and reverse reactions.
Dow Silicone Type R-671	PP 1016 (CI 42555) Leuco CN	Gives fair forward and reverse reactions.
Dow Silicone Type R-671	PP 2038 Leuco OH	Gives fair forward and reverse reactions.

PP 1016 (Crystal Violet CI 42555)	PP 2038 (A Polymethine Dye)
n-butanol	n-butanol
sec-butanol	1,3-butanediol
t-butanol	sec-butanol
1,3-butanediol	t-butanol

When other organic compounds were added to a solution of polymethine PP 2038 leucohydroxide in n-butanol, two different types of behavior were observed. The color of the dye was produced on contact without irradiation when compounds such as benzoic acid and benzaldehyde were added. But when compounds like benzil and benzoin were present, the photochromic capability was apparently destroyed. Addition of hydroquinone to the benzaldehyde to prevent its oxidation to benzoic acid did not affect the photochromic response of the dye.

Solutions of Crystal Violet (PP 1016; CI 42555) and PP 2038 were prepared by dissolving 0.1 gram of the leuco dye in a small portion of the solvent and diluting this to 50 ml. When a leuco compound did not completely dissolve after an hour of stirring, 50 ml of the saturated solution was used for the tests. Some of the solutions were colored initially and were bleached colorless with 0.05 M KCN in methanol. All the solutions containing bromoform, chloroform, and cyclohexanol required considerably more bleaching agent than the other solutions, indicating that these solvents generated more of the colored species than other solvents. Pure bromoform and chloroform solutions were very deeply colored before irradiation while most of the others had only a slight coloration or none at all. The haloform compounds are known to produce free radicals which can react with the leuco compound to produce a colored species.

The evaluations of the support of photochromism were made by determining the magnitude of and the time required for the color change of each solution under irradiation by ultraviolet light. The magnitude was determined by measuring the optical transmission at the absorption maxima before and after irradiation. This was 660 mμ for the triphenylmethane Crystal Violet (PP 1016; CI 42555) and 550 mμ for the polymethine PP 2038.

4. Resistance Studies

A group of solvents, many known to support photochromic reactions, was selected for resistance measurements to see if this parameter could be correlated with photochromic response. Sodium acetate and sodium benzoate were added to the solvents in order to measure the solvent's ability to dissociate an ionic salt. Table XVII summarizes the resistance measurements.

TABLE XVII

RESISTANCE OF SOLVENTS
BEFORE AND AFTER SALT ADDITION

		Resistance (KΩ)*	
Solvent	Pure	Addition of Sodium Acetate	Addition of Sodium Benzoate
Glycerol	9,000	70	100
Dimethyl Sulfoxide	110	3	3.5
Nitrobenzene	35,000	25,000	10,000
2-Methoxyethanol	310	2.4	3.8
2-Pentanol	15,000	600	600
Diethylene Glycol	410	6	40
Diethylene Glycol Monomethyl Ether	300	2.4	3
Pyridine	1,300	600	160
Acetonitrile	50	45	30
N,N-Dimethyl Formamide	45	3	2.4

*As measured with a platinum dipping cell and volt-ohm meter.

An interesting observation is that those solvents displaying a resistance of 3 KΩ or less in sodium acetate solution are the best media for photochromism. The resistance of the pure solvent seems irrelevant to the support of photochromism.

5. Effect on Activating Wavelength

A change in the peak activating wavelength was observed as a function of solvent as indicated by the data in Table XVIII. These data were obtained by activating samples of Crystal Violet (PP 1016; CI 42555) leuco cyanide in dimethyl sulfoxide, 2-methoxy ethanol and methanol with an AC xenon light source in conjunction with a monochromator. The photochromic responses to numerous wavelengths of monochromatic light were measured on a spectrophotometer. The three solvents were selected because Crystal Violet has good photochromic response in each solvent. These data tend to support the theory that an associated complex is the species which is activated.

TABLE XVIII

EFFECT OF SOLVENT ON THE
ACTIVATING WAVELENGTH PEAK OF
THE CRYSTAL VIOLET LEUCO CYANIDE SYSTEM

Solvent	Leuco Cyanide Concentration (g/l)	Activation Peak mμ
Dimethyl sulfoxide	1.00	340
2-Methoxy ethanol	0.81 (saturated)	330
Methanol	0.45 (saturated)	310

B. ADDITIVES

The photochromic system requires a number of components in the formulation. All components except the dye and the solvent are considered additives.

1. Sensitizers

Free radical generators such as bromoform, iodoform and carbon tetrachloride function as sensitizers in irreversible systems but their utility is hampered because many of them impart thermal instability to the resulting systems. Another type of free radical generating sensitizer, a halogenated semiquinone, is β-tetrachloro-1-ketonaphthalene which is discussed more thoroughly in Section V.

2. Oxygen

It has been observed that upon irradiation of reversible systems in open vessels the color formation is much greater at the air-liquid interface than in the bulk of the solution. It is felt that the oxygen in the air caused this. For verification, the following test was made. A solution of 2-methoxyethanol containing 2 g/l of polymethine PP 2017 leuco hydroxide was purged with oxygen-free nitrogen (N_2) for one hour under reflux. The solution was cooled to 25°C for one hour and re-irradiated. The oxygen-free system gave only a faint color change, compared to a significant color change for the air-purged system. Clearly then, oxygen plays a major role in the color formation observed.

3. Bleaches

The following two classes of bleaching reactions are known for the types of compounds under discussion:

(I) Replacement Reaction:

$$\underset{\text{salt form of dye}}{[\text{Dye}]^{+}\,\text{Cl}^{-}} + \underset{\substack{\text{Typical}\\ \text{Replacement}\\ \text{Bleach}}}{\text{KCN}} \longrightarrow \underset{\substack{\text{Covalent}\\ \text{leuco form}\\ \text{of dye}}}{\text{Dye CN}} + \text{KCl}$$

(II) Redox Reaction:

$$[\text{Dye}]^{+}\,\text{Cl}^{-} + \underset{\text{Redox Bleach}}{2\text{H}^{+} + 2\ \text{electrons}} \longrightarrow \text{Dye H} + \text{HCl}$$

Table XIX summarizes the reaction of various classes of dyes with each type of bleach.

It is interesting to compare the effect of bleach with the effect of solvent on the activating wavelength of a photochromic material. Apparently, replacement-type bleaches have no effect

TABLE XIX

SUMMARY OF BLEACH REACTIONS WITH DIFFERENT DYE TYPES

Bleach Type	Dye Type	Remarks
I	Triphenylmethane (example PP 1016; CI 42555)	Gives good photochromic response in either organic or aqueous solutions using KCN or $NaHSO_3$ as bleaches.
II	Triphenylmethane	Will bleach when fairly strong reducing agents are used (i.e., Zn dust and HCl). Shows no photo color response.
I	Polymethine (example PP 2038)	Gives good photochromic responses in organic solution using KOH as bleach. Dye has very limited aqueous solubility.
II	Polymethine	Will bleach when fairly strong reducing agents are used (i.e., Zn dust and HCl). Shows no photo color response.
I	Thiazine	Will not bleach with replacement-type bleaches.
II	Thiazine	Gives a variety of responses with reducing agents. The stronger reducing agents(i.e., acidified thiourea) give good photochromic response. Weaker reducing agents (i.e., allylthiourea or ascorbic acid) will give a system that can be photo bleached.

(Table XX) while solvents do (Table XVIII). However, the evidence is not conclusive because the experimental conditions and compounds used were not identical in both experiments.

In the bleach experiments, the replacement bleach anions used were the hydroxide, paramethoxycinnamate, and cyanide and the photochromic material was leuco polymethine PP 2038. The solvent was 2-methoxy ethanol. The samples were irradiated with a continuous xenon source through a monochromator. The results presented in Table XX show that the peak activating wavelength is the same for the different bleached solutions although the relative sensitivities are different.

TABLE XX
EFFECT OF BLEACH ANION ON THE ACTIVATING WAVELENGTH PEAK OF POLYMETHINE PP 2038

Bleach Anion	Relative Sensitivity of Solutions	Activating Wavelength
OH^-	1	355
CN^-	0.8	355
paramethoxycinnamate	1.4	355

4. Miscellaneous Compounds

Quite a number of chemical additives have been found which significantly improve the sensitivity of the photochromic response yet maintain a reversible system. These materials are primarily esters and soaps of carboxylic acids and give maximum results at concentrations of 1-5 percent of the total solvent. By using the better chemical additives, the change in steady state optical density can be increased by a factor approaching 10. The reason for this added sensitivity may be a buffer-like effect on the bleach anion of the photodissociated ion pair.

C. DYE-ANION CHARGE TRANSFER COMPLEXES

It may be desirable to form a complex of the solvent and the leuco dye which possesses an electron potential slightly under the threshold of spontaneous electron ejection. This complex would be activated only when the leuco compound is excited by absorption of an activating photon of energy. The anion portion of the complex would act as a Lewis base and the dye as a Lewis acid. Dye perchlorates are examples of this type of compound but they do not necessarily possess desirable electron potentials.

The relationship of the medium or solvent to the dye or the dye-anion complex is a most important factor in the occurrence and degree of photochromism. We have found that removal of dissolved oxygen from solvents such as methoxyethoxyethanol stops the forward reaction. On the other hand, with other solvents such as dimethyl sulfoxide, no dissolved oxygen is necessary for photochromism to occur. Also, a photochromic response can be induced, in dye-bleach systems formerly considered to be non-photochromic, by changing the solvent. The best solvent for one dye is not necessarily the best for another dye. Furthermore, for some photochromic materials, a mixture of solvents produces a greater response than either solvent alone.

Optimizing the dye-solvent system can sometimes be accomplished by addition of a buffer salt. It has been shown that the ability of a solvent to ionize the dye correlates with its ability to support photochromism. The literature(16) has stated that the dielectric constant of a solvent is a criterion for supporting the photochromic response. An oscillometer may be used to obtain a relative measurement of the dielectric constant to optimize the ratio of bleach, solvent and dye for maximum photochromism sensitivity.

The above indicates that there is a particular relationship between the solvent and the dye, a balance which, when properly adjusted, allows photochromism to occur. In general, the solvents used are of the electron donor type. Oxygen is known to form a donor-acceptor molecular complex or adduct with various solvents(28) and can complicate the adjustment of the dye solvent balance for optimum photochromism. The electron donor and acceptor properties of molecules can be expressed in terms of the energy coefficient (K), which, in turn, can be obtained by molecular orbital calculations(29).

The electron donor-acceptor properties correlate with ionization potentials, polarographic oxidation-reduction potentials, electron affinities and wavelengths of charge transfer bands.

The role of the energy transfer mechanism is important in the donor-acceptor hypothesis of the photochromic phenomenon. Energy transfer from the triplet level of a donor molecule to an acceptor molecule and thus elevation of the acceptor molecule from its singlet ground state to a triplet state has been observed between a number of donor-acceptor pairs in fluid solvents(30). Polar solvents are known to increase the probability for charge transfer with a donor-acceptor interaction(31). In order to transfer charges, the energy levels of the two structures involved must be closely matched(32). This could explain why one solvent is more effective for a given dye than another in producing an optimum photochromic response. The dielectric constant of the solvent, if sufficiently high, might also permit the dissociation of the donor-acceptor complexes into free radical ions(33). Thus, the donor-acceptor theory can be used to explain some of the phenomena associated with the photochromic response. Another factor in this theory is the influence of functional groups on both the solvent and the dye molecules. The improvement in photochromic sensitivity parallels the electrolytic dissociation in the substituted leuco materials(34).

Studies are in progress to determine if the above concepts can be used to provide a more sensitive system. This is being done by finding an acceptor which provides added sensitivity to the system when complexed with the leuco compound and effectively matches the leuco dye to the supporting system.

The results show that the more effective acceptor materials, e.g., tetranitromethane and chloranil, spontaneously react with the leuco form to give the colored form. To date, no material has been found which gives the amount of added sensitivity desired. However, the number of materials studied was limited so that the concept discussed above is not disproved.

D. COMBINATION DYE SYSTEMS

In the development of a photoactivated flashblindness protection device, the need for a neutral color system is considered important. Therefore, considerable effort was expended toward synthesizing a sensitive neutral density photochromic material. Also, the blending of photochromic materials to give a neutral system was examined briefly. However, this work was limited to materials with a broad spectrum of hues, each of which would exhibit photochromic response under the same set of conditions.

Thus, a number of triphenylmethane dyes of various hues were investigated which give a photochromic response in the same solvent with the same bleach. Studies were carried out to determine if these systems could be blended and give a mixed system which would exhibit a neutral photochromic response. Such a system was obtained by mixing PC 1023 (CI 42510) (a bright red dye) with PC 1090 (CI 42590) (a blue-green dye). The mixture was purple. An aqueous solution of the mixture with sodium bisulfite was colorless as desired. Upon activation with a xenon flash, the purple color was reproduced. This color appeared to be identical to the original color of the solution, that is, before bleaching with bisulfite. However, the back reaction rate was different for each component of the mixture so that progressive coloration during the back reaction was purple to red to colorless.

E. PLASTIC SYSTEMS

1. Homogeneous

A reversible photochromic system would be most useful if the physical form were a rigid or semi-rigid plastic. Therefore, an attempt was made to incorporate the photochromic leuco compounds into resins.

