FEASIBILITY STUDY AND DESIGN OF A SELF-ATTENUATING LIGHT VALVE

SUPERSEDES WADC TR 59-81

JOHN F. DREYER

POLACOAT INCORPORATED

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LIFE SUPPORT SYSTEMS LABORATORY
AEROSPACE MEDICAL LABORATORY
WRIGHT AIR DEVELOPMENT DIVISION
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by John F. Dreyer, Head of Research, Polacoat Incorporated, Blue Ash, Ohio, under contract AF33(616)-6715, Project No. 7165, "Health Hazards of Materials and Radiation," Task No. 71839, "Protection Against Electromagnetic Radiations." Dr. Richard E. Horn of the Vision Section, Protection Branch, Life Support Systems Laboratory, Aerospace Medical Laboratory, Wright Air Development Division, served as contract monitor.

This report supersedes WADC TR 59-81 dated October 1959. Additional and more detailed calculations have modified some of the conclusions of the original report.
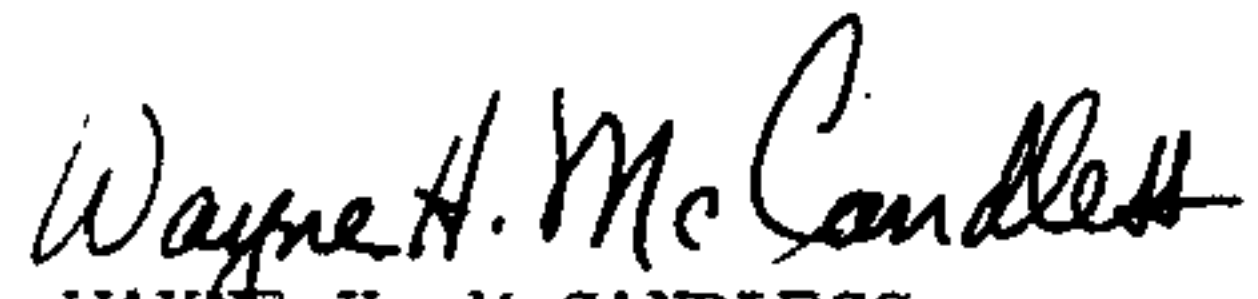
The following associates of Polacoat Incorporated have cooperated in the research and in the preparation of this report: Dr. Glenn H. Brown, Bibliographer; Donald Baltzer, Head of Laboratory; Frank Stevens, Senior Research Chemist; and Jerry Watkins, Laboratory Technician.

Theoretical study was prepared with the assistance of Dr. John McCarthy of the Physics Department of the University of Cincinnati.

ABSTRACT

The use of phototropic materials as self-attenuating light valves has been re-evaluated in the light of additional information. Sunglass application still appears to be feasible. As eye-protective devices to prevent flashblindness and retinal burns from nuclear detonations, phototropic filters appear to be feasible. However, it is impossible to state that they will provide complete eye protection under all operational conditions until more information is available on: (1) the absorption coefficients of the materials and (2) the tolerance of the human retina to short-duration, high-intensity radiation.

iii

TABLE OF CONTENTS

FEASIBILITY STUDY AND DESIGN OF A SELF-ATTENUATING LIGHT VALVE

INTRODUCTION

An investigation of the literature reveals that the use of phototropic material as a self-attenuating light valve of varying density has not been considered. The phenomenon of phototropy, known since 1881, is defined as one 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. The best general reviews of the subject are given by Brown (ref. 1) and Chalkley (ref. 2).

This study describes the principle of operation of such a light valve and its use as a protective device against the visible and ultraviolet radiation from an atomic flash or from the sun. An estimate of its sensitivity is made by some simple calculations of the energies involved. Some of the other practical considerations in the design of a valve employing the phototropic principle are also discussed.

1.

ABSORPTION OF LIGHT

When light is absorbed by a material, the absorbed energy can produce a number of different effects:

a) It can be converted to fluorescent radiation which is always of longer wavelength than the incident light. This radiation takes place within 10^{-8} sec.

b) It can be converted to heat, as, for example, in compounds having groups such as $C = O$ and $-OH$, oriented as in
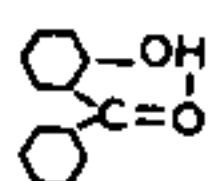
These materials can act as protective energy absorbers.

c) It can be converted to electrical energy, as in photocells.

d) It can be stored within the material and later released in the form of phosphorescent radiation.

e) It can produce chemical reactions which are referred to as photo-chemical reactions. Certain chemical reactions which will not proceed under the influence of a given frequency of light can be stimulated by adding a substance which is sensitive to this light frequency. The added substance, called a "sensitizer," is not changed in composition during the reaction.

Fluorescent compounds are in general very sensitive photochemically. They owe both properties to the fact that they are able to remain in an excited state for a comparatively long time without converting the absorbed energy into heat. This same property enables them to transfer the energy to some other compound and makes them good photosensitizers. The fluorescence itself plays no role in this energy transfer, since the photochemical reaction takes place before the excitation energy is lost by fluorescence.

Certain well accepted facts which are pertinent to the study are presented in the following: (a) only light which is absorbed can act chemically (Grotthus-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 of energy or each photon 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

2.

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); (h) viscosity and the bound state of the molecules also exert an influence; (i) the wavelengths of the absorption bands vary for each material.

From these facts it can be seen two conditions must be satisfied in order for an incident beam of light to cause an appreciable amount of a given reaction:

1) The beam must contain some photons, each of which has an energy greater than a certain minimum amount.

2) These photons must correspond to wavelengths lying within one of the absorption bands of the material.

