



WADC TECHNICAL REPORT 59-81

**FEASIBILITY STUDY AND DESIGN OF
A SELF-ATTENUATING LIGHT VALVE**

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FOREWORD

This report was prepared by John F. Dreyer, Head of Research, Polacoat Incorporated, Blue Ash, Ohio, under Contract No. AF 33(616)-5469, Project No. 7165, "Health Hazards of Materials and Radiation," Task No. 71839, "Protection against Electromagnetic Radiations." Captain Jerome A. Hirsch, USAF (MSC), of the Vision Section, Physiology Branch, Aerospace Medical Laboratory, Wright Air Development Center, served as contract monitor.

The following associates of Polacoat Incorporated have cooperated in the research and in the preparation of this report: Dr. Glenn H. Brown, Bibliographer; Donald Baltzer, Head of Laboratory; Frank Stevens, Senior Research Chemist; and Jerry Watkins, Laboratory Technician.

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This report was prepared in conjunction with WADC TR 59-436, Phototropy, A Literature Review.

Investigation of the phototropic phenomenon to determine the feasibility of phototropic material as a protective, self-attenuating light valve against the energy yields of high-intensity light sources has been accomplished. Although it has been found that the practical utilization of phototropic material as a protective eye device against an atomic flash is marginal, its use as a sunglass appears to be feasible.

PUBLICATION REVIEW

This report has been reviewed .

FOR THE COMMANDER:



ANDRES I. KARSTENS
Colonel, USAF (MC)
Ass't. Chief, Aerospace Medical Laboratory

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INTRODUCTION

An investigation of phototropic phenomenon literature reveals that the use of phototropic material as a self-attenuating, varying density light valve has not been considered.

The phototropic phenomenon, known since 1881, is defined as that in which a material not only changes color when exposed to light (the change depending on wavelength and amount of light) but also reverts to its original color following removal of the light. Since the advent of the concept of the phototropic phenomenon, the following terms have been introduced: photochromism, thermochromism, metachromism, and tenebrescence. Photochromism denotes color change caused by exposure to light; thermochromism, color change caused by exposure to heat; and metachromism, color change caused by interaction with environmental materials. Tenebrescence is a term used in connection with cathode-ray tubes and is the property of darkening visibly and bleaching reversibly under suitable irradiations.


There is a considerable amount of literature on phototropic compounds and their chemistry with much speculation on the method of operation of the phototropic process.^{1*} Chemical Reviews² provides the best general review of the phenomenon prior to this study.

Certain well accepted facts which are pertinent to the study are presented in the following: (a) only light which is absorbed can act chemically (Grothaus Draper Law); (b) in general, the amount of material transformed in a photochemical change is proportional to the product of the light intensity and the time of illumination (Bunsen Roscoe Law); (c) the amount of substance transformed in a photochemical reaction is proportional to the amount of light energy absorbed, rather than merely to the incident intensity (Vant Hoff); (d) each absorbed quantum should cause one light-absorbing molecule to react (Einstein Photoequivalent Law); (e) the quantum yield is the number of molecules which react for each quantum of light absorbed; (f) the primary process is the first step where each molecule absorbs a quantum; the subsequent secondary process which follows the law of mass action may be quite complex, and it may cause the quantum yield of the over-all reaction to vary from unity; (g) the concentration of molecules other than the ones which absorb radiation is an important factor in the velocity of the reaction (Rodenstein); and (h) viscosity and the bound state of the molecules also exert an influence.³

Absorbed light energy can be converted into: (a) fluorescence, (b) heat, (c) electric energy, (d) change in kinetic energy level, and (e) chemical reaction. Fluorescence, the conversion of absorbed light energy into longer wavelength

*Superscripts designate references.

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light, occurs at 10^{-8} seconds. The first order photochemical reaction must take place before the excitation energy is lost by fluorescence. Most sensitizers are compounds capable of fluorescence; however, they lose their fluorescence when acting as sensitizers since the energy is expended in the chemical reaction. Compounds which have groups such as $C=O$ and $-OH$, appropriately oriented as in , transform photoenergy into heat; and, as such, they can act as protective energy absorbers. Change to electric energy occurs in photocells. The storage of energy occurs as in phosphorescence. Chemical reaction caused by light is a well-known photochemical reaction. Most photochemical reactions are not reversed when the activating light is removed. Light energy can initiate a variety of chemical reactions including polymerization.