In one approach unplasticized resins were substituted for solvents in sensitive liquid photochromic systems. The resins contained functional groups similar to those contained in the solvents used for the dye-solvent systems. The resin systems were cast from solutions containing inert volatile solvents.

In a second approach plasticized resins were substituted for solvents in liquid photochromic systems. In this approach the plasticizer plays the role of the solvent for the photochromic dye and the resin is merely a supporting matrix. Plasticizers were chosen which contained functional groups similar to those of solvents known to support photochromism. The results of these studies are presented in Table XXI and XXII. The plasticized

TABLE XXI

RESINS EVALUATED FOR PHOTOCHROMIC SYSTEMS (UNPLASTICIZED)

	Resin	Leuco Dye	Resin System Cast From	Remarks & Response to Activating Light
1.	Cellulose Acetate	PC 1016 (CI 42555) Leuco CN (triphenylmethane type)	2-Methoxyethanol	Color response decreased as last traces of solvent volatilized. No response when completely dry.
2.	Cellulose Acetate	PP 2038 Leuco OH (polymethine type)	2-Methoxyethanol	Same as above.
3.	Cellulose Acetate Butyrate	PP 2038 Leuco OH	2-Methoxyethanol	Same as above.
4.	Cellulose Acetate Butyrate	PP 1016 (CI 42555) Leuco OH	2-Methoxyethanol	Same as above.
5.	Vinyl Acetate	PP 1016 (CI 42555) Leuco OH	Methanol	Same as above.
6.	Vinyl Acetate	PP 2038 Leuco CN	Methanol	Same as above.
7.	Vinyl Acetate-Vinyl Alcohol Copolymer	PC 1021 (CI 42000) Leuco Sulphonic Acid	Alcohol-Acetone Mixture	Gave slight reversible response when completely dry.

TABLE XXI (Cont'd)

RESINS EVALUATED FOR PHOTOCHROMIC SYSTEMS (UNPLASTICIZED)

Resin	Leuco Dye	Resin System Cast From	Remarks & Response to Activating Light
8. Polyvinyl Alcohol	PP 1016 (CI 42555) Leuco CN	Water-Alcohol Mixture	No response when completely dry.
9. Polyvinyl Alcohol	PC 1021 (CI 42000) Leuco Sulphonic Acid	Water	No response when completely dry.
10. Polyvinyl Pyrrolidone	PC 1021 (CI 42000) Leuco Sulphonic Acid	Water	No response when completely dry.
11. Methylvinyl Ether-Maleic Acid Copolymer	PC 1021 (CI 42000) Leuco Sulphonic Acid	Water	No response when completely dry.

TABLE XXII

PLASTICIZED RESIN-DYE SYSTEMS
EVALUATED FOR PHOTOCHROMIC RESPONSE

Resin	Plasticizer	Resin/ Plasticizer Ratio	Leuco Dye	Remarks & Response to Activating Light
1. Cellulose Acetate	Polyethylene Glycol 600	3/1	PP 2038 Leuco OH	Gives a faint photochromic response.
2. Cellulose Acetate	Dowanol I	3/1	PP 2038	Gives a faint photochromic response.
3. Cellulose Acetate	Polyethylene Glycol 600	3/1	PP 1016 CI 42555 Leuco CN	Gives a faint photochromic response .
4. Cellulose Acetate	Dowanol I	3/1	PP 1016 CI 42555 Leuco CN	Gives a faint photochromic response.
5. Cellulose Acetate	Polyethylene Glycol 600/Butyl Stearate (5/1)	3/1	PC 1021 CI 42000 Leuco CN	Gives a good photochromic response. Back reaction slow. Film very hazy and exudes the plasticizer.
6. Cellulose Acetate	Dowanol I/Butyl Stearate (5/1)	3/1	PC 1021 CI 42000 Leuco CN	Gives a fair forward photochromic response. Back reaction slow. Film exudes plasticizer.

TABLE XXII (Cont'd)

PLASTICIZED RESIN-DYE SYSTEMS
EVALUATED FOR PHOTOCHROMIC RESPONSE

	Resin	Plasticizer	Resin/ Plasticizer Ratio	Leuco Dye	Remarks & Response to Activating Light
7.	Cellulose Acetate	Polyethylene Glycol 600/Butyl Acetoxy Stearate (5/1)	3/1	PE 1021 CI 42000 Leuco CN	Gives a good forward photochromic response. Back reaction fairly slow. Film quality fair.
8.	Cellulose Acetate Butyrate	Dowanol I/Butyl Acetoxy Stearate (5/1)	3/1	PC 1021 CI 42000 Leuco CN	Gives a medium forward photochromic response. Back reaction slow. Film quality fair.
9.	Polyvinyl Alcohol	DMSO	5/1	PC 1021 CI 42000 Leuco SO_3H	Gives a good photochromic response. Back reaction slow. Film has poor dimensional stability. The DMSO may act only as a temporary plasticizer, i.e., it may evaporate eventually.

resin approach has been the most successful to date. However, a more thorough study of unplasticized resin systems containing more varied functional groups appears to be worthwhile. This approach, if successful, would definitely lead to a more satisfactory solution to the flashblindness protection than the plasticized resin systems.

2. Heterogeneous

This type of plastic system consists of a semi-solid or rigid plastic photochromic layer or film inclosed between transparent protective covers to insure its reliability. The covers are composed of a different plastic than the film. Some of the requirements of the cover material are that it be:

a. transparent to both the visible and near ultraviolet wavelengths.

b. of good optical quality.

c. dimensionally stable throughout the required temperature range. (The material will probably have to act as a heat sink where large amounts of energy must be withstood.)

d. inert to the photochromic formulation.

e. shatterproof and scratch-resistant.

f. inexpensive and readily available.

A large number of commercially available plastics and polymer films were screened and many seemed to fit most of the requirements. Polyester films were found best suited to the requirements although there was a tendency toward haze formation in the thickness used. A compromise in film thickness must be made between haze formation and film failure. Heat from radiant energy absorption builds up in thin films and causes film failure. If the irradiance level is constant, thick films last longer than thin films as indicated by the data in Table XXIII. In addition to polyester films, cellulose acetate films were irradiated because they were readily available in a variety of thicknesses. Before testing, a black coating having a 1 percent light transmission was applied to the films. This was done to absorb the energy and possibly simulate the photochromic material to be inclosed since otherwise the films were transparent. These coated films were then irradiated using a xenon lamp (constant source) and the time to failure for different thicknesses was recorded. Further work is desirable using a high intensity flash to provide higher irradiance per unit time than that provided by the constant source.

TABLE XXIII

EFFECT OF FILM THICKNESS ON THE ENERGY LEVEL AT WHICH FILMS FAIL

Film	Film Thickness (In)	Time to Failure (Sec)	Total Energy Absorbed Prior to Failure* (Cal/cm^2)
Cellulose Acetate	0.01	1.7	3.6
	0.015	2.3	4.8
	0.020	2.7	5.7
	0.030	3.4	7.2
Polyester film	0.005	1.1	2.3
	0.0075	1.5	3.2

*This number is necessarily small since the failure took place in the form of a spot where the energy level was higher than elsewhere on the film. The irradiance on the film was 2.3 cal/cm^2/sec as measured with a copper button calorimeter. Ninety-one percent of the incident energy was absorbed by each sample. The percentage was calculated using an energy distribution of 6000°K for the source and an absorption curve of the sample.

VII. SYSTEMS EVALUATION

A. SPECTRAL ABSORPTION CHARACTERISTICS

The spectral absorption characteristics for the near ultraviolet, visible and near infrared wavelength ranges of the colored form of the photochromic materials were determined using a Beckman DK-2 Spectrophotometer. The resulting curve can be used to compare absorption maxima between systems and materials and can also be related to any modification of the molecular structure. Curves were run on the original dye solution*, and a solution of the leuco form prior to irradiation, using the solvent as a reference. Known concentrations of the dye were used so that molar absorption coefficients could be calculated for any particular wavelength or wavelength bands. Curves showing the spectral absorption characteristics of some of the dyes synthesized during this effort are shown in Appendix B. The concentration of the dyes used to obtain these curves was not necessarily the same. Accordingly, these curves as shown can be used only to interpret the spectral absorption characteristics of the systems in general terms. Also, these curves should not be used for a detailed comparison of the original and irradiated leuco dyes in the near ultraviolet because their characteristics are not necessarily the same for this wavelength range.

B. ACTIVATING WAVELENGTH

An important parameter of a photosensitive system is the wavelength(s) of light which activate the photochromic mechanism and thus cause the material to produce its colored form. It is desirable for the activating wavelength band to be wide rather than narrow so that among other considerations, more energy can be absorbed for activation.

To determine the activating wavelengths, a colorless dye solution was placed in a quartz cell 4 inches long, 3/8-inch deep and approximately 1 inch high. The cell was divided into 23 cross-sectional compartments (3/8-inch deep x 1-inch high) by glass partitions.

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*The original dye is the dye as synthesized prior to conversion to the leuco compound.

These partitions reduced diffusion and circulation of any activated liquid along the length of the cell. The filled cell was placed in a spectrometer and its 1-inch x 4-inch surface was irradiated so that narrow bands could strike each section of the cell. Irradiation was continued until substantial color was developed. Then the optical density was measured for each compartment at right angles to the irradiated surface. Thus, each compartment became a cell with 1 inch pathlength. The apparent activating range and activating wavelength peak were obtained by recording optical density vs wavelength of irradiation. The source of light for the spectrometer was a xenon arc lamp.

To evaluate the effect of the dye structure on the activating wavelength range, the colorless dye forms must be formulated as reversible systems and the back reactions retarded to facilitate detection of color changes. The dye structures vary so widely that in some cases deviations from the standard formulation were required to give a photochromic system. The activating wavelength range for several of the dyes is given in Table XXIV.

This technique was also used to investigate the solvent dependency of the activating wavelength. When determining this dependency, corrections must be made for the transmission characteristics of the solvents in the activating wavelength range and the solubility of the photochromic materials in each solvent. Since these corrections presented difficulties, an accurate means of comparing activating wavelengths in different solvents has not yet been evolved. However, there is some indication that the solvent does influence the activating wavelength and additional study is desirable.

TABLE XXIV

ACTIVATING WAVELENGTH DATA
FOR PHOTOCHROMIC DYES

Polymethine Code Number	Activating Wavelength Range (mμ)
PP 2019	300 - 400
PP 2110	300 - 375
PP 2112	325 - 375
PP 2119	320 - 367
PP 2120	285 - 360
PP 2128	295 - 375
PP 2130	260 - 350
PP 2136	275 - 350

C. ACTIVATION BY ELECTRON BOMBARDMENT

A few of the photochromic dyes were subjected to electron bombardment to determine whether they would respond in a manner similar to photon bombardment. The sample to be tested for activation by electron bombardment was placed on an anode platform in a vacuum chamber. Half of the sample was covered with a ground and polished quartz plate so that it would be subjected to the same conditions as the exposed half of the sample with the exception of the electron impingement. Comparison could thus be made between the two halves. A cold cathode Geissler tube was also set in the vacuum chamber to act as the source of electrons. The chamber was evacuated and the sample was bombarded for 10 to 20 minutes, during which time visual observations were made of any changes in the character of the sample. The sample was removed and measurements of the transmission changes were made.

Irreversible light-sensitive film containing polymethine PP 2056 showed a definite darkening under electron bombardment. A sample of polymethine PP 2038 leuco dye in Acryloid resin, while not sensitive to light, exhibited a reversible color formation. Reversible photosensitive film also exhibited transmission changes with activation by electrons.

D. ACTIVATION BY GAMMA IRRADIATION

Information pertaining to gamma irradiation effects on the photochromic systems was of interest for two reasons:

1. Gamma radiation might enhance the photochromic capability.

2. This knowledge might help in understanding the mechanism of the photochromic response.

Two identical samples of each material (one for testing and one for control) were prepared for exposure to a cobalt-60 source. The exposures (doses) consisted of 1000 to 1200 rads. This amount of radiation is well above the LD 50 level for personnel. The following polymethine systems were tested:

1. Single component PP 2038 irreversible photo-thermosensitive liquid formulation.

2. Single component PP 2056 irreversible photo-thermosensitive liquid formulation.

3. Irreversible PP 2017 in a photo-thermosensitive liquid formulation (split components).

4. Single component PP 2017 irreversible photo-thermosensitive liquid formulation.

5. PP 2056 irreversible photo-thermosensitive plastic film.

6. Photochromic (reversible) PP 2017 liquid formulation.

7. Photochromic (reversible) PP 2038 liquid formulation.

During irradiation, the samples were visually observed and compared frequently to the unexposed controls. After exposure, the transmissions of the control and exposed samples were compared. No difference between the irradiated and control samples could be detected. The samples and control were then exposed to ultraviolet light. It was concluded that gamma irradiation neither activates the photosensitive materials nor reduces their response for the dose given.

E. REACTION RESPONSE TIME

The response time is defined as the time required for a measureable photo-induced coloration to take place subsequent to the incident activating energy.