The following Table I is derived from the equation $E = \frac{hc}{\lambda}$ where E = ergs per quanta, h = Plank's constant, 6.62×10^{-27}, C = velocity of light, 3.0×10^{10} cm/sec., λ is the wavelength in cm., and electron-volts = 1.6020×10^{12} ergs.

TABLE I

ENERGY OF LIGHT PHOTONS AT DIFFERENT WAVELENGTHS

Wavelength in $\overset{o}{A}$	Electron-volts/photon	Calories/photon $X10^{-19}$
2000	6.100	2.373
2500	4.959	1.899
3000	4.132	1.582
3500	3.542	1.365
4000	3.099	1.187
4500	2.755	1.055
5000	2.479	0.949
5500	2.254	0.863
6000	2.066	0.791
6500	1.907	0.730
7000	1.771	0.678
10000	1.240	0.475
15000	0.826	0.316
20000	0.620	0.237

Table I gives the energies, both in electron volts and in calories, for photons corresponding to different wavelengths. The greater energy possessed by photons of ultraviolet light explains why this type of light is especially effective in causing reactions. In general, the longer waves influence the chemical reactions in which there is a decrease in energy and the short waves influence the reactions in which there is an increase in energy (ref. 4). In some phototropic reactions, ultraviolet light increases one reaction and infrared increases the opposite reaction (Herschel Effect).

3.

Most photochemical reactions are not reversed when the activating light is removed and quantum yields much greater than one have been obtained for non-reversible systems. In spite of these advantageously high quantum yields, there are difficulties in using these nonreversible materials as light valves because no precise light-intensity threshold is needed to trigger them. Therefore, this study is limited to reversible systems for which the quantum yield is never appreciably greater than one. In fact, a quantum yield of 0.9 is assumed in the calculations below, since there is good evidence that this is a practical figure (ref. 6).

4.

PROPERTIES OF PHOTOTROPIC MATERIALS

The phototropic phenomenon is a photochemical reaction wherein the energy change is not too great to prevent its reversal. The activating light causes some of the material to change from one form to a second form and the light-absorption properties of the two forms are often quite different. In some reactions the compound becomes more transparent to visible light and is said to fade, but, in others (especially those activated by ultraviolet light), the substance becomes darker. Compounds of the latter type are considered in this study as a possible light valve since the absorption in the visible wavelengths can be greatly increased in a short time by the ultraviolet light in the incident radiation.

There appears to be no definite threshold for the amount of light to cause reactions. There are some materials which, as soon as the absorption of ultra-violet light has transformed some of the phototropic material from the light (transparent in the visible) to the dark (absorbing in the visible) form, a reverse reaction takes place at a rate which depends upon the law of mass action. When this type of material has been irradiated at a constant rate for sufficient time, an equilibrium exists between the light-to-dark and dark-to-light reactions. The effectiveness of a light valve and the speed with which it operates depends upon the rates of reactions in the two directions.

It is recognized that speed and fatigue considerations are important in the present study. Although little information is available on the speeds of phototropic reactions, there is a report that one type of reaction occurs in 10^{-5} sec. and the favorable fact that many photochemical reactions take place very quickly (ref. 8), some within 10^{-10} to 10^{-13} sec. The fatigue characteristics vary markedly with the different materials used, but some are excellent (refs. 2,10,11).

The molecular changes taking place during phototropic reactions can be of several different kinds and it is believed useful for the present report to give three examples:

1) A change in isomerization, as from cis to trans forms of stilbene. These forms have different absorption characteristics because of their different transition moments and their absorption curves in the ultra-violet are shown in figure 1 (ref.5). It is found experimentally that the higher absorbing planar trans form is changed by ultraviolet light to the cis nonplanar form. This type of reaction is not sensitive to air oxidation.
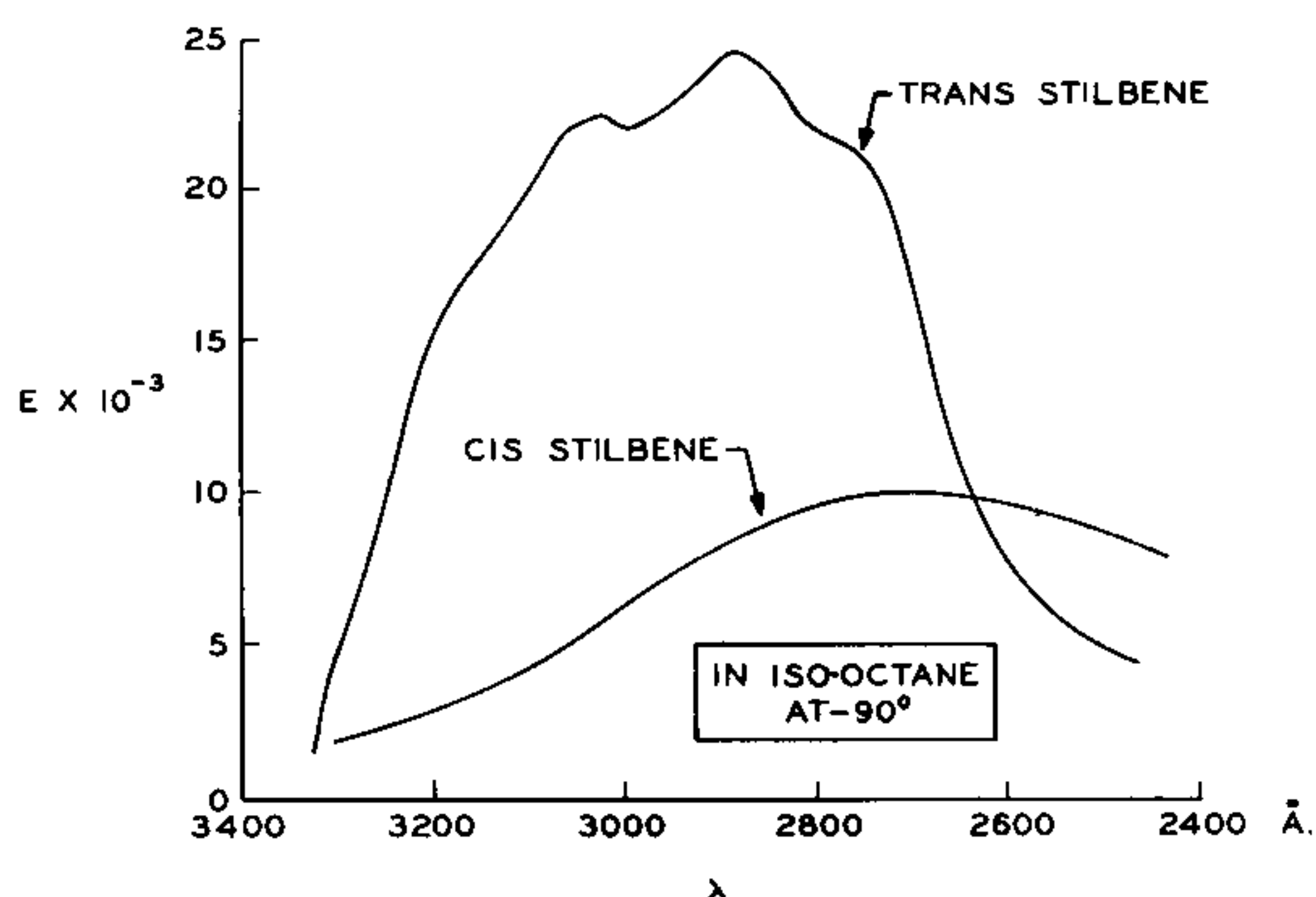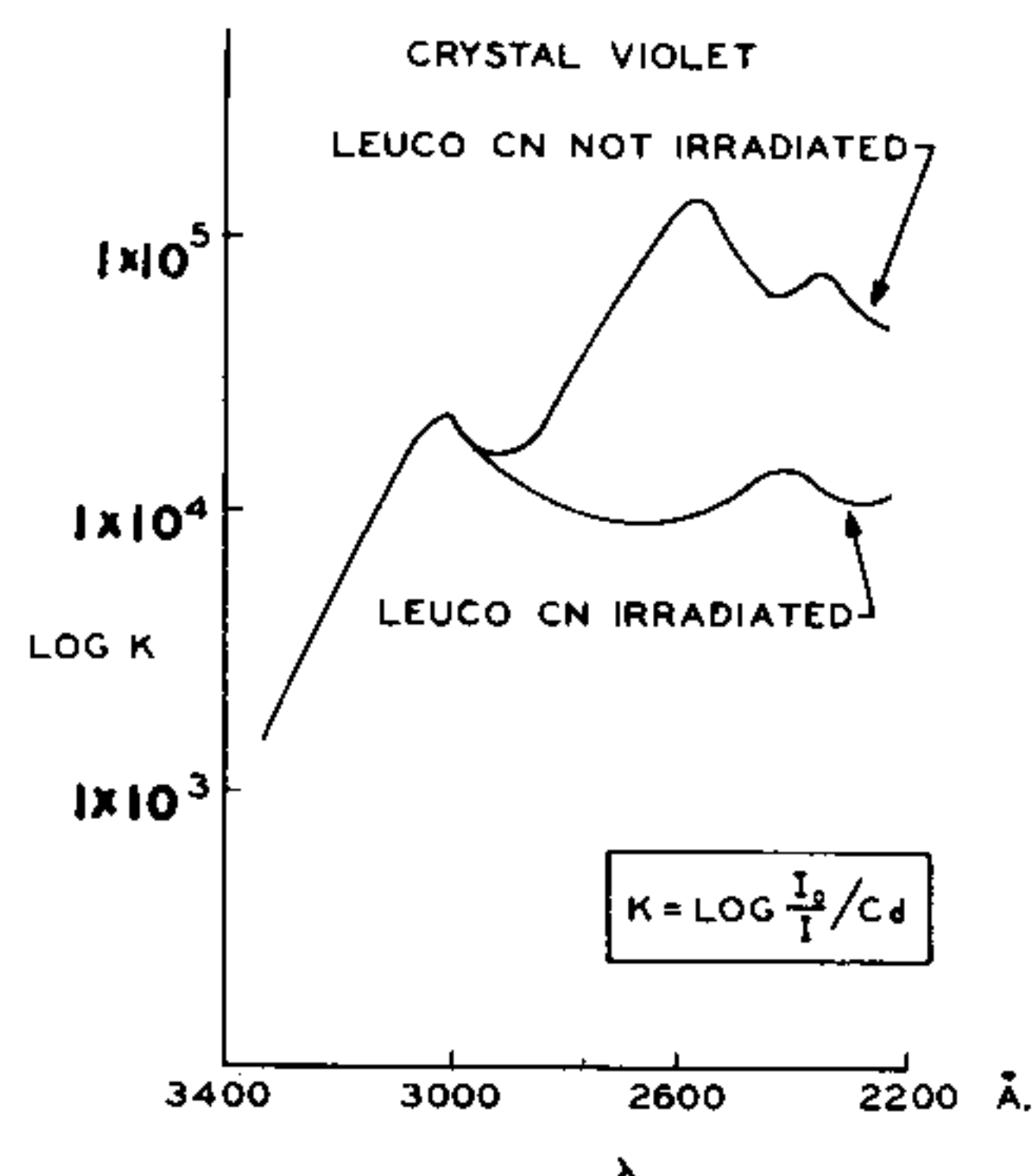
Figure 1.

