

## Protection Against Intense Light. III. The Use of Commercial Dyes in Thermal Protection

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### Synopsis

Experimental evidence is offered showing that commercial dyes can be used to provide protection against intense light energy. An estimate of the amount of material required/cm<sup>2</sup> to protect the skin, clothing, or houses is given.

### INTRODUCTION

Evidence was presented in a prior article<sup>1</sup> indicating that some materials provide unusually good thermal protection by the following three-step mechanism: (1) the material decomposes yielding gases and compounds containing chromophoric groups; (2) the compounds containing chromophoric groups vaporize and expand or are propelled by the gases into the region between the target and the source of radiant energy; and (3) the compounds containing chromophoric groups intercept photons and reradiate or dissipate the energy to the air as heat. The obvious ramification of this mechanism is that, if it is valid, one should be able to reduce the system to its essentials, dyes and a carrier, and obtain substantial, perhaps adequate, thermal protection with a feasible weight of material. The dyes (a) should have low molecular weights, (b) should have high molar absorptivities, (c) should volatilize before they decompose, (d) should not ignite nor decompose to toxic materials, (e) should cover the range of injurious radiation, and (f) should be stable for at least 1-2 min in air at elevated temperatures. The dyes should be dispersible in the carrier and preferably dissolve therein. The carrier should be a material which is inert to the substrate and to the dyes, should adhere or be attachable to the surface to be protected, and should decompose mainly into gases (which do not ignite, are not toxic, and do not react with the dye or substrate) before the substrate is injured or the dyes decompose. The weight of the dye-carrier system should be so low that it does not impose an appreciable burden on the substrate. The dyes probably need not be stable at temperatures much above that at which their vapor pressures are substantial because such temperatures probably will not be reached. There are two cooling processes which will operate to keep the temperature of the dyes down. First, the energy intercepted by the dye vapors is transferred to the air. Second, this air expands

rapidly thereby cooling itself and the dyes. (A quenching agent would also help to transfer the energy from the dye molecules to the air.)

The present objective is to show that commercial dyes and a carrier can be used to provide a substrate with substantial thermal protection via a mechanism analogous to the above three-step mechanism: when intense light energy strikes the dye-carrier combination, (1) the light is absorbed decomposing the carrier mainly into gases, (2) the gases propel the dyes toward the source of light, and (3) the dyes volatilize, intercept the photons, and reradiate or dissipate the energy to the air as heat thereby protecting the substrate. The use of dyes in the protection of the skin, clothing, and real estate will be discussed. For brevity, the word "dyes" will be used in place of the technically accurate phrase "compounds containing chromophoric groups" and will be defined to be any material or substance (including pigments) which can intercept photons of any wavelength and possibly fluoresce.

### EXPERIMENTAL

A cream<sup>2</sup> was developed over a period of years by the U.S. Army Natick Laboratories for the thermal protection of the hands and face against the intense light energy of a thermonuclear explosion. Of all the immediately available materials and compositions thereof, this cream was found to be the best usable system. The carrier chosen for these experiments was a modification of this cream. The modification consisted primarily of the omission of those constituents which conferred compatibility with the skin and the replacement of titanium dioxide by iron oxide. One formulation of the modified cream is given in Table I. This mixture was put through a three-roll mill twice at room temperature as quickly as possible. Milling is required to disperse the ingredients evenly, especially when dyes are present. Because of the evaporation of the water and CCl<sub>4</sub> during milling, the percentages of the constituents after milling were no longer precisely those given in Table I. The tetrachlorohexafluorobutane, a solid, was added be-

TABLE I  
Composition of the Modified Cream Used as the Carrier

| Material  | Per cent | Supplier            |
|---|----------|---------------------|
| Chlorowax 40 (liquid)                                   | 11       | Diamond Alkali      |
| Chlorowax 70 (solid)                                    | 34       | Diamond Alkali      |
| Iron oxide  | 11       |                     |
| Methyl cellulose (thickening agent)                     | 0.5      | Hercules Powder     |
| Halocarbon 446 (solid)<br>(tetrachlorohexafluorobutane) | 8.8      | Halocarbon Products |
| CCl <sub>4</sub>  | 18       |                     |
| Triethanolamine   | 0.1      |                     |
| Water   | 16       |                     |
| Dye (if used)   | 0.6      |                     |

cause it should not volatilize as rapidly as the water and  $\text{CCl}_4$  during milling. The modified cream without any dyes is the control.