The wavelengths of the absorption bands vary with different materials. Since only absorbed light can cause chemical action, useful materials must receive light having those wavelengths which they are capable of absorbing. The energy in a quantum of light varies in accordance with the wavelength. Table I gives the energy and voltage for different wavelengths. The shorter ultraviolet waves have more energy than the visible wavelengths. Ultraviolet light causes greater chemical action than visible light because of its higher potential. In general, the longer waves influence the reactions in which there is a decrease in energy, and the short waves influence the reactions where there is an increase in energy.⁴ In many phototropic reactions, ultraviolet light increases one reaction and infrared increases the opposite reaction (Herschel effect).

Generally, the phototropic phenomenon can be considered as a means whereby the absorption of high-potential light can be restricted. The material is pressured by the absorbed light, and it escapes this pressure by changing to another form which does not absorb the activating light. The majority of phototropic reactions occurs when the compound becomes transparent and is said to fade. The reactions where the substance becomes darker are those activated by the shorter, higher energy ultraviolet waves. The substance changes to a new compound with an increase in transmission in the ultraviolet but with a decrease in transmission in the visible.

The phototropic phenomenon is a chemical reaction wherein the energy change is not too great to prevent its reversal. The electron voltage for the reaction cannot be more than that provided by the light quantum. For example, light at a wavelength of 350 μ provides 81 Cal. per mol (table I). The activating light must have an electron voltage higher than that required to initiate the phototropic reaction. The quantum yield cannot be greater than one (100% efficiency) for a reversible reaction. Quantum yields, much greater than one—even in the thousands—have been obtained for nonreversible systems. The problem in using these materials as light valves is that no precise light intensity threshold will trigger them.

Chemical reactions, reversible by the presence or absence of light, are few. They include change in isomerization as from cis to trans, salt isomerization,

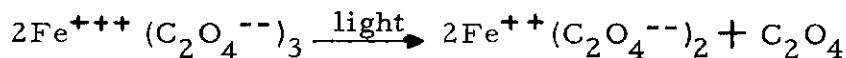
TABLE I

ENERGY OF LIGHT AT DIFFERENT WAVELENGTHS

| Wavelength Å | Electron Volts | Einstein Cal./mol | Cal./photon $\times 10^{-19}$ |
|-----------------|-------------------|----------------------|----------------------------------|
| 2000 | 6.199 | 142.95 | 2.373 |
| 2500 | 4.959 | 113.0 | 1.899 |
| 3000 | 4.132 | 95.27 | 1.582 |
| 3500 | 3.542 | 81.00 | 1.365 |
| 4000 | 3.099 | 71.48 | 1.187 |
| 4500 | 2.755 | 63.00 | 1.055 |
| 5000 | 2.479 | 57.18 | 0.9493 |
| 5500 | 2.254 | 52.00 | 0.8630 |
| 6000 | 2.066 | 47.65 | 0.7911 |
| 6500 | 1.907 | 43.50 | 0.7301 |
| 7000 | 1.771 | 40.84 | 0.6780 |
| 7500 | 1.653 | 38.00 | 0.6329 |
| 8000 | 1.550 | 35.74 | 0.5934 |
| 8500 | 1.458 | 33.63 | 0.5583 |
| 9000 | 1.377 | 31.75 | 0.5272 |
| 9500 | 1.305 | 30.10 | 0.4998 |
| 10000 | 1.240 | 28.59 | 0.4747 |
| 10500 | 1.180 | 27.27 | 0.4520 |
| 11000 | 1.127 | 25.98 | 0.4314 |
| 11500 | 1.077 | 24.84 | 0.4125 |
| 12000 | 1.033 | 23.83 | 0.3956 |
| 12500 | 0.9918 | 22.88 | 0.3798 |
| 13000 | 0.9538 | 22.00 | 0.3652 |
| 13500 | 0.9182 | 21.18 | 0.3516 |
| 14000 | 0.8858 | 20.42 | 0.3391 |
| 14500 | 0.8552 | 19.72 | 0.3274 |
| 15000 | 0.8265 | 19.06 | 0.3164 |
| 20000 | 0.62 | 14.2 | 0.233 |

and oxidation reduction, color center, ring closure, and other systems. An example of isomeric change is stilbene. The cis and trans forms of the stilbene group have different absorption intensities because of their different transition moments. The higher absorbing planar trans form is pressured by light to change to the cis nonplanar form. Figure 1 presents the absorption curves of cis and trans stilbene for different wavelengths in the ultraviolet.⁵ This type of reaction is not sensitive to air oxidation. An example of the salt isomerization type is Crystal Violet of the triphenyl methane class. The cyanide, borate, sulfide, or hydroxide strongly basic anion solution is phototropic. When exposed to light containing near ultraviolet rays, it changes rapidly from a colorless to a deeply colored violet solution. The curve of the absorption in the ultraviolet for Crystal Violet cyanide is depicted in figure 2.⁶ Colorless nitrite changes to the colored cyanide