Figure 2.

2) An example of the salt-isomerization type is Crystal Violet of the triphenyl methane class. The cyanide, borate, sulfide, or hydroxide in a strongly basic anion solution is phototropic. For example, the colorless leuco cyanide is changed by ultraviolet light to the colored form, and the absorption curve changes as shown in figure 2 (ref. 6). This type of reaction also has the advantage of being insensitive to change by air oxidation.

3) The oxidation-reduction type of reaction is most common and occurs with both organic and inorganic compounds. The reaction does not necessarily involve oxygen; usually a transfer of one or more electrons takes place, with a resulting change in the ability to resonate.

In inorganic compounds, elements of multiple valence (e.g., chromium, iron, mercury, titanium, etc.) have different colors at different valences. In the presence of a donor or an acceptor of an electron, incident light can cause them to change valence. One example is molybdenum oxide which, under proper conditions, changes from a yellow in the dark to blue in the light. Another example involves the following reaction:

$$2Fe^{+++}(C_2O_4^{--})_3 \xrightarrow{\text{light}} 2Fe^{++}(C_2O_4^{--})_2 + C_2O_4$$
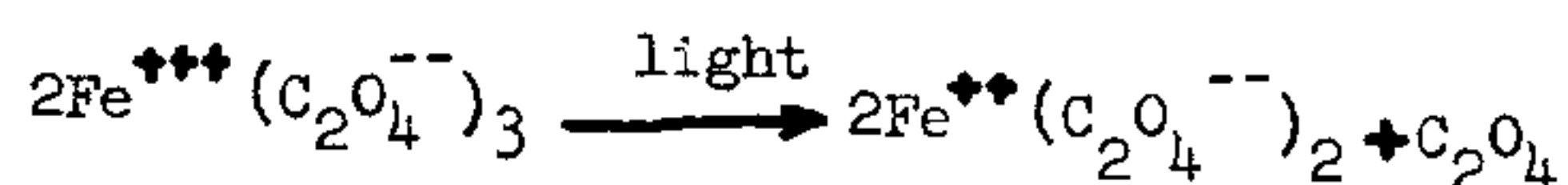
The use of these inorganic compounds in light valves is hampered by the difficulty of dissolving them for use in manufacture of optically clear films.

Perhaps the most common example of oxidation-reduction type of phototropy in an organic compound is methylene blue. The oxidized form is a strong blue and can be changed by irradiation to the reduced leuco (colorless) form by the addition of a reducing agent (e.g., ascorbic acid). As illustrated in figure 3 (ref.7), the reaction is sensitive to pH, since the redox voltage for the two compounds changes with pH.

ENERGY CALCULATIONS

In this section calculations are made on the energy aspects of the phototropic phenomenon in order to investigate the necessary conditions for its use in a self-attenuating light valve. An estimate is made of the visible light energy coming through a typical slab of phototropic material when the radiation from a nuclear flash is incident upon it. This result is compared with the amount of radiant energy required to produce a burn in the eye.

For these calculations a time lag of zero is assumed for the phototropic reaction and the effect of a reverse reaction is ignored. More refined calculations would have to consider the kinetics of the reactions.

A. Ultraviolet Energy Needed to Close Valve

The energy transmitted by a colored layer of phototropic material can be calculated by Beer's Law. According to this Law, the transmission may be expressed as:

$$T = 10^{-ACL}$$

or

$$\log \frac{1}{T} = D = ACL$$

where D = Optical Density
A = Molar Absorption Coefficient
C = Concentration Expressed as Moles/liter
L = Path Length in Centimeters

Table II gives some data on measured values for A. For these calculations, a molar absorption coefficient of 1.5×10^4 has been chosen as a reasonable average over the band spread for the visible wavelengths.

TABLE II

MOLAR ABSORPTION COEFFICIENTS

Compound	Wavelengths in Å	A
Malachite Green (657) in water	6250-6750	2.7×10^4
Malachite Green (657) in methanol	5940-6350	5.5
Methyl Violet (680) in water	5400-5900	4.0
Crystal Violet (681) in methanol	5425-5925	5.7
Normal for highly colored dyes (Hiskey[12])		10
Theoretical Maximum (Hiskey[12])		100

8.