### APPARATUS AND PROCEDURE

The test block consists of: (1) a transite block 1 in. thick and 4 in. square containing a butt-welded, 0.005-in.-diameter thermocouple in the center of one face, and (2) a sheet of stainless steel  $\frac{1}{16}$  in. thick and 4 in. square with a centered hole 2 in. in diameter. The stainless steel sheet is fastened to the surface of the transite block which has the thermocouple and is centered so that the thermocouple is at the center of the hole. The test block now offers a "well"  $\frac{1}{16}$  in. deep and 2 in. in diameter. The well is then filled with the test material, i.e., the modified cream with or without dyes, and smoothed with a spatula to provide a disc of material  $\frac{1}{16}$  in. thick and 2 in. in diameter with a thermocouple in the center of the rear surface.

The test block containing the material is placed in a vertical position at one focus of the single elliptical carbon arc-image furnace<sup>1,2,3,4</sup> and exposed for 3 sec at 18.5 cal/cm<sup>2</sup> sec. (The carbon electrodes are at the other focus, and the major axis of the ellipse is horizontal.) The change in temperature of the thermocouple was recorded on a strip-chart recorder, and the maximum temperature rise,  $\Delta T$ , was determined. Three exposures were made using 3 samples of each modified cream with or without a dye and the resulting  $\Delta T$  values were averaged.

### RESULTS AND DISCUSSION

Data for 15 dyes (all that could be tested before this investigation was terminated) are given in Table II. Although three significant figures are reported, the test results are not that accurate. Judging from the spread of the three  $\Delta T$  values for each modified cream-dye combination, the data are within  $\pm 1^\circ\text{C}$ . The response of the test sample to the radiant energy was instantaneous, vigorous, and steady.

Xanthone gave the best performance, which was a drop in the  $\Delta T$  value of  $18 - 11.3^\circ\text{C} = 6.7^\circ\text{C}$ , or 37%. Although this improvement is certainly not phenomenal, other factors must be considered before reaching an opinion. These are (a) the mechanism by which the modified cream provides protection, (b) the temperature at which the mechanism operates, and (c) the effect of dyes on surface charring. They will be discussed in that order.

In order to demonstrate the effectiveness of dyes in attenuating light energy, the mechanism by which the modified cream (carrier) provides protection should not involve dyes. Unfortunately, this does not appear to be the case. Excluding the iron oxide from consideration for the moment, the modified cream (Table I) consists mainly of Chlorowax and volatile materials. Chlorowax 40 and Chlorowax 70 are straight-chain compounds and contain 40% and 70% chlorine, respectively, with the chlorine atoms randomly distributed along the chain. The average constituent of

TABLE II  
Some Dyes and Their Average  $\Delta T$  Values

| Carrier        | Dye                 | % Dye | $\Delta T$ , °C |
|----------------|---------------------|-------|-----------------|
| Modified cream | No dye, control     | —     | 18.0            |
| "              | Congo Red           | 0.6   | 19.9            |
| "              | Rosaniline HCl      | 0.6   | 19.3            |
| "              | du Pont TLA 1351    | 0.6   | 16.2            |
| "              | 9-Fluorenone        | 0.6   | 16.1            |
| "              | du Pont TLA 1350    | 0.6   | 16.0            |
| "              | du Pont TLA 1352    | 0.6   | 15.9            |
| "              | Phenolphthalein     | 0.6   | 15.8            |
| "              | Fluorene            | 0.6   | 15.4            |
| "              | Heliogen Green      | 0.6   | 15.3            |
| "              | Naphthol Yellow     | 0.6   | 15.2            |
| "              | Sherdye Blue        | 0.6   | 14.9            |
| "              | Heliogen Blue       | 0.6   | 14.6            |
| "              | $\beta$ -Carotene   | 0.6   | 11.7            |
| "              | Orange G (83% pure) | 0.6   | 11.5            |
| "              | Xanthone            | 0.6   | 11.3            |