Present measurements indicate that the reaction response times are less than 40 nanoseconds (earlier reports stated: less than 50 microseconds). A portion of an oscillogram illustrating how the response time is determined is shown in Figure 6. The top trace (C) on this oscillogram represents the light which penetrated a fixed filter with an open-state transmission approximately 1 percent less than the photochromic filter. The slight rise of the trace indicates the low light output from the flash during the first 100 nanoseconds. The bottom trace (D) is the light which was transmitted by the photosensitive filter for the same time period. A reversible photosensitive liquid formulation of Crystal Violet (PC 1016; CI 42555) in a thick (5 cm) cell was used to obtain this oscillogram and was observed at 600 mμ, the major absorption wavelength of the PC 1016 dye. The sweeps were separated so they could be easily detected. To indicate where (C) and (D) separate, a line (E) was drawn on the oscillogram parallel to sweep (D), but starting from the same point as the top sweep (C). This line separates from the top sweep at a point less than 40 nanoseconds from time 0. The trace shows that the photochromic filter at this time was transmitting less light than the fixed filter and thus it took less than 40 nanoseconds to begin responding to the flash.

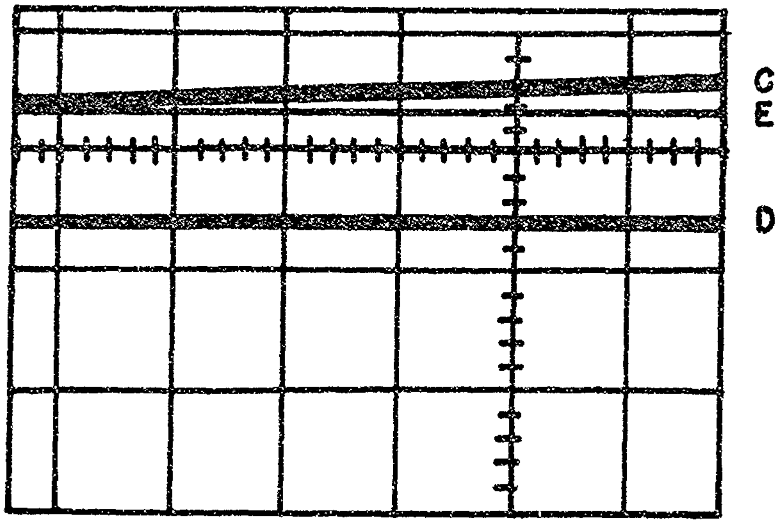


Figure 6. Drawing of Oscillogram Showing Reaction Response Speed to be Less than 40 Nanoseconds. Sweep C; Light Through Fixed Filter (Non-photochromic). Sweep D; Light Through Photochromic Filter. Line E; Drawn Parallel to D. Scale: 20 Nanoseconds per Division.

F. SYSTEM CLOSURE

1. Activation

The speed with which a photosensitive filter closes, that is, becomes less transparent when exposed to a high intensity flash source, gives a practical evaluation of its sensitivity. Since closure is energy dependent, a percent transmission versus time curve is good only for that flash condition under which it is measured. The method used for determining the percent transmission microseconds after the initiation of the flash was to record and compare on a single oscillogram the percent T vs time curves of both a photosensitive filter and a fixed filter.

The apparatus consisted of a flash tube with an appropriate power supply, trigger mechanism and shutter, and a sensing and recording device. The flash tube had a rating of 200 watt-seconds output and 200 µ sec duration. The optical train had, consecutively, a heat absorbing filter next to the flash tube, then the test cell followed by a UV absorbing filter. Approximately four (4) feet away from the UV filter was the phototube. This was placed at a distance for two reasons: (1) to prevent phototube saturation and (2) to keep the recording electronics away from the static fields caused by the flash and thereby minimize the electronic noise level. The output section of the phototube was connected to an oscilloscope and the curves or traces were recorded photographically. The light pulse of the flash tube was reproducible as measured on a given phototube.

The apparatus was operated first with a fixed filter, then with a light sensitive filter in the test cell position. The fixed filter was made from the dye being tested by irradiating an irreversible formulation of the dye to its colored form and diluting this colored solution to the desired transmission with the solvents of choice. A cell containing this solution was placed in the test cell position. Consider, for example, that the transmission of this fixed filter is 50 percent as measured with a Welch Densichron densitometer. With the filter in place, the camera shutter was opened, the flash triggered and the shutter closed. The resulting oscillogram showed the amount of light transmitted by the 50 percent T filter for any time after the flash was initiated.

The filter blank was then removed and replaced with the unexposed light-sensitive filter to be tested (transmission of about 90 percent). The flash was repeated for the photochromic filter and the oscilloscope trace was recorded over that of the fixed filter. The point of intersection between the two traces was the point where the photochromic filter was transmitting the same amount of light as the fixed filter, that is, where both filters had a transmittance of 50 percent T. By measuring the time between the ignition of the flash and this intersection of traces, the time to go from 90 percent T to 50 percent T was obtained. This was repeated for different fixed filter transmissions and for the different solutions being studied. Table XXV shows some of these measurements for an irreversible system, while Table XXVI shows the results obtained for a reversible system.

TABLE XXV

CLOSURE TIME OF IRREVERSIBLE MATERIAL
Compound: PP 2038 (Polymethine)
Activation: 200 Watt-Second Flash

Transmission (%)	Time (Microseconds)
87 (initial)	0
64	30
55	50
45	65
33	70
28	110
20	350
13	700
0.1	5×10^6

The data from Table XXV were correlated with the energy output of the flash tube used for the tests. These results are shown in Figure 7, which also shows a hypothetical energy output curve for a nuclear detonation. The energy curves show that a nuclear source has a continuously increasing energy output up to 100 microseconds whereas the flash tube reaches a maximum energy output at this time. The transmission curve for the dye shows a decrease in transmission with an increase in energy output of the flash tube. Since the energy output of a nuclear source continues to increase, this source could produce a lower transmission (faster closure) in the photochromic material than could the flash tube.

2. Energy Transmitted

Reversible photochromic solutions containing "new" additives transmit less energy and are thus better than the irreversible systems for short exposures to light. This is indicated by the data in Table XXVII.

For long exposures, irreversible systems transmit less energy than reversible systems because irreversible systems darken cumulatively and because the back reaction in the reversible systems opposes the darkening reaction.

TABLE XXVI

CLOSURE TIME OF
REVERSIBLE PROTECTIVE SYSTEMS

Compound: PP 2038 (Polymethine)
Activation: 200 Watt-Second Flash

	Time (Microseconds)	
Transmission (%)*	78% initial trans.	82% initial trans.
64	30	44
55	54	45
45	65	62
33	80	110
28	110	120
20	128	136

*Reduced from the initial transmission by flashing.

TABLE XXVII

ENERGY TRANSMITTED BY
PP 2038 SYSTEMS AT TWO
RATES OF ENERGY INPUT

	Energy Transmitted* (cal/cm^2)	
Source	Irreversible	Reversible
120 millisecond, 2400 watt-second flash	0.084	0.075 with additive "J"
200 microsecond, 200 watt-second flash	0.037	0.028 with additive "D"

*measured with a copper button calorimeter

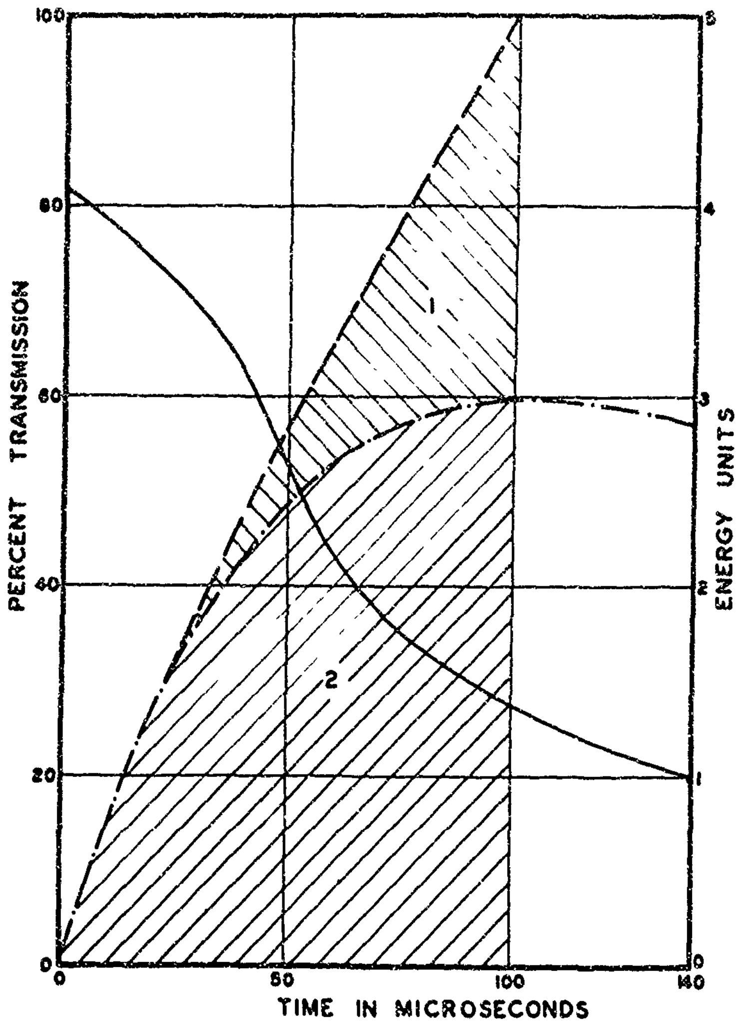


Figure 7. A Comparison of System Closure with Source Energy for PP 2038

———	Transmission versus time for PP 2038 irreversible photochromic material when activated by an XE1-3 flash tube.
— —	Supposed rate of energy input from a nuclear flash.
—·—	Rate of energy input from an XE1-3, 200 watt-second, flash tube. (Reaches peak at ~100 μ sec; this tube has a total incident energy of 0.3 cal/cm^2 for heating the glass and cell.)
Area 1	Additional energy that would be available for closing filter from nuclear flash up to 100 μ sec.
Area 2	Energy striking cell from XE1-3 flash unit up to 100 μ sec.

3. Effect of Temperature

The temperature of both reversible and irreversible photochromic filters has little or no effect upon the rate of closure of the system. This is shown by the following experiments:

An irreversible system was chilled in a freezer and activated by a flash tube while the sample was cold. The energy transmitted through the filter was measured with a copper button calorimeter. Another sample was heated and flashed. The energy transmitted was the same in both cases and equal to the energy transmitted at room temperature.

Samples of the components of the polymethine PP 2038 formulation designed for the separate-component stable system were stored for some time at -110°F. They were then brought to room temperature and mixed. The mixtures were found to be no different in response than other mixtures whose components had not been stored at this temperature.

Samples of polymethine PP 2038 in both irreversible and reversible formulations were held at -70°C for several hours and then warmed to +77°C and held for several hours. They showed the same photochromic response as other samples that had not been exposed to these temperature conditions.

Reversible photochromic systems were stored at temperatures between -70°C and +70°C for several hours and allowed to return to room temperature prior to exposure. Again there was no change in photochromic response.

Samples of a reversible system were cooled to -70°C with dry ice and acetone and exposed to a flash of light from a 2400 watt-second flash tube. The energy transmitted during "closing" was measured with a copper button calorimeter. Other samples were heated with hot water and then exposed to the flash and the transmitted energy measured. No significant differences in closure were observed. Data from some of the high and low temperature experiments are recorded in Table XXVIII.

TABLE XXVIII

RELATIVE ENERGIES TRANSMITTED
BY HOT AND COLD
IRREVERSIBLE FILTERS

Temperature (°C)	Initial Transmission (%)	Energy Transmitted (cal/cm^2)
95	38	0.042
-50	38	0.042
-50	90	0.11
90	90	0.08

4. Effect of System Thickness

In general, when the thickness of a sample is increased, the closure time is decreased. This was determined by measuring the closure at the peak absorption wavelength of photochromic materials in cells having different thicknesses. The procedure for obtaining these measurements with a flash source was discussed previously in part 1, Activation. The apparatus discussed was used with a monochromator between the cell and the phototube.

Initial experiments were with Crystal Violet (PC 1016; CI 42555) in a 1/16-inch cell. This dye has a major absorption peak near 600 millimicrons in its colored form. A heat-absorbing glass filter was used between the flash tube and the cell to prevent the flash from overheating the liquid in the cell. This filter had to be removed when polymethine PP 2038 was used because it prevented observation of the major absorption peak of the dye at 800 millimicrons. The closure curves (percent transmission vs time curves) for both PC 1016 and PP 2038 are shown in Figure 8.