form when subjected to ultraviolet. This type of reaction has the advantage of not being sensitive to change by air oxidation. The oxidation-reduction type photochemical reaction is most common. It occurs with both organic and inorganic compounds. The reaction is a transfer of one or more electrons with a change in the ability to resonate and without necessarily involving oxygen. Compounds of elements of multiple valence—chromium, iron, mercury, titanium, etc.—have different colors at different valences. In the presence of a donor or an acceptor of an electron, they can be pressured by light to change valence. One of these is molybdenum oxide which, under proper conditions, changes from a yellow in the dark to blue in the light. The following chemical expression presents another example:



An example of the color center type is the mineral Hackmanite, said to reversibly change from pink to purple under suitable irradiation.

An example of ring closure is the spiran.

The action of compounds like mercury halide thiocyanide has not been classified as to type.

The anion combined must be strongly polarizable—for example, oxides or sulfides where there is absorption in the near ultraviolet or in the visible. The problem in the use of the inorganic compounds is the difficulty of dissolving them for use in the manufacture of clear films.

**ABSORPTION CURVES FOR CIS
STILBENE AND TRANS STILBENE**

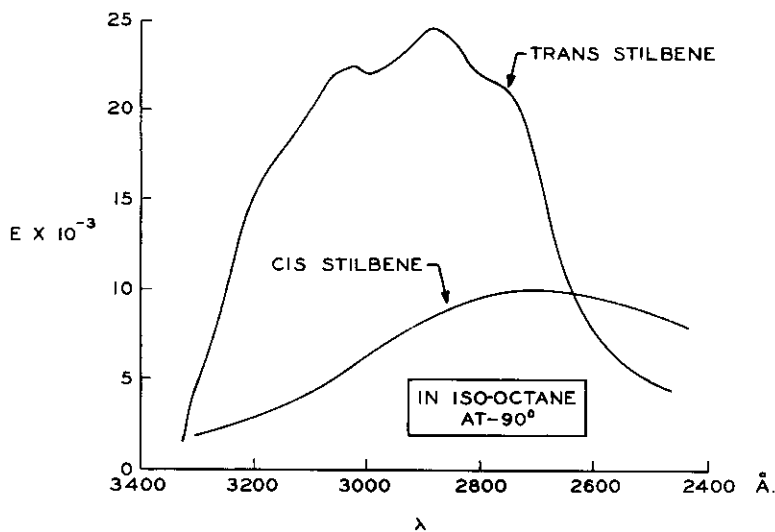


Figure 1.

**ABSORPTION CURVES FOR
CRYSTAL VIOLET
CYANIDE**

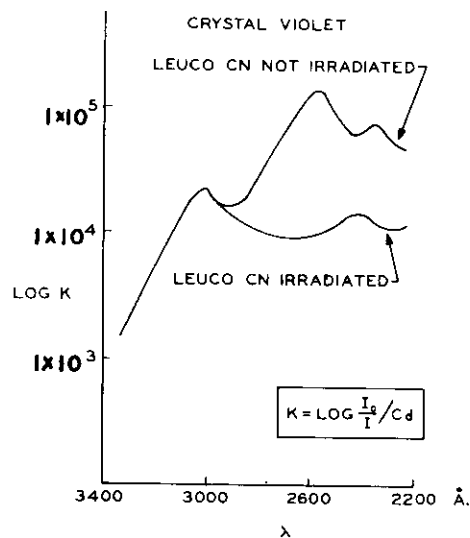


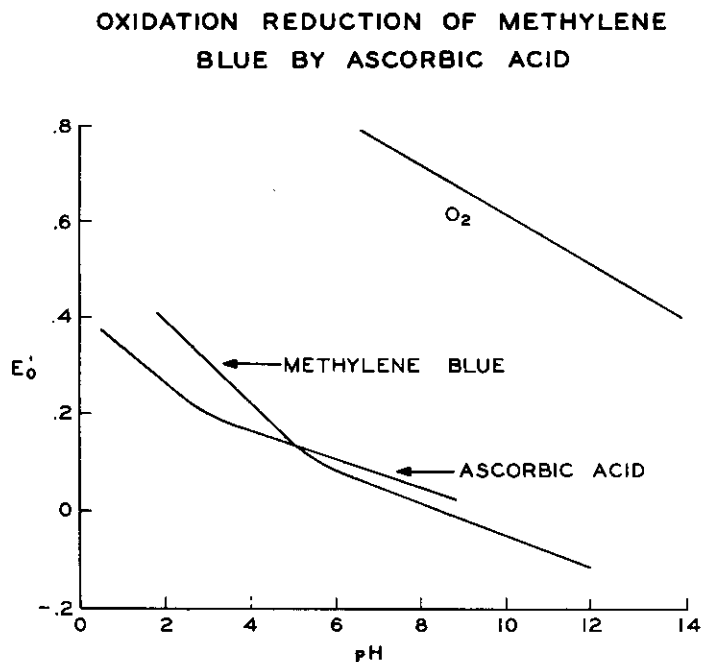
Figure 2.