OXIDATION REDUCTION OF METHYLENE
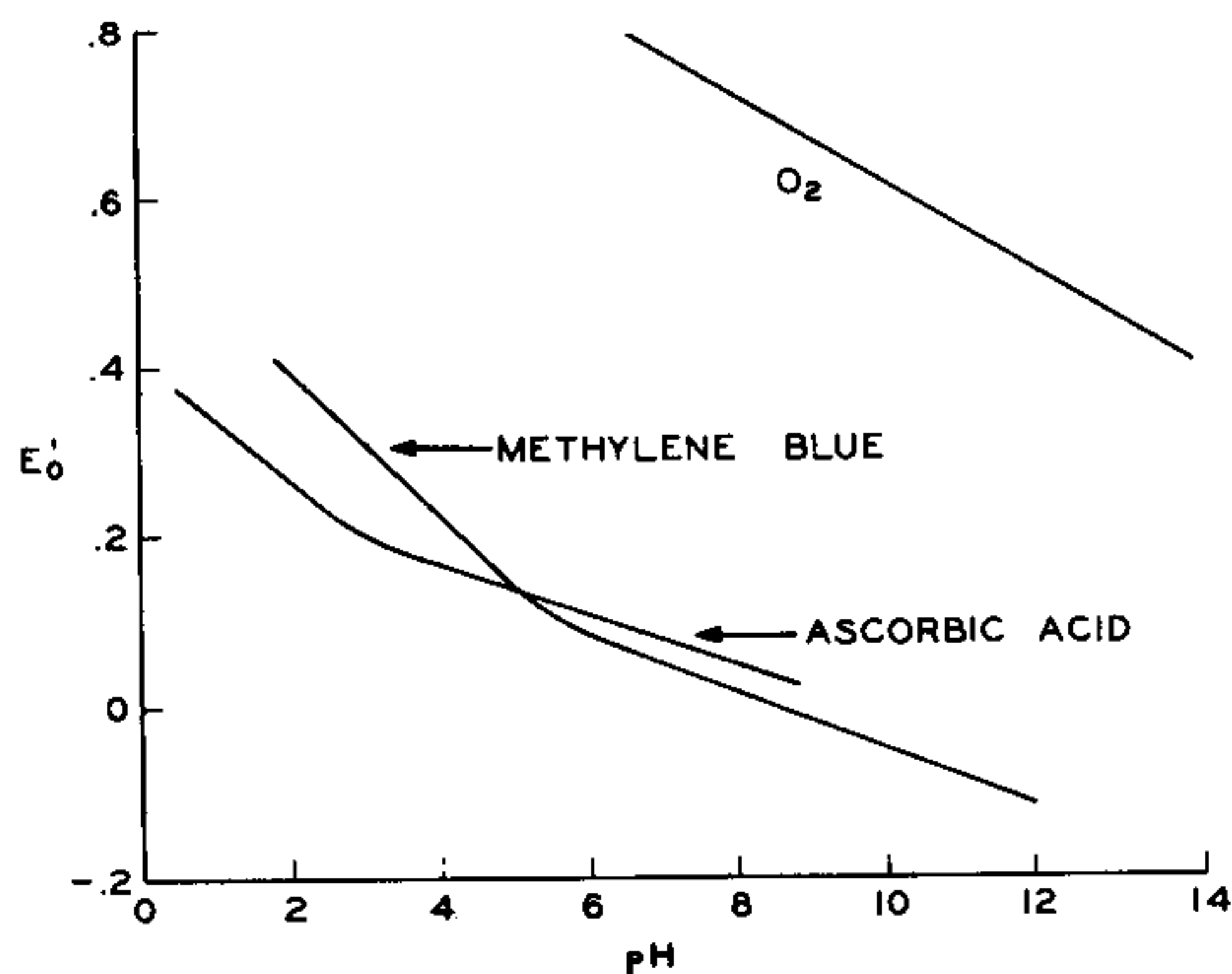## BLUE BY ASCORBIC ACID

Figure 3.

This is a good example of how the behavior of a compound toward light can be influenced by the presence of another compound. From a pH of approximately 1 to 5, the absorbic acid will reduce the methylene blue to the colorless form even without the presence of light. From a pH of 5 upwards, this same reaction occurs only with the addition of energy and figure 3 shows that the amount of energy needed is less than one electron-volt. Therefore, in this pH region, the photons of the visible light absorbed by the blue form have enough energy (see Table I) to cause the reduction reaction and thus to cause the fading in the visible. Visible light will bleach the mixture and the blue color will be restored in the dark. In the presence of oxygen, the ascorbic acid is irreversibly oxidized and consumed, whereas the methylene blue changes reversibly back and forth between the two forms. Ultraviolet light causes the reaction to proceed toward the colorless form.

The concentration of molecules in the colored form can be found from Beer's Law by the following equation:

$$K = \frac{D \times N}{A \times L} \times 10^3$$

where
K = Number of Molecules Converted Per Cubic Centimeter
D = Optical Density
N = Avagadro's Number (6.03×10^{23} molecules/mole)
A = Molar Absorption Coefficient
L = Length of Cell Path

When D = 4, the result we obtain is 1.61×10^{17} molecules/cm^2.

This number also represents the number of molecules changed from the light to the dark form by the ultraviolet light which has been absorbed. The ultraviolet wavelengths which pass through a methylmethacrylate airplane canopy are longer than 3200 Å. From Table I we find that the average energy per photon between 3200 Å and 4000 Å is $\frac{1.482 + 1.187}{2} \times 10^{19}$ or 1.33×10^{-19} calories/photon. Assuming a quantum yield of 0.9, the ultraviolet energy per molecule required to cause a change becomes $\frac{1.33 \times 10^{-19}}{0.9} = 1.48 \times 10^{-19}$ calories per molecule.

The total ultraviolet energy which must be absorbed to attain a density of 4 in the visible is $1.48 \times 10^{-19} \times 1.61 \times 10^{17} = 2.38 \times 10^{-2}$ calories/cm^2. Because of the high density of the phototropic layer for ultraviolet, this number is also, except for a 4 percent reflection loss, the total ultraviolet energy that must be incident upon the valve while it is closing. Assuming an equivalent black body temperature of 6500° K for a nuclear flash, we find (from a Radiation Calculator*) that the radiant energy between 3200 Å and 4000 Å is 11.0 percent (20.5-9.5) of the total. Thus, $2.38 \times 10^{-2} \times 1.04 \times \frac{100}{11.0} = 0.224$ calories/cm^2 is the total radiant energy necessary to cause a photochemical reaction resulting in an optical density of 4 in the visible wavelengths. For a 6500° K source, the percentage of the total radiant energy between 4000 Å and 7000 Å is 39 percent (from the Radiation Calculator). Thus, when 2.38×10^{-2} calories/cm^2 of ultraviolet energy enters the valve, $\frac{39}{11} \times 2.38 \times 10^{-2} = 8.45 \times 10^{-2}$ calories/cm^2 of visible energy enters. This assumes that the percentage of reflection is the same for both visible and ultraviolet.