In another measurement with PC 1016, a 1/4-inch thick cell was used. The time required to reduce transmission to 37 percent at 600 millimicrons was measured by the fixed-filter comparison technique described previously and compared to the 37 percent transmission point on the PC 1016 curve in Figure 8. Less than

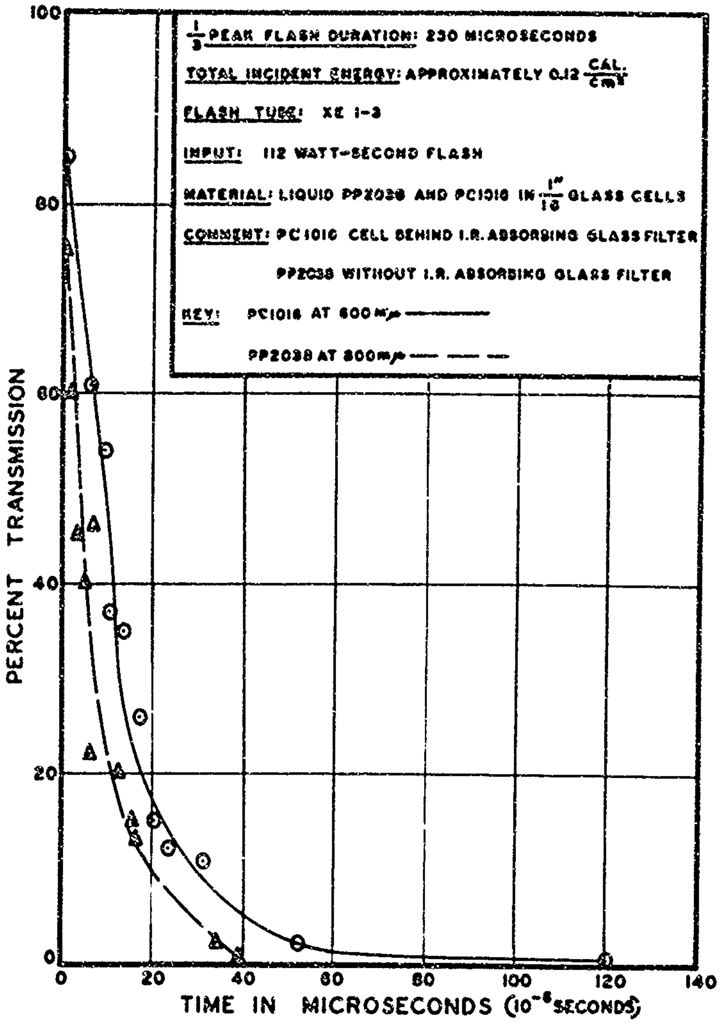


Figure 8. Closure of Reversible Crystal Violet (PC 1016; CI 42555) and Polymethine PP 2038 Systems

8 microseconds were required for the 1/4-inch cell to reach 37 percent transmission, whereas thirteen microseconds were required by the 1/16-inch cell. The same dye concentration was used in both tests.

It was then assumed that a cell of still greater thickness would show a still better response and this assumption was tested with a 5 centimeter quartz cell. It was recognized that this cell was too thick for a practical system, but it was thick enough to indicate the maximum density which could be obtained by increasing cell thickness. After the flash, color was observed in the cell to a depth of at least 2 centimeters. Figure 9 shows a curve based on five measurements using the 5 centimeter cell containing PC 1016 photosensitive material. At the fifth data point, an optical density greater than 4 was measured approximately 250 microseconds after the flash initiation. Since the flash duration was approximately 230 microseconds, light input to the filter from the flash at 250 microseconds had essentially ceased and very little additional darkening due to the flash could occur after this time. Also, after 100 microseconds the light output of the flash tube was decreasing and thus the rate of response of the photosensitive material was similarly decreasing. In some nuclear flashes, the light input to the filter may continue to increase after 100 microseconds and produce a somewhat darker filter.

The data points in Figure 9 were each obtained from oscillograms. For example, the third data point, optical density 1.69 in 21 microseconds, is the average of data from four oscillograms, one of which is shown in Figure 10. Sweep line A in this Figure is the light energy that is transmitted by a 2 percent fixed filter for the first 27 microseconds of the flash. Sweep line B is the light transmitted by the photochromic material for the first 45 microseconds of the flash. Initially, the photochromic filter (B) transmits more light than the fixed filter (A) until they both transmit the same amount of light (after about 20 microseconds). After this time, the photochromic filter transmits considerably less light than the 2 percent fixed filter. Thus, it took 20 microseconds for the photochromic filter to attain a transmission of 2 percent or an optical density of 1.69. This was repeated three times giving results of 22, 20 and 21 microseconds, an average of 21 microseconds.

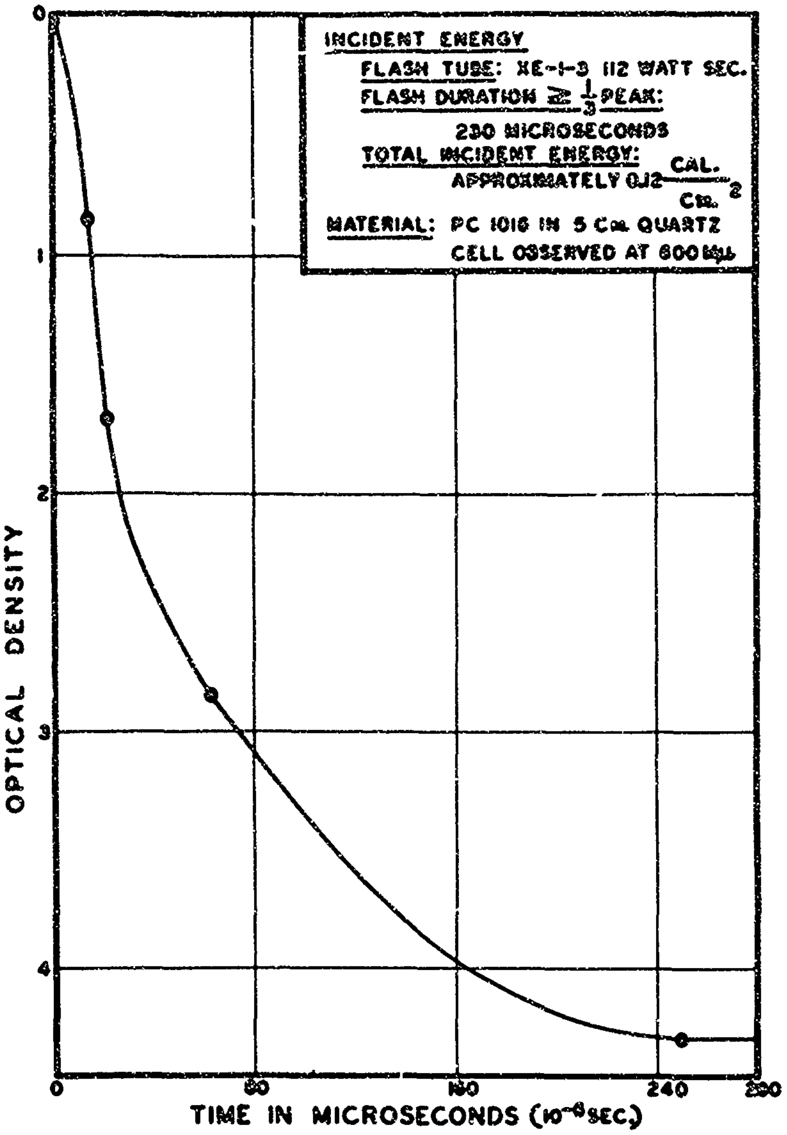


Figure 9. Closure of Crystal Violet (PC 1016; CI 42555) at its Major Absorption Peak

5. Effective Closure

a. Measured by Relative Degree of Flashblindness

The protective capability or effective closure of a directly actuated reversible system was illustrated by an approximate measure of the degree of flashblindness protection afforded. A 6 mil thick cell containing the thiazine PP 4000 (Methylene Blue; CI 52015) photochromic material and a complementary red-colored fixed filter were placed in front of a 2400 watt-second flash unit.

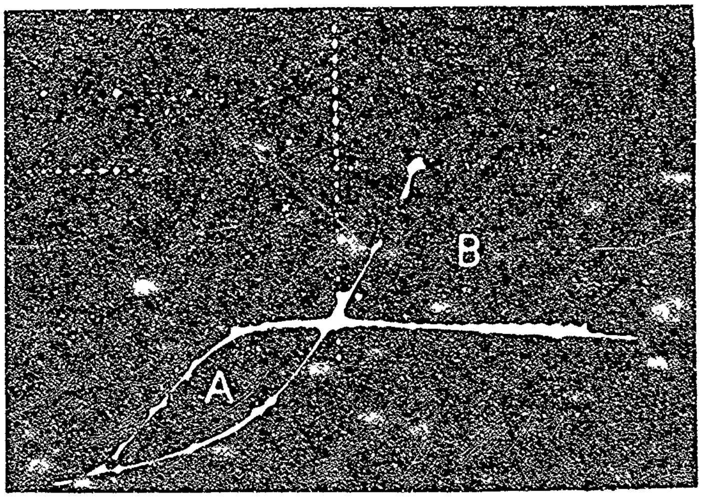


Figure 10. Oscillogram Comparing Light Transmitted by a Crystal Violet (PC 1016; CI 42555) Photochromic Filter and a 2 Percent Transmitting Fixed Filter. (Sweep Rate: 5 μ sec/cm)

Several observers approximately three feet from the flash source were requested to announce when they were able to see a number written within a visually subtended area less than that of the flash source. They made the observations and announcements with the filters both in place and removed. The results obtained from this crude experiment demonstrated a 2-6 fold improvement (decrease) in visual recovery time, as shown in Table XXIX. This experiment demonstrated that directly actuated reversible materials are capable of providing some degree of flashblindness protection.

b. Measured Photographically

When the human eye in the above experiments (Section 5) was replaced with a camera, the 2400 watt-second flash tube destroyed the effectiveness of the film even when large f-stops were used. Consequently, a neutral OD 2 filter was added between the flash and the camera to prevent over-exposure. The camera was located several inches from the flash tube. A black numeral "7" was placed over an aperture in front of the flash tube to provide an object for viewing. With the OD 2 neutral filter, the complementary red filter and the PP 4000 (Methylene Blue, CI 52015) filter in place between the flash tube and the camera, the shutter was opened, the flash was fired, and the shutter was closed. The PP 4000 photosensitive filter was then removed and the flash was repeated. The photographic results are shown in Figures 11 and 12, respectively. In Figure 12, where the PP 4000 photosensitive filter was absent, the complete field of view was washed out and nothing is distinguishable. This illustrates the flashblindness condition described in Section 5. When the PP 4000 photosensitive filter was used, even with its high initial transmission of 80 percent, the filter darkened enough during the flash duration to attenuate the light and permit the numeral 7 to be photographed clearly.

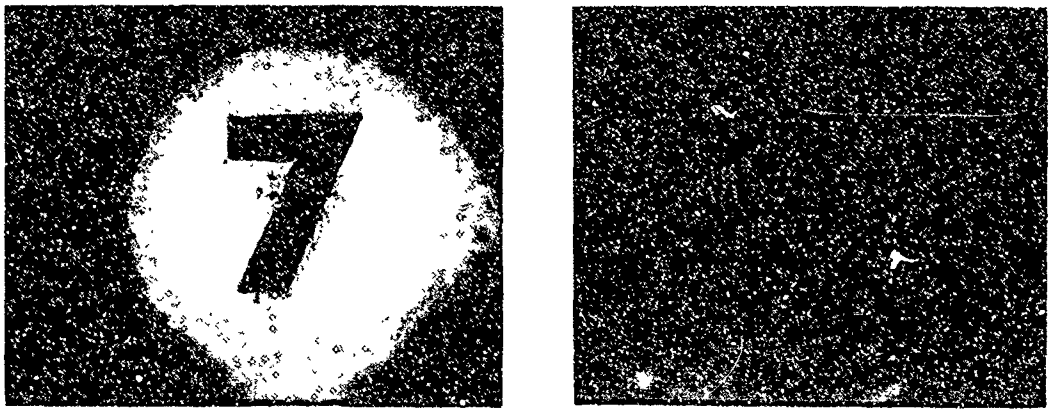


Figure 11 Figure 12

Photographs Illustrating Effective Closure of PP 4000 (Methylene Blue)

TABLE XXIX

FLASHBLINDNESS RECOVERY TEST DATA

Source and Conditions	Filters*	Recovery Time (sec)	
		Observer A	Observer B
2400 watt-second flash with Ambient Room Lighting	None	30.1	----
Ambient Room Lighting	Complementary Red and Photochromic	5.6	----
Dark Adaptation**	None	68	68
Dark Adaptation**	Complementary Red Only	----	60
Dark Adaptation**	Photochromic Only	25.5	24.5
Dark Adaptation**	Complementary Red and Photochromic	16.5	8

*The red filter is fixed; the photochromic filter contains Methylene Blue PP 4000

**Dark adaptation for these tests consisted of spending approximately 5 minutes under a black velvet photographer's hood having a slit to permit seeing the target.

c. Measured by Oscilloscope Trace

The effective closure of a photochromic material was demonstrated by recording light flashes with and without a photochromic filter. A monochromator was used to monitor the major absorption peak of the activated material in the filter. The intensity of the monochromator beam was sensed by a phototube and recorded with an oscilloscope and camera. The oscilloscope was adjusted so that the peak of the light pulse coming through a solvent blank appeared at near full-scale deflection on the oscilloscope screen. The sweep rate was set so that almost the entire flash could be traced. A trace of the light transmitted by the solvent blank was then photographed after which the blank was replaced with a photochromic solution and a flash through this solution was recorded on the same photograph. Both the solvent blank and the photochromic solution had the same initial transmission.

The photograph of the oscilloscope traces is shown in Figure 13 where trace 1 represents the light which was transmitted by the solvent and trace 2 shows the light transmitted by a PC 1016 (Crystal Violet; CI 42555) photochromic solution. The sweep rate was 50 microseconds per centimeter. This shows dramatically the light attenuation capability of the photochromic material.