Perhaps the most common example of oxidation-reduction type phototropy in an organic compound is methylene blue. The reduced leuco form is colorless and the oxidized form is a strong blue. Methylene blue can be reduced to the leuco compound by, for example, ascorbic acid. As illustrated in figure 3,⁷ the reaction is sensitive to pH since the redox voltage for the two compounds changes differently with pH. From a pH of approximately 1 to 5, the ascorbic acid will reduce the methylene blue to the colorless form even without the presence of light. From an approximate 5 pH upwards, this same reaction occurs when light is absorbed. The difference of the electrical potential between methylene blue and ascorbic acid is only a fraction of an electron volt. In the absorption range of methylene blue, there is more than 1 volt potential available from light as is indicated by table I. Light will bleach the mixture, and the reaction will be reversed in the dark. In the presence of oxygen, the ascorbic acid is irreversibly oxidized and consumed, whereas the methylene blue changes back and forth between the leuco and the colored form.

Methylene blue absorbs in the visible portion of the spectrum and is activated by visible light. The action of the light causes fading in the visible. To obtain the reverse effect of increased absorption in the visible in the presence of visible light, it is necessary to have absorption and activation at higher potential, ultraviolet wavelengths. Then, the intensity of the ultraviolet light and the time of exposure will control the amount of the reaction and, hence, the amount of absorption in the visible portion of the spectrum.

There appears to be no definite threshold for the amount of light to cause reaction. For reversible systems, there is an equilibrium between light-to-dark and dark-to-light reactions which is influenced by the presence of the shorter wavelength light present. There is a threshold associated with the wavelength of the activating light which depends on the absorption characteristic of the material but there is no energy threshold.

Figure 3.



The speed fatigue and energy characteristics warrant critical examination in this study. Indication that good photochemical reaction speeds are obtainable, such as immediate dissociation speeds of less than 10^{-10} to 10^{-13} seconds, has been revealed.⁸ First order cis-trans formation occurs in 10^{-5} seconds.⁹ No

information is available on the speeds of phototropic materials. The fatigue characteristic varies markedly with the different materials used. The literature review revealed several examples where good fatigue characteristics were obtained. Salicylidene aniline contained in a sealed Pyrex tube evidenced no change in phototropic properties after exposure to daylight for a year.² Although a solution of molybdenum trioxide in selenium oxychloride changes from light yellow to indigo blue when placed in the sun, 8 years of exposure to light did not diminish its capability of changing color.¹⁰ A zinc sulfide complex, while observed during 1 year, continued to demonstrate its capability of changing from black to white within 2 minutes and of reverting to black within 2 hours.¹¹

SECTION II

METHOD OF APPROACH

A. Energy Considerations

Consideration of the energy aspects of the phototropic phenomenon contributes to the knowledge of the necessary conditions for use of the phototropic material as a self-attenuating light valve.

Both the density of the phototropic color and the time required for the evolvment of the color depend on the following: (a) the quantum yield of the phototropic material; (b) the degree of absorption—i. e., the absorption coefficient and the band spread at the activating wavelengths and at the visible; (c) the back pressure of the reversing reaction; and (d) the amount and wavelength of energy available to activate in any given time. Quantum yields close to unity have been obtained.⁶ The value of 0.9 is used in the subsequent calculations.

In accordance with Beer's Law, the transmission may be expressed as $T = 10^{-Ac}$ and $\log \frac{1}{T} = Ac$, where A is the molar absorption coefficient to the base 10, c is the concentration in gram molecules or mols per liter, and l is the path length in centimeters. Several materials were measured to obtain the value of A . Malachite green (657) in water between 6250 and 6750 Å measured 2.7×10^4 . Malachite green (657) in methanal between 5940 and 6350 Å measured 5.5×10^4 . Methyl violet (680) in water between 5400 and 5900 Å measured 4.0×10^4 . Crystal violet (681) in methanal between 5425 and 5925 Å measured 5.7×10^4 . According to C. F. Hiskey,¹² a coefficient of 10×10^4 is normal for highly colored dyes and 100×10^4 is the theoretical maximum. A coefficient of 1.5×10^4 has been chosen as a reasonable average over the band spread for both the ultraviolet and the visible.