B. Visible Light Energy Transmitted by Valve

The exponential function shows that the visible energy transmitted is not in direct proportion to the activating light. Consequently, on receiving light at a constant rate, the transmission will reduce quickly at first and then more slowly as further ultraviolet energy is absorbed. The visible radiant energy that gets through the valve while it is in the process of closing is calculated as follows:

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*The Radiation Calculator is supplied by the General Electric Co., Schenectady, N. Y.

The optical density D is equal to the product ACL at any time during this process. This is directly proportional to n, the total ultraviolet energy which has been absorbed up to this time. This assumes that sufficient material is available for the utilization of all the activating energy for the forward reaction and that the ultraviolet transmission of the molecules in the converted form is 100 percent.

Since, it was calculated that 2.38×10^{-2} calories/cm^2 are required to produce a density of 4, the proportion:

$$\frac{D}{4} = \frac{n}{0.0238}$$

may be set up. Translating the equation, we obtain:

$$D = \frac{4n}{0.0238} = \log \frac{1}{T}$$

Thus, the transmission at any instant of the closing is: $T = e^{-386n}$

Then the total visible energy transmitted during the closing of the valve is given by the formula:

$$No = \int_{0}^{No} dN$$

In which n = Total ultraviolet energy/cm^2 that has been absorbed up to some time when the transmission is T.

dn = Ultraviolet energy/cm^2 absorbed during some short time interval.

This also equals the incident ultraviolet energy and so the incident visible light during this time interval is $\frac{39}{11}$ dn

dN = Visible light energy transmitted during this time interval or $T = \frac{39}{11}$ dn

Substituting the data into the above equation, we obtain:

$$\frac{39}{11}\int_{0}^{.0238} T\, dn = \frac{39}{11}\int_{0}^{.0238} e^{-386n}\, dn$$

$$= \frac{39}{11 \times 386}\left[1 - e^{\frac{1}{386(0.0238)}} \right]$$

$$= 0.0092 \text{ cal/cm}^2$$

It was determined that the total cal/cm^2 in the visible can be obtained by the use of the formula:

$$\text{Total calories/cm}^2 = \frac{V \times 1.24 \times 10^4}{U \times W \times Q \times M} \times \left(1 - \frac{1}{10^D}\right)$$

10.

In which V = Percent of Energy in Visible
U = Percent of Energy in Ultraviolet
W = Average Activating Wavelength in Millimicrons
Q = Quantum Yield
M = Molar Absorption Coefficient to base ten

This formula assumes a zero lag time for the photochemical reaction and also that the system is "one-way", i.e., has no back reaction.

The density, D, that the valve reaches equals $M \times Q \times W \times 3.5 \times 10^{-5} \times$ cal/cm^2 in UV. Then the total calories/cm^2 transmitted in the visible =

$$\frac{U \times 0.435 \times calories/cm^2 \text{ in UV}}{V \times D} \times (1 - \frac{1}{10^D})$$

In the fully open position the transmission of the active material is high and the surface reflection losses are the only major concern.

By arguments similar to the above, it can quite simply be shown that the visible radiant energy transmitted by the light valve, as it closes from an initial density, D_1, to a final density, D_2, is given by the equation:

$$No = \frac{137}{A} (\frac{1}{10^{D_1}} - \frac{1}{10^{D_2}})$$

This is valid only for a $6500^{o}K$ source. In this form, the dependence of No upon the choice of A, D_1, and D_2 is clearly seen. It is obvious that the amount of visible energy which will pass through the valve after it is closed (i.e., for D^4) is negligible.

Few single materials have a uniform absorption coefficient of 1.5×10^4 over the entire visible spectrum. In reality sufficient absorption should be expected only for a portion of the visible, but additional filters could be used to restrict the remaining energy.

C.   Ultraviolet and Infrared Energy Transmitted by Valve

It has been explained above that the ultraviolet light is very greatly attenuated by the phototropic layer. In any case additional filters are readily available so that the transmitted ultraviolet energy could be made negligible.

Since the energy in the near infrared for a $6500^{o}K$ body is 45 percent of the total, the transmission characteristics of the light valve in the infrared region are of importance. A simple calculation can be made for a valve in combination with an absorbing glass and filter which transmits approximately 75 percent in the visible and 1.6 percent in the near infrared. We find that the energy transmitted by the combination while the valve is closing is:

(1)   Zero in the ultraviolet wavelength range
(2)   0.75 to 0.0092 = 0.0069 cal/cm^2 in the visible wavelength range
(3)   0.016 x 0.45 x 0.224 = 0.0016 in the infrared wavelength range
(4)   The total is 0.0085 cal/cm^2

D. Minimum Energy Required to Cause Damage to the Eye

Information on the radiant energy capable of causing damage to the eye is provided by Ham et al. (ref. 13) and Glasstone (ref. 14). A quantitative estimate can be made from the experimental data taken on rabbits by Ham et al. From the curves in this paper, the minimum rate of thermal energy needed to produce a lesion on the retina is 37 cal/cm^2 sec. for an exposure time of 0.025 sec. and for a retinal image which is 1.1 mm in diameter. An equation is given, enabling us to calculate the minimum energy, incident upon the cornea, needed to produce a lesion. This is $\emptyset_c t = \emptyset_R t \dfrac{d^2 f}{D^2 K}$.