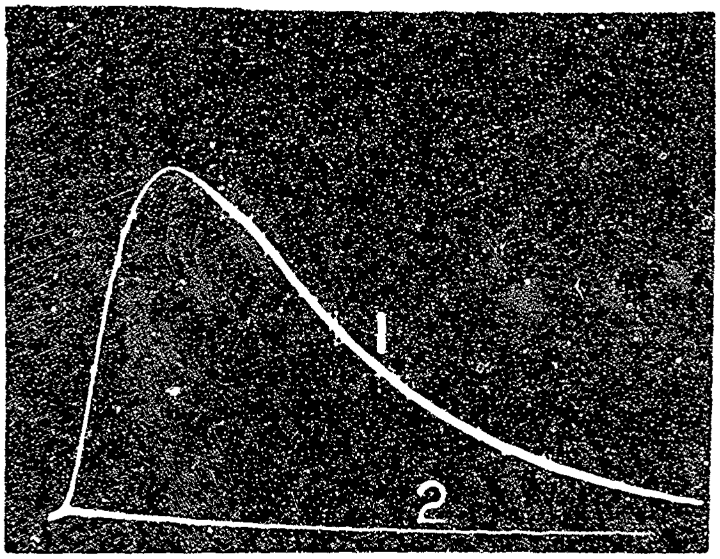


Figure 13. Attenuation of light by a photosensitive solution. (Trace 1 - Light transmitted by the solvent; Trace 2 - Light transmitted by the photochromic material and solvent; Sweep rate - 50 µsec/cm; Light source - Xenon flash.)

VIII. EYE PROTECTION DEVICE CONCEPTS

A. GENERAL

The intense luminous and thermal energy emanating from a nuclear detonation can produce permanent damage in the form of a thermal lesion on the retina when the fireball is viewed by the eye. In addition, the rapid changes in the illumination level are capable of producing a visual incapacitation, "flashblindness", which can last for many seconds but from which there is eventual recovery. These problems become particularly acute when observations through an optical fire control or other optical magnification instrument are required and when vision is required constantly for a particular task such as operating an aircraft.

Thermal lesions on the retina, caused by directly viewing a nuclear detonation, are produced by the energy being focused onto the retina by the lens of the eye. The extent of damage to the retina is determined by:

(1) The intensity of the radiant energy.

(2) The duration of exposure.

(3) The distance from the fireball.

When considering retinal burns, a basic principle must be kept in mind, that is, the retinal image of the detonation receives a constant energy per unit area (cal/cm^2) regardless of the distance of the viewer from the detonation under most circumstances of concern in this study. Only the size of the retinal image will change with distance.

Although flashblindness is a temporary effect, it also varies considerably in both severity and duration depending upon the conditions of exposure. The degree of flashblindness which can be caused is dependent upon at least three factors:

(1) The level of light adaptation of the eye.

(2) The intensity and brightness of the light source.

(3) The duration of the irradiation by the source.

It is highly desirable to have a simple and reliable device which can protect the eye when protection is needed and yet not impair normal vision. The device also should not be triggerable by non-harmful flash sources. One way to provide the protection desired is to use a self-attenuating light filter, i.e., one which becomes opaque to a degree dependent upon the level of illumination. Such a device should also provide rapid return to the normal clear condition as the damaging light radiation subsides. This type of filter is possible with the use of certain photochromic materials and systems. By definition, photochromism is the photochemical phenomenon of changing the color of a substance by exposure to electromagnetic radiation (usually UV or visible light) and, after removal of the activating source, returning the substance to its original state. Systems of this type can be activated directly or indirectly.

B. INDIRECTLY ACTUATED SYSTEMS

The photosensitive material in an indirectly actuated system is activated by a secondary light source which is triggered by detecting an increase in illumination caused by a detonation. The indirectly actuated system has the unique advantage that, regardless of distance or direction from the detonation, as long as the detonation can be detected, a protective response will be obtained.

The major disadvantages are:

(1) that there is a finite delay time required for detection and activation, and

(2) that light sources other than those coming from a nuclear flash can activate an indirect system.

Although the finite time required for operation may be 50-100 microseconds, no protection is being afforded during this time. This problem becomes particularly acute when the system must be used in close proximity to the detonation. Sufficient amounts of energy to cause eye damage can be transmitted by the filter during the detection period. For the modern low yield nuclear weapons, the entire first pulse could be transmitted within the first 100 microseconds. If protection against this first pulse is desired, closure must take place much faster than 100 microseconds.

C. DIRECTLY ACTUATED SYSTEMS

The photosensitive material in a directly actuated system is triggered directly by incident electromagnetic radiation to obtain a protective response. Thus, there is no time lost in the closure of the system as there is in an indirectly actuated system. Directly actuated systems can be utilized in two types of eye protection devices:

(1) Direct-line-of-sight and

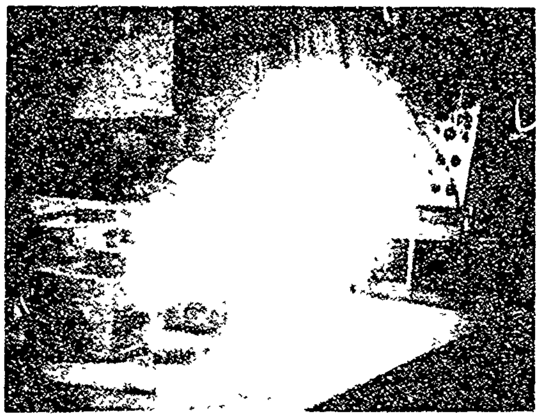
(2) Focal plane

A direct-line-of-sight device can be visualized simply as a protective filter in the form of a sheet of plastic or glass placed in front of the eyes while viewing the detonation. This system is simple and lightweight. A major limitation is the distance factor. When placed in the direct line of vision, a photochromic or photosensitive filter produces a darkening which is in proportion to the amount of activating energy received per unit area. This level of energy is inversely proportional to the square of the distance from the source. Because of the characteristics of the human eye, the energy received per unit area at the retina remains the same regardless of the distance from the source (as long as the viewer is far enough distant so that the image resembles a point source). Accordingly, there may be some distance at which the eye can focus sufficient energy to cause damage in the form of a retinal burn while insufficient energy is available to close the filter adequately. By the same token, there is a range where sufficient activating energy is available to provide protective response. This range varies with the sensitivity of the system used.

A way to overcome the distance limitation while utilizing the advantage of a directly actuated system, may be the focal plane concept where a photochromic or irreversible material is placed at the focal plane of an optical system. The optics would focus the fireball image on a photosensitive filter. The response of such a device would not be distance dependent; rather, it would function in proportion to the intensity of the image. Therefore, the greater the source intensity, the greater the protective response. The major limitation of such a system is that the optical train must utilize a real focal plane rather than an imaginary focal plane.

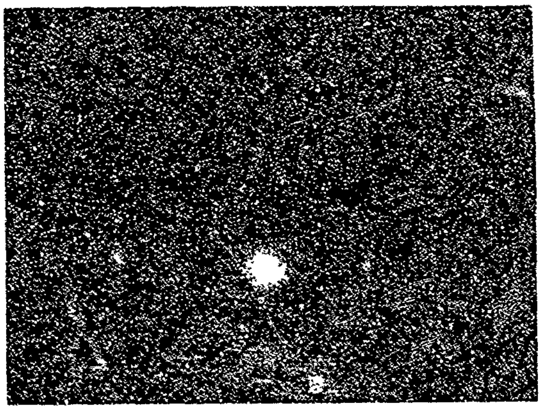
The focal plane concept offers a unique advantage because only that portion of the field of view encompassing the image of an intense illumination source is attenuated. The remaining visual field remains normal. This is illustrated by the three photographs in Figure 14. Accordingly, it is recommended that directly actuated focal plane filters be studied for use in optical fire control and other optical magnification instruments.

PHOTOGRAPH 1*



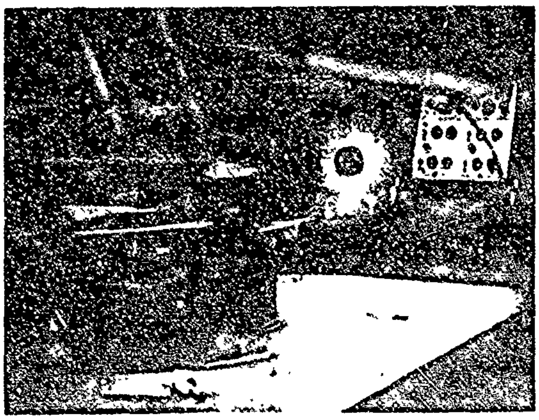
View of a Sylvania Sun Gun (upper right) and Mercury Arc Lamp (lower left) through a 1X Focal Plane Demonstrator with no protective filter. Notice the overexposure in the image area of the two light sources.

PHOTOGRAPH 2*



View of Sylvania Sun Gun (upper left) and Mercury Arc Lamp (lower right) through a 1X Focal Plane Demonstrator with a 1.2 neutral optical density fixed filter at the focal plane. Notice that there is sufficient light present from the two light sources to cause overexposure.

PHOTOGRAPH 3*



View of Sylvania Sun Gun (upper right) and Mercury Arc Lamp (lower left) through a 1X Focal Plane Demonstrator with a preactivated Polacoat Photosensitive Ophthalmic Protective Filter placed at the focal plane. Notice the self-attenuating filter completely "blacked out" the Mercury Arc Light Source while attenuating the sun gun image to the extent of rendering the filaments visible. Also, note the increased visibility in the surroundings.

Figure 14. Photographs Illustrating the Focal Plane Concept. (*All exposures at $f16$, 1/2 sec)

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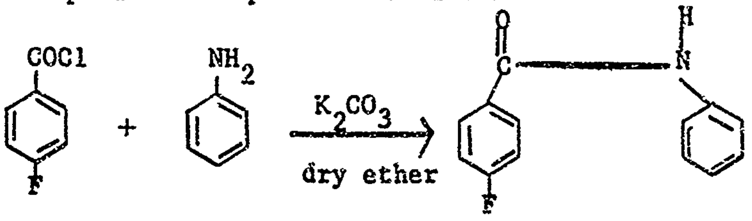
APPENDIX A

ORGANIC SYNTHESIS PROCEDURES

APPENDIX A

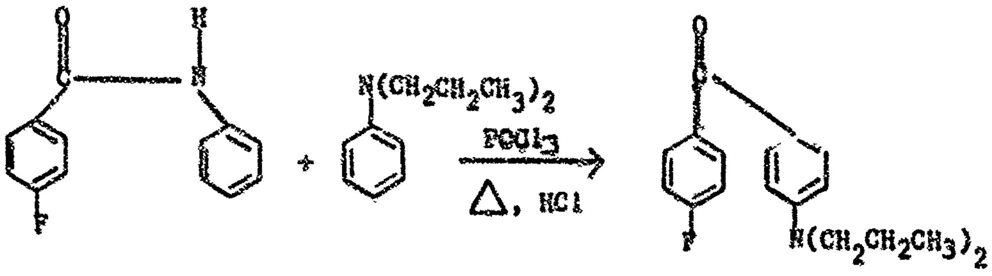
ORGANIC SYNTHESIS PROCEDURES

Method No. 1: Polymethine dyes
Example: Preparation of dye PP 2109
Step A: Preparation of p-Fluorobenzanilide



A solution of aniline, 23.7 g (0.255 mole) in 250 ml of dry ether containing 55.3 g of potassium carbonate was heated to reflux temperature. To the refluxing mixture, 50 g (0.32 mole) of p-fluorobenzoyl chloride was added over a period of one hour. The reaction mixture was refluxed for four hours and the ether distilled off. Cold water was added to the residue and the p-fluorobenzanilide collected by filtration. Yield: 64 g, melting point 196°C, white crystalline powder.

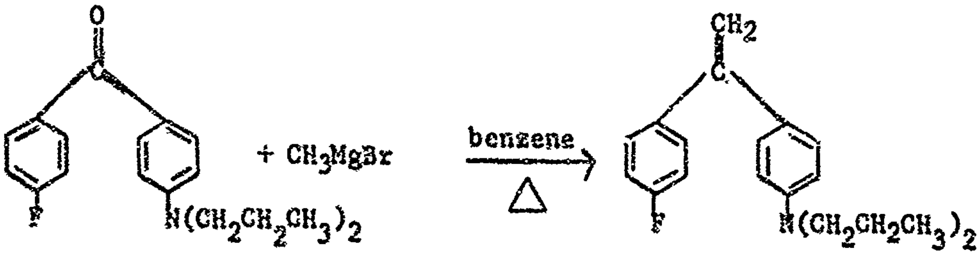
Step B: Preparation of p-N,N-Di-n-propylamino-p-fluorobenzophenone



64 g (0.3 mole) of dry, powdered p-fluorobenzanilide, 100 g (0.6 mole) of N,N-di-n-propylaniline, and 55 ml of phosphorous oxychloride were