With $A = 1.5 \times 10^4$, $l = \frac{1}{10}$ cm., and transmission = 10% (or density of one)

then, $\log \left(\frac{1}{0.1} \right) = 1.5 \times 10^4 \times c \times \frac{1}{10}$

and, $c = 6.67 \times 10^{-4}$ mols per liter for $\frac{1}{10}$ cm. thick filter

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Assuming a volume of 1 square cm. by $\frac{1}{10}$ cm. thick = $\frac{1}{10000}$ liter

$$\text{then, } \frac{6.67 \times 10^{-4}}{10000} = 6.67 \times 10^{-8} \text{ mols/cm.}^2 \text{ of area}$$

Since Avagadro's number = 6.023×10^{23} molecules/mol

$$\text{then, } 6.023 \times 10^{23} \times 6.67 \times 10^{-8} = 4.02 \times 10^{16} \text{ molecules/cm.}^2,$$

the area required for a density of one.

The absolute quantity of light energy can be expressed in terms of calories per second per square centimeter. Considering the energy from an atomic flash, the ultraviolet waves which pass through a methylmethacrylate airplane canopy are longer than 3200 Å. Assuming an equivalent black body temperature of 6500 °K. for the flash, the average calory per photon or calory per quantum between 3200 and 4000 Å. is $\frac{(1.482 \times 1.187)}{2} \times 10^{-19} = 1.334 \times 10^{-19}$ as indicated by table I. The quantum yield is the ratio of the number of molecules chemically changed to the number of quanta absorbed. With a quantum yield of 0.90, $\frac{1.334 \times 10^{-19}}{0.90} = 1.48 \times 10^{-19}$

calories per molecule. The energy required in the ultraviolet region to convert to a density of one in the visible is $1.48 \times 10^{-19} \times 4 \times 10^{16} = 0.0059$ calories/cm.²

Assuming a 4% fresnel loss by the front surface of the valve, the radiant energy in the ultraviolet between 3200 and 4000 Å. is $20.5 - 9.5 = 11 \times 0.96 = 10.5\%$ of the spectrum (from a Radiation Calculator).^{*} Therefore, $0.0059 \times \frac{100}{10.5} = 0.056$

calories/cm.² Hence, a 6500 °K. temperature radiator must have a total radiant energy of 0.056 calories/cm.² to provide sufficient ultraviolet in the 3200 to 4000 Å. range to cause a photochemical reaction on a material having an absorption coefficient of 1.5×10^4 in the ultraviolet and in the visible and a quantum efficiency of 90% to produce a density of one in the visible. The density is directly proportional to the radiation energy provided that sufficient material is available for the utilization of the activating energy for the first order reaction and the ultraviolet transmission of the activated state is 100%. A density of four requires approximately 0.224 calories/cm.² total radiant energy. The optical density is proportional to the log of the reciprocal of the transmission. Consequently, the transmission will not be in direct proportion to the activating light. Also, on receiving light at a constant rate, the valve will close slowly at first, then faster as further energy is received. At the 40% transmission point, the rate of closing is directly proportional to the activating energy and from then on it will close at an increasingly faster rate. The radiant energy that gets through the valve while it is in the process of closing is calculated as follows. A time lag of zero is assumed for the photochemical reaction.

^{*}The Radiation Calculator is supplied by the General Electric Company, Schenectady, New York.

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$$\text{Optical density } D = \log_{10} \frac{1}{T}$$

$$D = (\log_{10} e) (-\log_e T)$$

$$D = \frac{1}{2.303} (-\ln T)$$

where T is the transmission ratio in the visible spectrum.

Let n = the increment of energy transmitted at any particular value T . Since density D is proportional to the energy N , i. e.:

$$\frac{D}{N} = \frac{(\text{Neutral Density of 4})}{0.224 \text{ cal./cm.}^2}$$

or

$$D = \frac{N (\text{Neutral Density of 4})}{0.224 \text{ cal./cm.}^2}$$

then, the transmission ratio T can be related to the energy n by:

$$\frac{1}{2.303} (-\ln T) = \frac{N \times 4 \text{ Neutral Density}}{0.224 \text{ cal./cm.}^2}$$

or

$$-\ln T = \frac{2.303 \times N \times 4}{0.224 \text{ cal./cm.}^2}$$

Therefore, $T = e^{-41.12n}$

Then, if N is allowed to equal the net total energy transmitted before the given density is reached, then:

$$dN = Tdn$$

or

$$dN = e^{-41.12n} dn$$

and

$$N = \int_0^{0.224} e^{-41.12n} dn$$

$$N = \frac{-1}{41.1 \times e^{-41.12} \times 0.224 \text{ cal./cm.}^2} + \frac{1}{41.12}$$

$$N = 0.0243 - 0.00000243$$

$$N = 0.0243 \text{ cal./cm.}^2$$

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The per cent of the total radiant energy for a 6500 °K. radiator between 4000 and 7000 Å. is 39% (from Radiation Calculator). The maximum amount of energy in the visible which can pass through the activated valve is $0.0243 \times \frac{39}{100} = 0.0095$ cal./cm.² In the fully open position, the transmission of the active material is high and the surface reflection losses at the outside faces are the only major concern.

Few materials have a uniform absorption coefficient of 1.5×10^4 and a quantum efficiency of 0.9 over the entire spectrum. In reality, sufficient absorption should be expected only over a portion of the visible. A green with limits of operation between 4500 and 6500 Å. is practical. This could be combined with additional filters to restrict the remaining energy. Filters providing satisfactory ultraviolet absorption are available. An absorbing glass such as Ezeve or Solex transmits approximately 75% in the visible and 30% in the near infrared. As the energy in the near infrared for a 6500 °K. body from 6500 Å. out is 45% of the total, $0.0243 \times \frac{45}{100} \times \frac{30}{100} = 0.0033$ cal./cm.² Then, at a 0.0243 cal./cm.² ambient light level, the valve permits the transmission of nothing in the NUV, $0.0095 \times \frac{75}{100} = 0.0071$ cal./sec. in the visible, and 0.0033 cal./cm.² of the NIR. These transmissions total 0.0104 calories/cm.² As the ambient light increases, the amount of energy in the visible transmitted by the valve will decrease, whereas the energy in the near infrared will increase in direct proportion to the ambient radiation.

Information of the radiant energy capable of causing burn in the eye is provided in the references.^{13, 14} Minimum thermal energy for lesion is

$$\frac{37 \times 30}{1000} = 1.11 \text{ cal./cm.}^2 \text{ at the retina;}^{13} \text{ this quantity becomes } 1.11 =$$

$$\frac{\emptyset C \times 8 \times 8 \times 0.80}{1.1 \times 1.1 \times 0.873} \text{ cal./cm.}^2 \text{ at the exterior of the eye, where } \emptyset C = \frac{1.11}{48.5} =$$

0.023 cal./cm.², the minimum thermal energy from an atomic flash capable of causing a burn.

Operation of the valve as a protective device against the visible and ultraviolet rays of an atomic flash would be marginal. Further, its operation would depend on the practical absorption band width, absorption coefficients, reaction speeds, and quantum yields time lag and near infrared filter efficiency obtainable. If a valve were to serve practically, it would have to remain open when exposed to a certain ambient level of ultraviolet which would require a balancing back pressure. However, a zero back pressure has been considered in these reactions. Also, an additional filter to eliminate a large portion of the near infrared rays would be required to make the valve feasible as an eye protective device. The valve must provide protection using the available energy before the expiration of the 150 milliseconds during which period the eye blink affords protection. It has to reduce the transmission of the radiant energy to a rate which the eye can withstand. This device will have a transmission which varies in accordance with the amount of ultraviolet connected with ambient light to which it is subjected and, if exposed to the sun or sky light, will darken accordingly.

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To use the valve as a protective device against the high ambient light conditions produced by the sun, the light to density of the valve is the amount of activated material and the time available for exposure and the ultraviolet transmission of the activated state. To produce a density of 2, approximately 8×10^{16} molecules/cm.² of absorbing compound and 0.112 calories/cm.² are required for activation. The sun may be considered as a black body of temperature 5800 °K. for spectral energy distribution. There is 7.7% of the total radiant energy within the 3200 to 4000 Å. range (from Radiation Calculator). As the sun produces 0.0323 cal./cm.²/sec., it requires $\frac{0.112}{0.0323}$, i.e., 3.47 seconds, to develop a density of 2

and 7 seconds for a density of 4. The speed of reversal depends on temperature, the amount of infrared which is absorbed, and the dark reaction speed of the material used. These conditions vary for both different materials and various chemical conditions, such as pH and concentration. The device which has been calculated depends on energy in the ultraviolet between 320 and 400 mu for activation. The incandescent lamp light has but a small proportion of its energy within this range. As a tungsten filament lamp at 2700 °F. has less than 0.0003% of its energy within this range, it would not exert any appreciable effect on the operation of the valve. The transmission of the device will not necessarily be in proportion to the amount of visible light, but it will vary as the amount of near ultraviolet light varies.