Chlorowax 40 would probably be near  $C_{21}H_{37}Cl_7$ , and for Chlorowax 70, near  $C_{24}H_{28}Cl_{22}$ .<sup>5</sup>

Since the original cream gave excellent thermal protection, and since the three-step mechanism listed above can also result in excellent protection, we will investigate this route of energy attenuation. It has been found<sup>1</sup> that when the three-step mechanism is operable, it usually surpasses all other routes of energy attenuation. Keeping the total weight of Chlorowax 40 and Chlorowax 70 the same and starting with only Chlorowax 40 in the modified cream (carrier), as the Chlorowax 40 was replaced by Chlorowax 70, the  $\Delta T$  values fell to a minimum of 50% of the initial value. (Replacement of all of the Chlorowax 40 by Chlorowax 70 gave an intractable system, since the former is a liquid and the latter a solid at room tempera-

TABLE III  
Spectra of Conjugated Polyenes,  $H(CH=CH)_nH$ ,  
in 2,2,4-Trimethylpentane

| $n$            | $\lambda_{max}$ , $m\mu$ | $\epsilon_{max}$ |
|----------------|--------------------------|------------------|
| 2 <sup>a</sup> | 217                      | 21,000           |
| 3              | 268                      | 34,000           |
| 4 <sup>b</sup> | 304                      | —                |
| 5              | 334                      | 121,000          |
| 6              | 364                      | 138,000          |
| 7              | 390                      | —                |
| 8              | 410                      | —                |
| 10             | 447                      | —                |

<sup>a</sup> In hexane.

<sup>b</sup> In cyclohexane.

ture.) Since the H/Cl ratio in Chlorowax 40 is about 5/1 and in Chlorowax 70, about 1.3/1 (these ratios are essentially independent of the molecular weight), it is apparent that much more HCl can split off from the Chlorowax 70 than from the Chlorowax 40, hence increasing significantly the probability of obtaining conjugated sequences of double bonds called polyenes. Polyenes have a high molar absorptivity,  $\epsilon$ , in the ultraviolet (UV).<sup>6</sup> See Table III.<sup>7</sup>

It appears that during irradiation the water, the  $\text{CCl}_4$ , and the tetrachlorohexafluorobutane simply volatilize and propel the degraded Chlorowax molecules containing various polyene segments between the target and light source, where they intercept energy across the UV and part of the visible spectrum and dissipate it to the air as heat. On this basis, since the Chlorowax 70 will provide greater concentrations of polyenes, use of the Chlorowax 70 should show improved performance, which it does.

In the original cream, titanium dioxide was used on the basis that it was white and would reflect much of the light energy. This may be the case. However, replacement of the titanium dioxide by an equal weight of iron oxide ( $\text{Fe}_2\text{O}_3$ ), which is red, also in the finely pulverized state, gave a substantially lower  $\Delta T$ , indicating that reflectance is not that important a factor, a conclusion reached earlier.<sup>28</sup>