In which $\emptyset_c$ = Minimum rate of radiant energy incident upon cornea in cal/cm^2 sec.

$\quad\quad\quad\emptyset_R$ = Minimum rate of radiant energy incident upon retina in cal/cm^2 sec.

$\quad\quad\quad$ t = Exposure time

$\quad\quad\quad$ D = Pupillary diameter at time of exposure, taken as 8 mm

$\quad\quad\quad$ d = Diameter of image on retina in mm

$\quad\quad\quad$ k = Average transmission coefficient of eye for the given spectral distribution

$\quad\quad\quad$ f = Form factor to correct for shadow of carbon arc holder on retina

Substituting, we obtain:

$$\emptyset_c t = \emptyset_R t \cdot \frac{d^2 f}{D^2 K} = 37(0.025) \frac{(1.1)^2 \times 0.873}{(8)^2 \times 0.8}$$

$$= 0.021 \text{ cal/cm}^2$$

E. Valve Performance at Different Distances from Atomic Flash

For the calculations in the original report a retinal image of 1.1 mm diameter was assumed, since it seemed that damage was more likely in the case of large images. The size of the image is determined by the distance from the explosion and by the size of the resulting fireball. Therefore, consideration must be given to the behavior of the proposed valve under two unfavorable circumstances:

1) The distance from the explosion is so great that the valve closes only partly.

2) The distance from the explosion is so small that the energy in the first pulse of thermal radiation is enough to damage the retina. During this short time the average diameter of the fireball is smaller and therefore injury is more probable.

In order to illustrate the results of effects like these, calculations are made for various distances from a 20-kiloton explosion. These distances were chosen so that the results of Ham's group (ref. 13) could easily be applied. Other numerical data were taken from Glasstone (ref.14). The results are summarized in Table III, in which all energies are in cal/cm^2.

We felt that the probability of an eye blinking within 150 milliseconds is great, so that some of the calculations are based on that time interval. The proper values for the fireball diameter and threshold energy for this time are in some doubt. The values (R = 780 feet and the threshold energy for 100-millisecond exposure) were chosen for arithmetical convenience and appear conservative. In the final column an attempt is made to show the effects during

12.

the initial short pulse of thermal radiation at a distance of 2.3 miles. It is assumed that, during this short time, the diameter of the fireball is only 390 feet and, therefore, the image size is reduced accordingly. The increased hazard under these conditions can be clearly seen. However, at the present time only a guess can be made of threshold energy for such a short exposure time.

The benefits of a phototropic valve for a variety of conditions are clearly shown in this table. It should be noted that the calculations assume a very clear atmosphere and complete dark adaptation for the eye. The results would be more favorable for a normal pupillary diameter of 4 or 5 mm.

TABLE III

ENERGY RELATIONSHIPS FOR DIFFERENT DISTANCES FROM 20KT EXPLOSION

d = diameter of retinal image	mm	0.18	0.24	0.365	0.71	1.1	0.55
Q_R = threshold energy on retina to produce damage during 100-millisecond exposure	cal/cm²	7.0 (est)	5.3	4.1	2.2	1.3	1.3
Q_c = threshold energy on cornea to produce damage during 100-millisecond exposure	" "	0.0049	0.0063	0.011	0.0256	0.0308	0.0077
R = distance from fireball needed for image size Diam. of fireball = 780 ft.	miles	14.2	10.5	7.0	3.5	2.3	2.3
Total energy incident upon cornea from fireball	cal/cm²	0.0105	0.034	0.14	0.51	2.7	2.7
Energy incident upon cornea before blink = 20% of total	" "	0.0021	0.0068	0.028	0.12	0.54	0.027 (0.015 sec.)
Visible energy passing through phototropic valve in 150 milliseconds. Initial density = 0	" "	0.00092	0.0023	0.0053	0.002	0.0032	0.0059 (0.015 sec.)
Visible energy passing through phototropic valve in 150 milliseconds. Initial density = 0.3	" "	0.00040	0.0011	0.0031	0.004	0.0013	0.0034 (0.015 sec.)
Total visible light energy passing through a valve in 3 sec. initial density = 0.3	" "	0.0016	0.0034	0.004	0.004	0.004	0.004

F. Results

A comparison of the results in Parts C and D above show that the operation of the valve as a protective device against thermal radiation from a nuclear flash would be marginal. Furthermore, its operation would depend upon the practical absorption band width, absorption coefficients, speed of the phototropic reaction, the quantum yield and the efficiency of a near infrared filter. The valve must close quickly in order to provide adequate protection.

G. Response to Solar Radiation

When exposed to the indirect radiation from the sun, the valve should not close to an extent so as to impair visibility. The total density produced depends upon the rate of the incident radiation and the rate of the reverse reaction. An estimate of its importance can be made when data on reaction rates are available.

13.

A valve of this type might also serve as a protective device against the high ambient light conditions (e.g., sun glasses of variable density). For this application some of the requirements are not quite the same as those considered above; e.g., reversibility is very important and the rates of opening and closing might be much different from those for a nuclear flash. For the present purpose, it can be shown that the ultraviolet energy absorbed from the sun's radiation is capable of closing a valve within a reasonable time. We assume that the sun may be considered as a black body at a temperature of 5800° K, and find (from the Radiation Calculator) that 7.7 percent of the total radiant energy lies between 3200 Å and 4000 Å. Since the total rate of radiation from the sun is 0.0323 calories/cm^2/sec., the rate of ultraviolet energy is 0.077 x 0.0332 = 0.00256 cal/cm^2/sec. By the method used in part A of this Section, it is found that the ultraviolet energy required to close the valve to a condition where optical density (D) equals 2 is 0.0119 cal/cm^2. The time required for the sun's radiation to close the valve to this condition is then:

Time to develop a density of two for sun glasses = $\frac{0.0119}{0.00256}$ = 4.6 sec.