B. Design

To be useful as a self-attenuating light valve for eye protection, the system should provide an area of at least 2 inches in diameter which is clear with high transmission when in the open state. It should absorb in the visible proportionately to the ambient light. Preferably, the absorption should be uniform throughout the visible portion of the spectrum which is within the range of eye sensitivity—i.e., approximately 400 to 700 mu. A useful system would also be a green where the absorption is in proportion to the eye sensitivity. Another useful system would employ a valve operating between cut-off limits of, respectively, from the near ultraviolet to 450 mu and from 650 mu to the near infrared.

The construction could comprise, as an example, a laminated sandwich having the following elements: (a) a near ultraviolet and visible transmitting, scratch-resistant, optically flat rigid sheet; this could be methyl methacrylate, quartz, glass, or other; (b) a phototropic material; this could be utilized as a solid layer coating either in a liquid solution or incorporated in a plastic; the latter is preferable with the plastic being a material, such as polyvinyl butyral, capable of being laminated for good adhesion and optical contact with the other elements of the sandwich; and (c) a near ultraviolet and infrared absorbing material with good visual transmission; the material should be rigid, scratch-resistant, and optically flat; it could be either glass or plastic, for example, Ezeve or Solex glass, with a coating of an ultraviolet absorbing material, such as phenyl salicylate in cellulose nitrate; or, it could consist of a plastic, such as a cast polyester resin, containing an ultraviolet absorber, such as cinnamaldazine with a near infrared absorber such as a copper compound.

Continued

Another combination could be a clear plastic coating containing the phototropic material on a rigid support, such as glass containing iron. Further, still another combination could install the infrared absorbing portion within the first section or incorporate it together with the phototropic material.

If the infrared rays tend to reverse the action of the ultraviolet to an excessive extent, the infrared absorber should be placed in front of the phototropic material. If it is desirable to accelerate the reversed reaction, the infrared absorber should be installed together with or adjacent to the phototropic material. The phototropic material could consist of one material with an appropriate absorption band, or it could comprise a mixture of materials having, for example, complementary colors to broaden the absorption band or to intensify one particular portion. If ultraviolet-absorbing materials act as sensitizers for the reaction, they could be incorporated together with the phototropic material.

It is essential that the design permit the transmission of the useful activating and visible wavelengths to the phototropic material. If sufficient ultraviolet energy is not available to activate the device to the proper level, the design could include an optical system which would concentrate the rays within a smaller area to increase the activating energy per square centimeter. Further, if the ambient light cannot produce the desired reaction, it could trigger a secondary source of activating ultraviolet provided as an integral part of the system.

Initial laboratory work was devoted to evaluating phototropic properties of methylene blue and thionine dyes. Water solutions of duPont's methylene blue Zx (C.I. 922) photobleached under a 75-watt flood lamp within periods varying from a few seconds to 30 minutes depending on the type and concentration of reducing agents. Stannous chloride produced a slow bleaching within approximately 30 minutes, while ascorbic acid and phenyl hydrazine produced a photobleaching within 2 to 5 seconds. The methylene blue systems were observed to be sensitive to visible blue light and to be reversible. However, their reversal times were relatively slow, the time requirements varying from 2 to 30 minutes. Further testing revealed that reversal occurred only when ready access to air was provided. The testing also indicated that color developed only because of reoxidation of the leuco methylene blue by atmospheric oxygen. Since the reducing reagents were invariably destroyed in the photobleaching reaction, the phototropic oxidation of the methylene blue was not strictly reversible. The number of photobleaching cycle performances with a given solution depended on the original quantity of the reducing agent. When all of the reducing agent was consumed, the solution became insensitive to light. The speed of both the forward and reverse reactions depended on the ratio of dye to reducing agent. Larger proportions of the reducing agent increased the speed and degree of photobleaching, but decreased the speed and degree of reversal. Clear plastic films consisting of polyvinyl alcohol incorporating both methylene blue and an ascorbic acid reducing agent were prepared and observed to photobleach in approximately 1 minute. However, the reversal was slow. This was probably due to the slow molecular migration which can take place in solid solutions.

An unusual effect was revealed when methylene blue reduced while in the dark by titanous chloride resulted in a solution of leuco methylene blue and colloidal titanium dioxide. When illuminated, the methylene blue color developed due to the reoxidation by the insoluble TiO_2 . The color development in consuming less than 1 minute was fairly fast. This example of color development following illumination is noteworthy in contrast to the usual photobleaching processing of methylene blue.