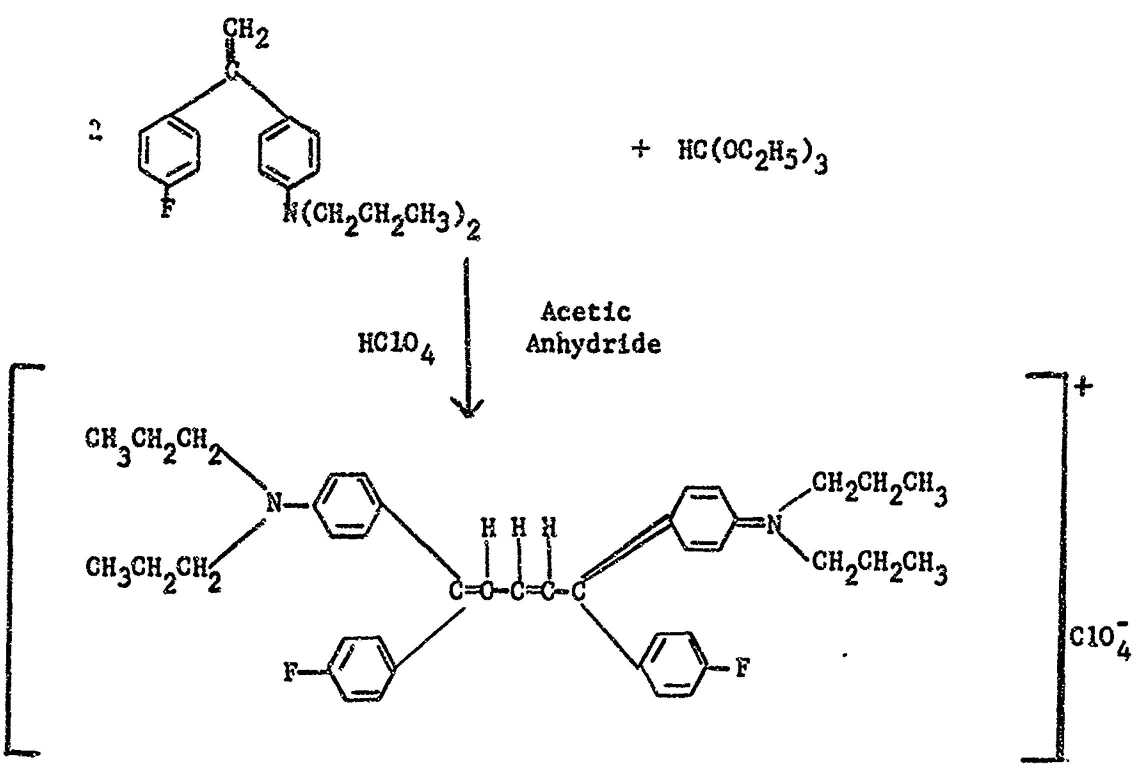
mixed in a 500 ml three-necked flask fitted with a stopper, a thermometer and a reflux condenser having a $CaCl_2$ drying tube on top. The reaction mixture was warmed gently until the temperature reached 110°-112°C, at which point an exothermic reaction occurred and the temperature rose to 160°C. As soon as the exothermic reaction was noted, the mixture was immediately cooled by swirling the flask in ice water. The cooling was continued until the temperature dropped to 100°-105°C. This temperature range was held for three hours. The reaction mixture was then hydrolyzed in a three liter beaker by the addition of 58 ml concentrated hydrochloric acid in 445 ml water. The reaction mixture was allowed to stand for eight to twelve hours to complete the hydrolysis. An additional 4100 ml of water was then added to precipitate the ketone formed. This was filtered, washed thoroughly with cold water, reslurried and refiltered. Yield: 45 g, light green sandy crystals, melting point 85°-87°C.

Step C: Preparation of 1-(4-N,N-Di-n-propylaminophenyl)-1-(4-fluorophenyl) ethylene



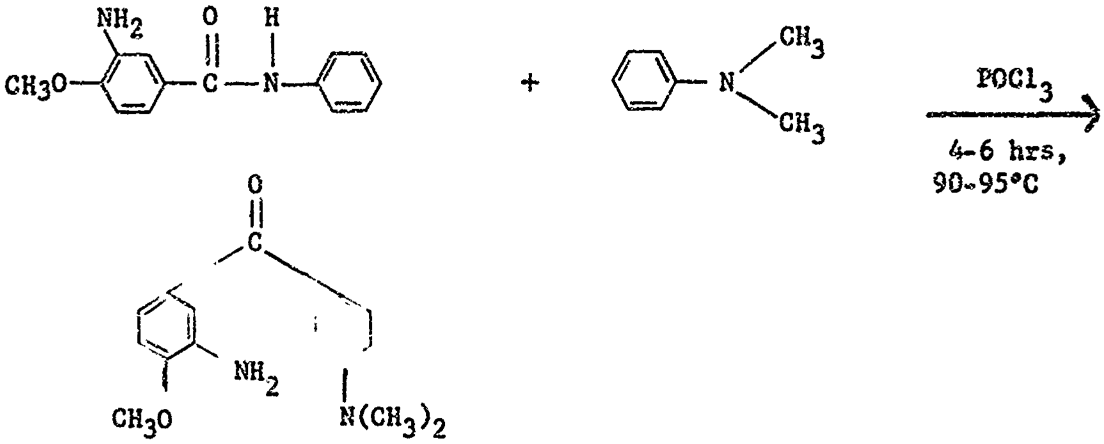
Sixty ml of a 3 molar etherial solution of methyl magnesium bromide was evaporated almost to dryness under reduced pressure in a 500 ml three-necked flask equipped with thermometer and nitrogen sparger. The grey moist residue was suspended in 75 ml of dry benzene. The flask was then equipped for refluxing by the addition of a condenser fitted with a $CaCl_2$ drying tube and an addition funnel. A 0.1 mole portion of the ketone dissolved in 250 ml of boiling benzene was then placed in the addition funnel and added dropwise to the warmed methyl magnesium bromide-benzene slurry over a half-hour period. The resulting reddish solution was refluxed for three hours. The termination of the reaction was indicated by the fading of the initial reddish color to a pale yellow. The reaction mixture was then cooled to room temperature and cautiously treated with 45 ml of saturated ammonium chloride solution. This mixture was filtered and the filtrate boiled with 0.1 g of p-toluenesulphonic acid until the evolution of water was completed. The acid contained in the reaction mixture was then removed by the addition of 0.5 g of sodium bicarbonate. The volume was reduced to one half by evaporation under reduced pressure. Five hundred ml of dry ethanol was added to the remaining solution, which was then allowed to cool with the subsequent precipitation of the ethylene compound. The precipitate was filtered, washed with 50 ml of ice cold ethanol, and the crystals dried in a vacuum oven. Yield: 86 percent of theory; melting point 101°-102°C.

Step D: Preparation of dye PP 2109 (a perchlorate of 1,5-di-(p-fluorophenyl)-1,5-bis-(p-N,N-di-n-propylanilino)-1,3-pentadiene



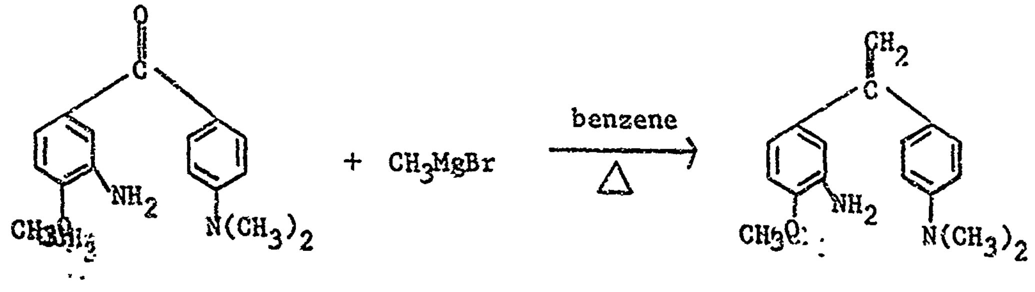
A mixture of 23.6 g (0.08 mole) of 1(4-N,N-di-n-propylaminophenyl)-1-(4-fluorophenyl)ethylene, 12 ml of ethyl orthoformate and 50 ml of acetic anhydride was treated with an ice-cold solution of 4 ml of 72 percent perchloric acid dissolved in 50 ml of acetic anhydride. The resulting dark red solution was heated in a water bath at 85°C for one hour, after which another 12 ml of ethyl orthoformate was added. The mixture was then allowed to stand at room temperature for 18 hours to precipitate the condensation product. The precipitate was collected and washed with acetic acid, ethanol and ether. Yield: 68 percent based on perchloric acid, golden brown crystals melting with decomposition at 277°C.

Method No. 2: Polymethine dyes
Example: Preparation of dye PP 2110
Step A: Preparation of 3-Amino-4-methoxy-4'-N,N-Dimethylaminobenzophenone



Fifty grams (0.2 mole) of 3-amino-4-methoxybenzanilide, 70 g (0.58 mole) N,N-dimethylaniline and 36 g $POCl_3$ were heated on a water bath at 90°C to 95°C for 4 to 6 hours. The product was then cautiously poured into a solution of 25 ml of concentrated hydrochloric acid in 250 ml water. The resulting solution was warmed at 80°C until the initial reddish color disappeared, indicating that the aniline was completely hydrolyzed. A liter of water was added to precipitate the ketone, which was filtered, washed with cold water, and recrystallized from a 2:1 aqueous alcohol solution. Yield: 38 g of slightly yellowish crystals, melting point 82°C.

Step B: Preparation of 1(4-N,N-Dimethylaminophenyl)-1-(3-amino-4-methoxyphenyl)ethylene



Fifty ml of a 3 M ethereal solution of methyl magnesium bromide was evaporated almost to dryness under reduced pressure. Dry nitrogen was admitted to the reaction flask and the gray residue was suspended in 75 ml of dry benzene. The slurry was warmed, then 26.6 g (0.1 mole) of the ketone compound dissolved in 250 ml boiling benzene was added over a 15-minute period. The resulting solution was refluxed until the pale yellow color faded to colorless (45 minutes). The mixture was cooled and treated with 50 ml of a saturated NH_4Cl solution. The colorless solution was filtered through a folded filter paper without applying vacuum and in the absence of strong light. The filtrate was boiled with 0.1 g p-toluenesulfonic acid until the evolution of water was complete. The cooled solution was neutralized by the addition of 0.2 g dry $NaHCO_3$ and then reduced to 1/4 volume by evaporating the solvent under reduced pressure. The remaining solution was diluted with 250 ml of dry ethanol and the ethylene product allowed to precipitate over 12 hours. Yield: 34 percent of theory, yellow hygroscopic flakes, melting point 118°C.

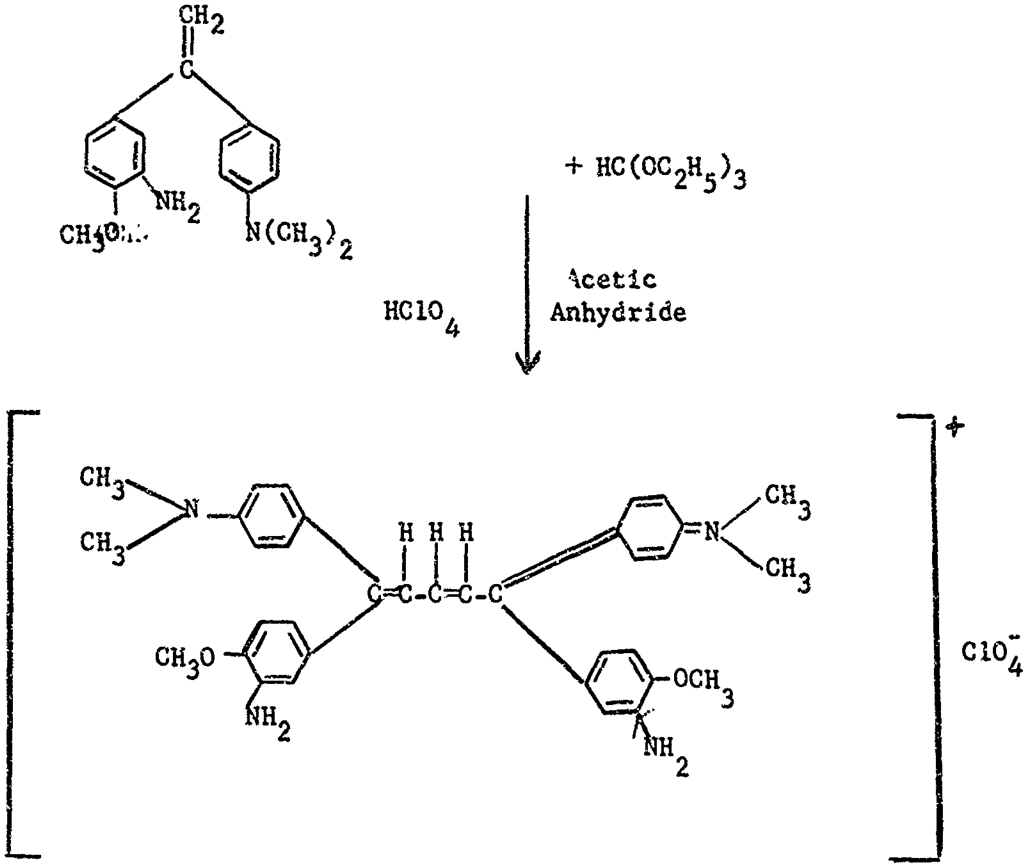
Step C: Condensation Reaction Leading to Dye (A perchlorate of 1,5-di-(3-amino-4-methoxyphenyl)-1,5-bis-(p-N,N-dimethylanilino)-1,3-pentadiene

A mixture of 26.9 g (0.1 mole) of 1(4-N,N-dimethylaminophenyl)-1-(3-amino-4-methoxyphenyl)ethylene, 15 ml of ethyl orthoformate and 45 ml acetic anhydride was treated with a solution of 4 ml of