It should also be noted that the ultraviolet energy radiated by a tungsten lamp is so small that it would have a negligible effect upon the valve.

14.

DESIGN CONSIDERATIONS FOR PHOTOTROPIC VALVE

A.   Design

The valve system should provide an area of at least 2 inches in diameter which is clear with high transmission when in the open state. In the closed state the absorption in the visible should be proportional to the ultraviolet energy in the ambient light. Preferably the absorption should be uniform throughout the visible position of the spectrum, but other spectral distributions might be acceptable.

The construction could comprise, for example, a laminated sandwich having the following elements:

(a)   A scratch-resistant, optically flat rigid sheet of material trans-parent to near ultraviolet and visible light. This might be quartz, glass, or methyl methacrylate.

(b)   A layer of phototropic material, either in a liquid solution or incorporated in a plastic. The latter arrangement is preferable. The plastic must be capable of being laminated for good adhesion and optical contact with the other elements of the sandwich. One possible material is polyvinyl butyral. It might be desirable to use a mixture of phototropic materials having, for example, comple-mentary colors to broaden the absorption band. If ultraviolet-absorbing materials act as sensitizers for the reaction, they could be mixed with the phototropic materials.

(c)   An ultraviolet and infrared absorbing material with good visual transmission. This should be rigid, scratch-resistant, and optically flat. One possibility is E-Z eye or Solex glass with a coating of an ultraviolet absorbing material, such as phenyl salicylate in cellulose nitrate. Another is cast polyester resin, containing an ultraviolet absorber, such as cinnamaldazine and an infrared absorber such as a copper compound.

Where infrared rays tend to aid the reverse chemical reaction, i.e., to open the valve, the location of an infrared absorber within the assembly will depend upon whether it is desirable to discourage or accelerate the reverse reaction. For example, if it is placed in front of the phototropic layer, the reverse reaction will be retarded.

The rise in temperature of the phototropic layer, arising from the absorption of radiation from a nuclear flash, is of importance and the thickness of the layer will be largely determined by this factor. Calculations of this temperature rise will be made for one extreme condition.

B.   Temperature Rise in Phototropic Layer

One important factor in the design of a phototropic valve is the temperature rise of the plastic layer containing the phototropic material. The expected rise is calculated for an exposure at a distance of 1 mile from a 20KT flash. In this calculation the dissipation of heat is neglected because of the short time.

It is assumed that all of the radiation between 3200 Å and 7000 Å is absorbed and that the layer has properties similar to those of methyl methacrylate plastic (specific heat of 0.35 cal/gm°C and specific gravity of 1.1).

From Glasstone (see ref. 14) it is found that the total radiant energy is 20 cal/cm² and from the Radiation Calculator (6500° K), it is found that 50 percent of the energy is included between 3200 Å and 7000 Å . Then for a layer 1 cm thick:

$$\text{Temperature Rise} = \frac{20 \times 0.50}{0.35 \times 1.1 \times 1} = 25° \text{ C.}$$

A layer 1 millimeter thick would have an intolerable temperature rise of 250° C.

If sufficient ultraviolet energy is not available to activate the devices to the proper level, one of the two following arrangements might be useful:

1. The design could include an optical system which would concentrate the rays within a smaller area to increase the activating energy per square centimeter.

2. The incident light could trigger a secondary source of activating ultraviolet provided as an integral part of the system.

There would also be some advantage in maintaining the phototropic layer at some tolerable initial density D_1 (chemically, thermally, or by a lamp), so that the valve is partially closed when the radiation from the atomic flash strikes it. If D_1 is chosen as 0.3, so that the initial transmission is about 50 percent, the visible energy coming through the valve as it closes is only one-half that calculated in "Visible Light Energy Transmitted by Valve," pages 9 to 11.

16.

LOCAL EXPERIMENTS ON PHOTOTROPIC MATERIALS

The results of some of our preliminary experiments on phototropic materials are as follows:

Initial laboratory work was devoted to evaluating phototropic properties of methylene blue and thionine dyes. It was found that water solutions of methylene blue 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, also, 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 ascorbic acid as the 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 takes place in solid solutions.

An unusual effect was revealed with methylene blue when it was reduced in the dark by titanous chloride. A solution of the leuco methylene blue and colloidal titanium dioxide resulted. When illuminated, the methylene blue color developed due to the reoxidation by the insoluble titanium dioxide. 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.

17.

The crystal violet color is bleached out by the judicious addition of an alcoholic solution of potassium cyanide or hydroxide. When the colorless solution is placed in sunlight or in some other source of 3000Å to 4000Å irradiation, the original crystal violet color developed 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 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. The forward reaction is not sensitive to temperature. Continued exposure to light results in a fading of the color which is attributed principally to the increase in back reaction caused by the increased temperature due to 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 were revealed to be phototropic as listed in Table IV. 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.

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 IV

PHOTOTROPIC TRIPHENYL METHANE DYES

Color Index No.	Name
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

18.

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 dyestuffs and several inorganic compounds. Although many exhibited photochemical characteristics, they were discarded generally because of lack of reversibility, slow reaction, or insufficient color change.

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