The major drawback to the use of an oxidation-reduction phototropic system is the interference caused by atmospheric oxygen. Having tested stilbene dyes as an example of the cis-trans change, the readily available compounds revealed but slight color change in the visible from colorless to yellow.

Triphenyl methane dyes, such as Crystal Violet and Malachite Green, reported as evidencing phototropy in the carbonyl or cyanide form were evaluated. These dyes were considered to have promising possibilities without high oxygen sensitivity. A phototropic system using a dilute methyl alcohol solution and stressing the importance of the type solvent used could be prepared. The crystal violet color is bleached out by the judicious addition of KCN or KOH. When the colorless solution is placed in sunlight or in some other source of 3000 to 4000 \AA . radiation results in the development of the original crystal violet color within a very short time—i. e., usually within 10 to 30 seconds, depending on concentrations, temperature, pH, and intensity of light source. Extensive investigation of this and other triphenyl methanes indicates that this system is fast in both the forward and reverse directions. However, the system has several drawbacks in its present form. After each forward-reverse cycle, the degree of color change becomes progressively less with the system completely lacking sensitivity on attaining approximately the fiftieth cycle. Yet, it is quite likely that the fatigue could be reduced to increase the useful life of the system. As the system is sensitive to temperature, continued exposure to light results in a fading of the color which is attributed principally to the increased temperature caused by the absorption of light. Still, if the exact mechanism of the fading were determined, it might be possible to effect a suitable stabilization. A number of triphenyl methane type dyes tested for phototropic character was revealed to be phototropic as listed in table II. The triphenyl methane systems have been successfully incorporated into plastic films—i. e., polyvinyl butyral—with some sacrifice of reversal speed.

Another system which was evaluated and indicated considerable promise was one utilizing ammonium molybdate in combination with an organic hydroxy compound, such as citric acid in aqueous solution, as a reducing agent. When illuminated, the hexavalent molybdenum is reduced to molybdenum blue. In hazy sunlight, the color development occurs within approximately 3 minutes. Although the system is reversible, the reversal depends on the availability of atmospheric oxygen for oxidation to the original form as is the requirement in the case of the thiazine dyes. To make the system usable, a reversible reducing agent would be required.

Controls

The molybdenum-citric acid combination exhibited its phototropic properties in clear films of polyvinyl alcohol. It is surmised that a reversible inorganic reducing agent used with the ammonium molybdate would provide a system evidencing less fatigue than the organic systems listed.

TABLE II

PHOTOTROPIC TRIPHENYL METHANE DYES

| <u>Color Index No.</u> | <u>Name</u> |
|------------------------|----------------------------|
| 657 | Malachite Green |
| 658 | Brilliant Blue |
| 662 | Brilliant Green B Crystals |
| 662 | Brilliant Green B Crystals |
| 658 | Brilliant Blue |
| 666 | Acid Green L Extra |
| 667 | Fast Acid Green |
| 669 | Light Green SF |
| 677 | Magenta Red Fuchsin Base |
| 679 | Iodine Violet |
| 680 | Methyl Violet |
| 681 | Crystal Violet |
| 686 | Iodine Green |
| 688 | Methyl Blue |
| 693 | Red Violet 5R |

Many other types of material were tested and evaluated for phototropic properties. Diamines, such as p-phenylene diamine in combination with potassium nitrate, were coated on paper and darkened when exposed to light, but they did not function in solution form. The investigated materials also included over 100 dye-stuffs and several inorganic compounds. Although many exhibited photochemical characteristics, they were discarded generally because of lack of reversibility, slow reaction, or insufficient color change.

SECTION III

SUMMARY AND RECOMMENDATIONS

A device using phototropic material would provide a simple, automatic means of controlling light intensity. It could be utilized in windows, shades, visors, and glasses to assist and protect the eye. The device could modify the intensity of sun illumination so that the light would not exceed the level of optimum visibility. It could also be usefully applied to photography and to visual sensing devices, such as photocells, television cameras, etc. It would contain the light level within the limit of the maximum sensitivity range and prevent the jamming caused by excessive illumination.

Certain applications, such as aviator glasses for protection against atomic flash, would require a rapid cut-off with a fast return to the open condition being preferred. However, other applications, such as devices for auto driving, would require a slower reaction to prevent the flicker which would otherwise occur when passing through the shadow of a tree, etc.

Although the device when applied as a protection against a sudden flash could utilize a disposable material designed for a single application, most applications would require a device capable of repeated usage.

As an inorganic-type material will probably provide the optimum conditions for the speed and fatigue requirements, future research should be guided accordingly.

Contrails
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