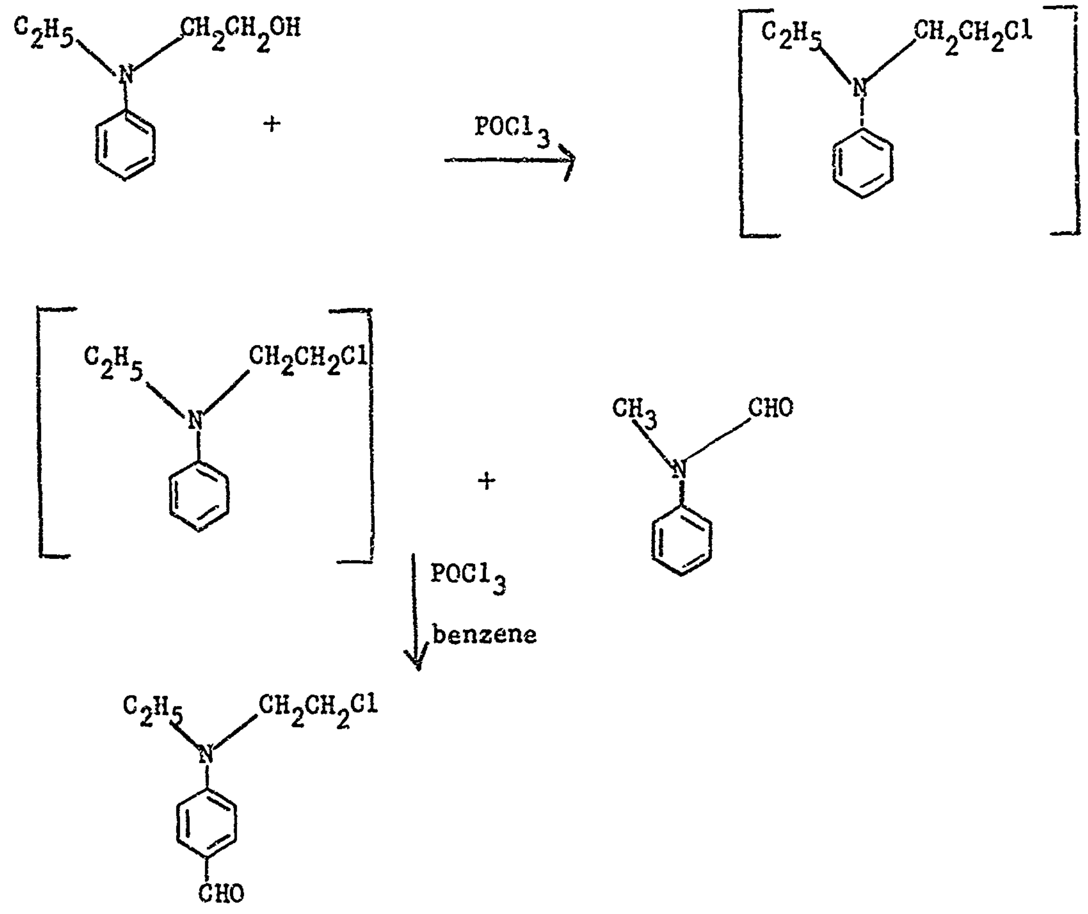
72 percent perchloric acid and 40 ml acetic acid previously cooled to 0°C. The resulting mixture was allowed to stand at room temperature for 5 days, after which it was treated with 25 ml of ether and kept an additional day at room temperature. The precipitate formed was filtered and washed with acetic acid, ethanol, and ether, and dried in a vacuum desiccator.

Product: sandy crystals, dark brown, melting point 209°-210°C

Note: The reaction should be run at room temperature. Condensation at elevated temperatures yields a black, insoluble polymerization product.



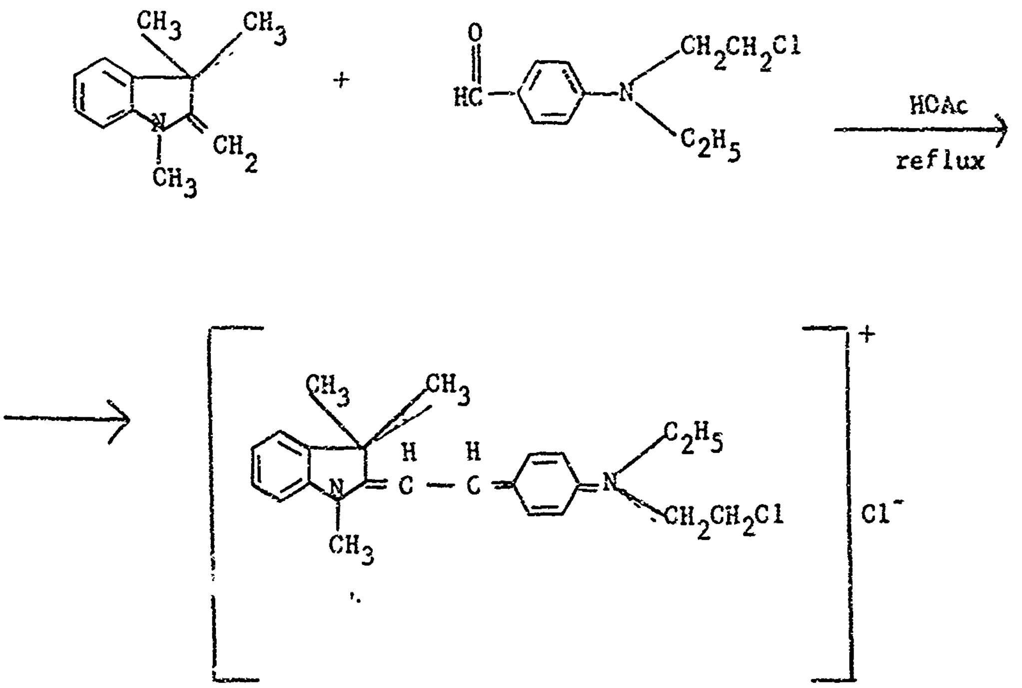
Method No. 3: Indoline base dyes
Example: Preparation of dye PP 2120
Step A: Synthesis of p-[N-(2-chloroethyl)-N-ethyl]aminobenzaldehyde



At 50°C, 82.5 parts by weight of N-(2-hydroxyethyl)-N-ethylaniline were added dropwise to 90 parts by weight of phosphorous oxychloride. The solution was then heated at 90°C for 6 hours. After cooling to 0°C, a mixture of 150 parts by weight of N-methylformanilide, 170 parts by weight of phosphorus oxychloride, and 120 parts by weight of benzene, was added to the above solution. The mixture was heated for a few hours at 30-35°C. After neutralization with an aqueous solution of sodium hydroxide, the benzene solution of the aldehyde product was separated. After evaporating the benzene, p-N-chloroethyl-N-ethylamino benzaldhyde remained as a slightly yellow oil which

[illegible]
The recrystallized [illegible]
melting point of 28[illegible]°C.

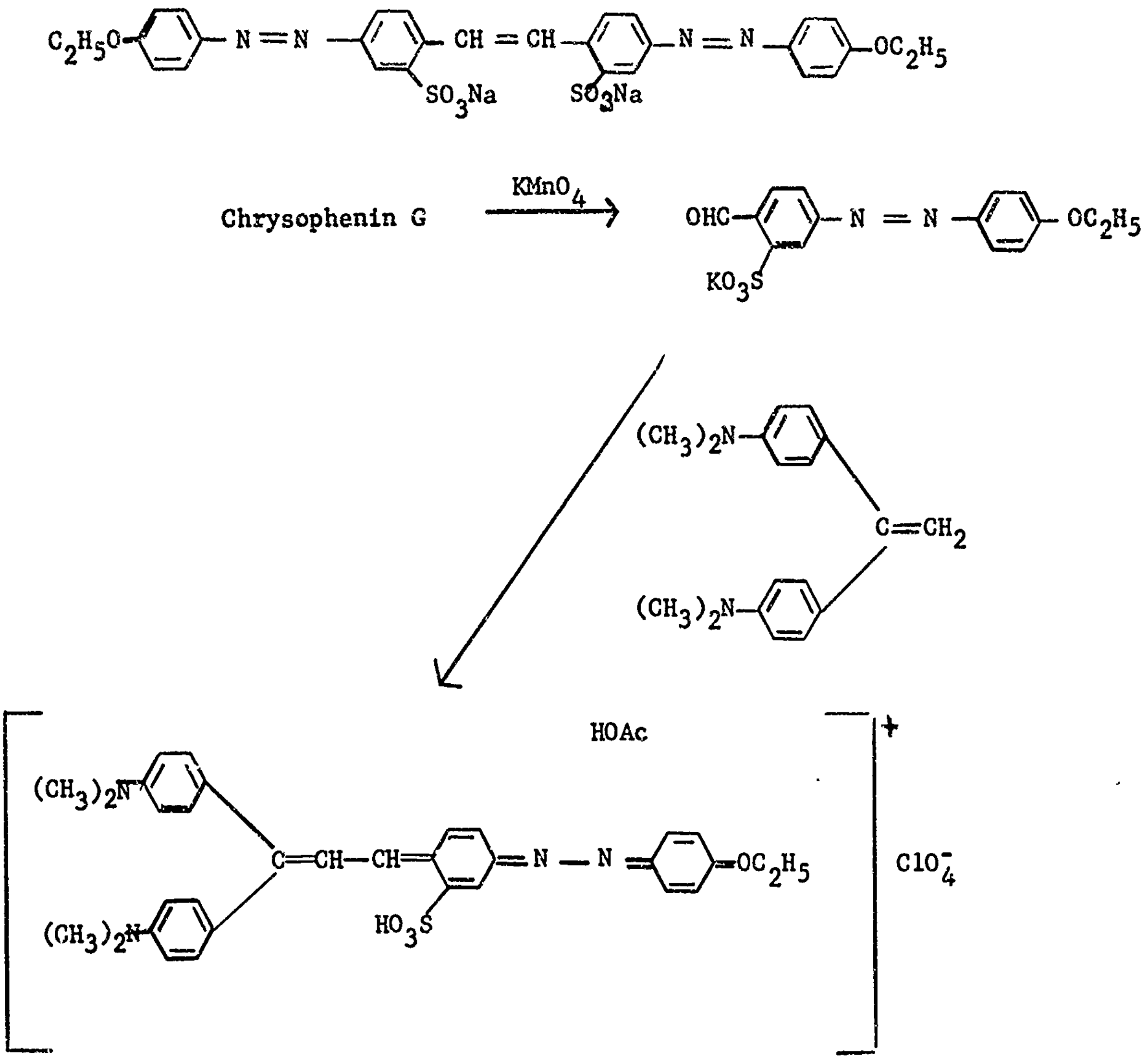
Step B: Synthesis of dye PP 2120, Chloride of [illegible]
[p-(N-2-chloroethyl-N-ethyl)amino-β-styryl]indoline.



p-(N-Chloroethyl-N-ethyl)amino benzaldehyde (12.5 parts by weight) was refluxed for 6 hours at 100°C with 8.5 parts by weight of 1,3,3-trimethyl-2-methylene-indoline in 60 parts by weight of glacial acetic acid. The mixture was then poured into water and the condensation product was salted out with sodium chloride. The crude dyestuff was obtained as a dark bronze resinous liquid which hardened upon standing and could be crushed into shiny bronze particles. The pure dye was obtained by recrystallization from hot water, m.p. 167-168°C.

Method No. 4: Dyes with more than one chromophore
Example: Preparation of dye PP 2131
Step A: Synthesis of phenetolazobenzaldehydesulphonic acid

One hundred grams of Chrysophenin G concentrate, which was equivalent to about 92 grams of the pure compound, was dissolved in 6 liters of boiling water. The solution was cooled to 0-5°C by the addition of ice and then saturated with sodium chloride.



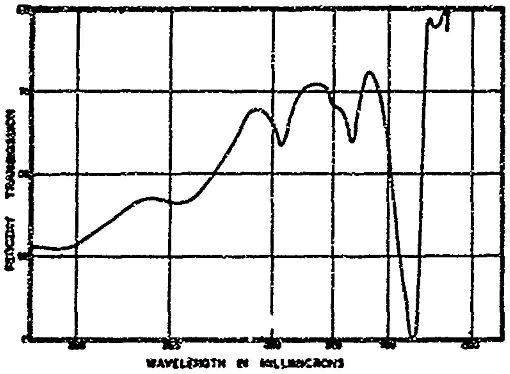
A 3 percent solution of potassium permanganate was slowly added with vigorous agitation until a pale pink color persisted. (The quantity of permanganate required was 29 grams.) The precipitate which formed during the reaction was allowed to settle and was collected by siphoning off the supernatant liquor. The product was isolated by boiling the precipitate two or three times with one liter of water, filtering off the manganese dioxide and adding potassium chloride to the hot water solution until precipitation was complete. An additional small quantity of aldehyde was isolated by salting it out of the supernatant liquor with potassium chloride. The product precipitated from water in orange-colored microscopic needles.

Step B: Synthesis of Dye PP 2131, perchlorate of 1,1-bis-(p-N,N-dimethylamino)phenyl-3-[2-sulfonato-4-(p-ethoxyphenylazo)]phenyl propene.

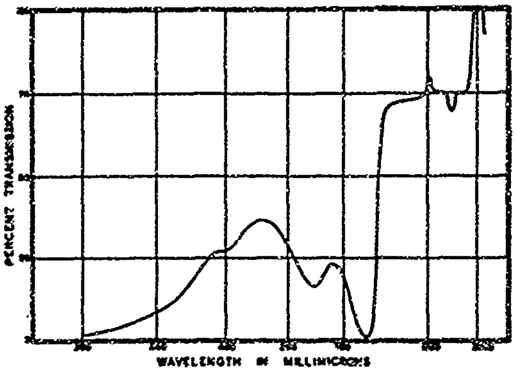
Phenetoleazobenzaldehyde sulphonic acid (1.86 parts by weight) was refluxed for 6 hours at 100°C with 1.33 parts by weight of 1,1-bis-(4-N,N-dimethylamino)phenyl ethylene in 25 parts by weight of glacial acetic acid. The condensation product was then poured into water and salted out. The dyestuff was obtained as a thick dark green liquid which hardened upon standing to a crushable solid, melting point 78-92°C. An attempt to recrystallize the dye using a variety of solvents was unsuccessful.

APPENDIX B

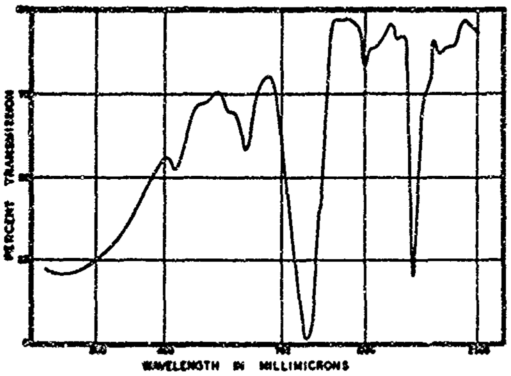
SPECTRAL ABSORPTION CHARACTERISTICS OF SYNTHESIZED DYES



PP-2109



PP-2110



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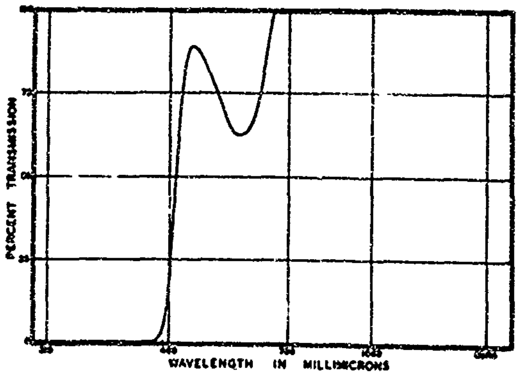

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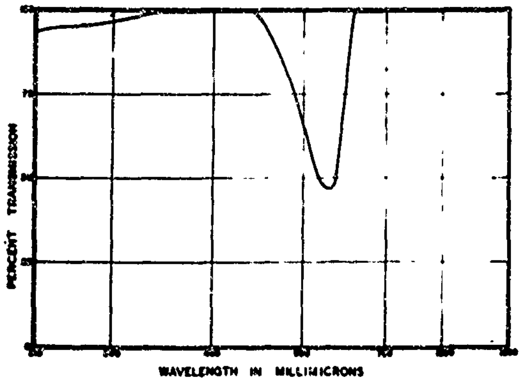

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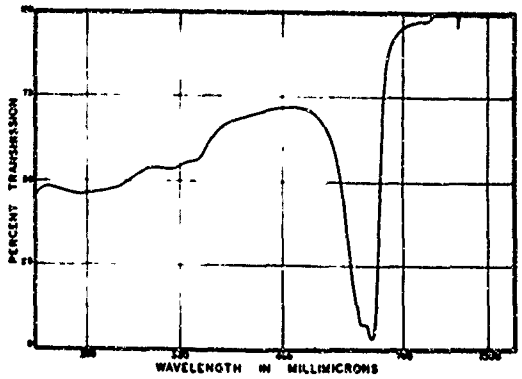

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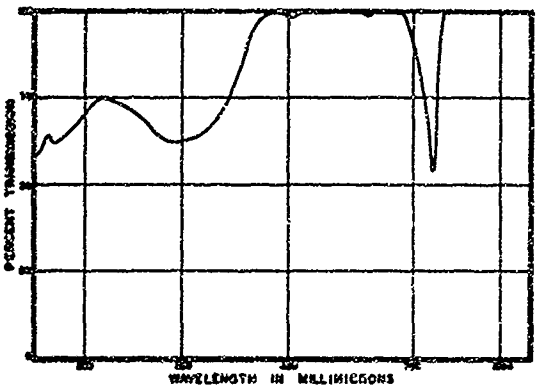

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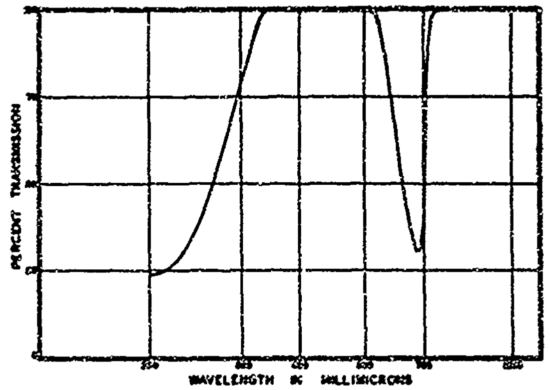

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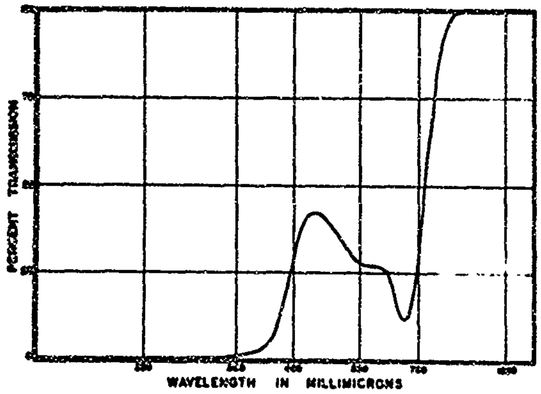
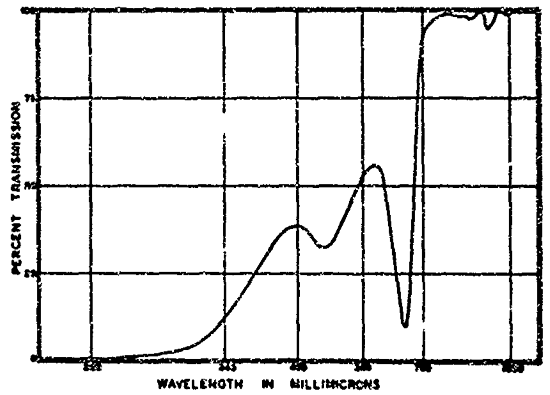


PP-2131



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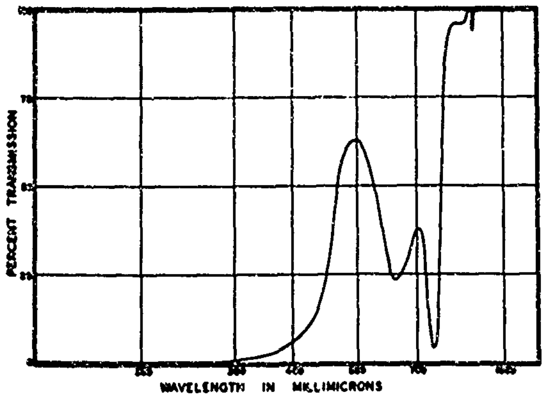

PP-2136

APPENDIX C

INDEX TO STRUCTURAL FORMULAS

APPENDIX C

INDEX TO STRUCTURAL FORMULAS

POLACOAT CODE NUMBER*	STRUCTURE PAGE	TABLE NO.
PC 1011R	39	V
PC 1016	39	V
PC 1016	57	X
PC 1021	57	X
PC 1023	--	See PC 1023R
PC 1023R	40	V
PC 1023R	57	X
PC 1024	--	See PC 1024R
PC 1024R	40	V
PC 1090	41	V
PC 1090	58	X
PC 1091	41	V
PC 1092	42	V
PC 1093	42	V
PC 1094	43	V
PC 1095	43	V
PC 1104	44	V
PC 1106	44	V

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*PC = Polacoat Commercial (purchased)

APPENDIX C (cont'd)

INDEX TO STRUCTURAL FORMULAS

POLACOAT CODE NUMBER*		STRUCTURE PAGE	TABLE NO.
PC 1113	------------------------------	45	V
PC 1115	------------------------------	45	V
PC 1117	------------------------------	46	V
PC 1118	------------------------------	57	X
PC 4000	------------------------------	60	XI
PC 4000	------------------------------	67	XIII
PC 4001	------------------------------	61	XI
PC 4002	------------------------------	61	XI
PC 4002	------------------------------	67	XIII
PC 4003	------------------------------	67	XIII
PC 4004	------------------------------	67	XIII
PC 4005	------------------------------	67	XIII
PC 5000	------------------------------	66	none
PC 6000	------------------------------	68	none
PC 6001	------------------------------	68	none
PC 6002	------------------------------	69	none
PC 6003	------------------------------	69	none
PC 7000	------------------------------	70	none
PP 1016	------------------------------	--	See PC 1016

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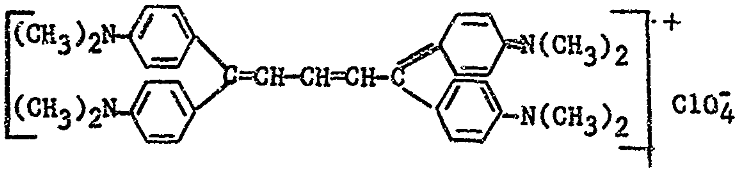
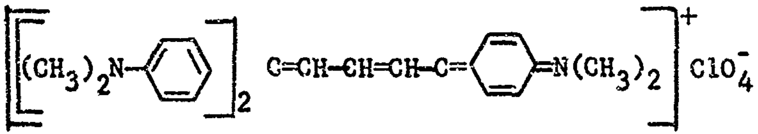
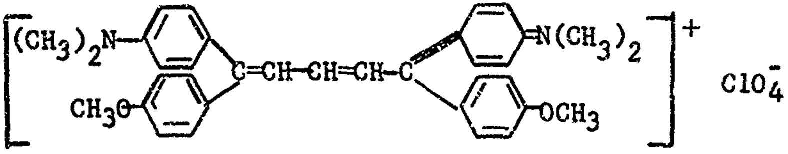
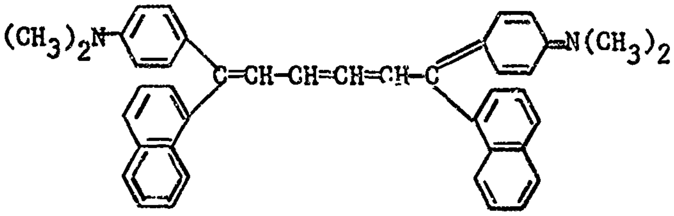
*PP = Polacoat Prepared (synthesized)

APPENDIX C (cont'd)

INDEX TO STRUCTURAL FORMULAS

POLACOAT		STRUCTURE	
CODE NUMBER		PAGE	TABLE NO.
PP 1085		26	II
PP 1086		26	II
PP 1115		26	II
PP 1116		27	II
PP 2017			
PP 2019			
PP 2038			
PP 2056			
PP 2109		Appendix A, p. 120	none
PP 2109C		29	III
PP 2110		29	III

APPENDIX C (cont'd)

INDEX TO STRUCTURAL FORMULAS

POLACOAT	STRUCTURE	
CODE NUMBER	PAGE	TABLE NO.
PP 2112	30	III
PP 2113	27	II
PP 2114	28	II
PP 2115	28	II
PP 2119	30	III
PP 2120	30	III
PP 2121	31	III
PP 2128	31	III
PP 2130	31	III
PP 2131	32	III
PP 2133	28	II
PP 2134	32	III
PP 2136	32	III
PP 4000	--	See PC 4000

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Security Classification

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4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
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13. ABSTRACT

The initial phases of a research effort to develop an ophthalmic protective device for use against flashblindness resulting from nuclear detonations are outlined. Efforts to develop a sensitive and relatively transparent photothermosensitive material, which can be prepared as a thin film and can become a filter having high optical density upon exposure to intense electromagnetic radiation, are described.

Several materials were prepared which possessed satisfactory spectral absorption characteristics and were suitable for application to nuclear flashblindness protection. Their absorption peaks were broad, located in the visible, and were relatively close to the peak of the eye sensitivity curve. The synthesized compounds were members of the triphenylmethane, azo, and polymethine dye classes. The formulation of these materials as photochromic thin film filters produced systems which became colored in less than 40 nanoseconds and reached an optical density of 3.8 in 100 microseconds, measured at the wavelength of the absorption maxima. The films prepared had an initial transmittance of 70-80%.

A variety of plastic substrates for both photo- and thermosensitive systems were evaluated. The more suitable substrates, polyester films, were studied in greater detail.

It was established that temperatures from -50° to +95° had no appreciable

(cont'd)

Unclassified
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Protection	8		4		4	
Flashblindness	9		4		4	
Photochromism	10		8		10	
Films	10		9		9	
Plastics	10					
Density					8	
Optical					0	

Unclassified
Security Classification

13. Abstract (cont'd)

effect on the functionality of the photothermosensitive materials as measured by the radiant energy transmitted during activation.

The problem of storage stability at -65°F to +125°F for periods of at least 6 months for the photothermosensitive materials was not solved. However, the problem may be circumvented if necessary. The feasibility of a two-component system which combines the two components and activates the system just prior to use was established.

Considerable effort was expended in an attempt to obtain an understanding of the basic mechanisms involved in the photo-process for a variety of systems. Electron donor-acceptor concepts appear to fit the theory and the experimental facts.