If the iron oxide is omitted from the control, on irradiation the temperature of the thermocouple rises abruptly immediately after the shutter of the carbon arc-image furnace opens at the start of the exposure. This information is obtained from a strip-chart recorder which records not only the output (temperature) of the thermocouple but the opening and closing of the shutters (using a separate pen). When the iron oxide is included, the temperature of the thermocouple begins to rise usually after the shutters close at the end of the exposure. There is no question that when the iron oxide is not present, radiant energy is reaching the thermocouple, and when the iron oxide is present, the energy reaching the thermocouple is primarily heat conducted through the disc from the pyrolyzed surface of the disc. Apparently, the iron oxide is absorbing radiant energy in the blue, violet, and perhaps UV, which is reasonable since the iron oxide is red. (Iron oxide transparent in the IR.<sup>8</sup>) The iron oxide therefore probably reaches a higher temperature than the titanium dioxide, since the latter is white. This will cause more extensive decomposition of the Chlorowax, resulting in a greater degree of polyene formation; it will also heat the propellants to a higher temperature, resulting in more efficient propulsion of the decomposition products in front of the target and thereby provide the improved thermal protection obtained.

From the behavior of the system as Chlorowax 40 is replaced by Chlorowax 70 and titanium dioxide is replaced by iron oxide, and from the known pyrolysis behavior (dehydrochlorination) of this type of material,<sup>1</sup> the thermal protection offered by the modified cream undoubtedly acts primarily via the three-step mechanism given in the introduction, with polyenes acting as the dyes.

Xanthone also absorbs mainly in the UV,<sup>9</sup> however. Consequently, if the polyenes and xanthone did not both absorb in the UV, the improvement in the  $\Delta T$  would be better than 37%. Apparently, the thermal conversion of the Chlorowax to polyenes is rather inefficient. This is not surprising since the chlorine atoms are randomly distributed along the carbon-carbon chain.

Since  $\beta$ -carotene and Orange G absorb in the UV and blue, whereas xanthone, being white, absorbs only in the UV, one would expect the  $\Delta T$  values for  $\beta$ -carotene and Orange G to be lower than the  $\Delta T$  value of xanthone. If all three compounds were equally stable, this would undoubtedly be the case, but xanthone is stable up to about 850°C<sup>10</sup> whereas the others are not. While it appears that the  $\beta$ -carotene and Orange G are decomposing rather rapidly, their vapors must survive the heat long enough and be replaced quickly enough to give considerable protection. A drop in the  $\Delta T$  of 37% appears large since light from the sun or a thermonuclear explosion does not have such a high proportion of energy in the UV. Those wavelengths shorter than 400 m $\mu$  constitute less than 5% of the total sunlight,<sup>11,12</sup> and the spectrum of light from a thermonuclear explosion is roughly similar to that of sunlight.<sup>13</sup> The carbon arc-image furnace, however, does provide a higher percentage of energy in the UV because of the cyanogen bands at about 360, 390, and 420 m $\mu$ . The combined bands at 360 and 390 m $\mu$  appear to be about 50% more intense than any other span of equal width in the carbon arc emission spectrum.

Turning now to the second consideration, the temperature at which the mechanism operates, the pyrolysis temperature of the Chlorowax is obviously a factor, since some dyes will not survive this temperature. After pyrolysis, since the surface of the control is charred, the Chlorowax must have decomposed. Poly(vinyl chloride) decomposes at about 230°C.<sup>14</sup> Since Chlorowax is somewhat similar in composition to PVC (excluding chain length) and both compounds dehydrohalogenate on pyrolysis, one would expect their decomposition temperatures to be about the same. Consequently, when dyes are included, they must also reach about 230°C. In many cases, the dyes will decompose below 230°C increasing the amount of char on the surface, which will not only impede the propulsion of the polyenes and deflect them to the side but also absorb more light energy and thereby increase the  $\Delta T$  value. If the dye survives 230°C, when expelled into the air it may ignite immediately and be destroyed or decompose, leaving the  $\Delta T$  value unaffected. Finally, if the dye survives 230°C and volatilizes significantly, it should provide a measure of thermal protection. Hence, one would expect to get a spread of  $\Delta T$  values below and above the control  $\Delta T$  value, and one does. If the carrier decomposed at 130°C instead of 230°C, substantial improvement in the  $\Delta T$  values could be expected in many cases because, if the dye is not very stable thermally, more dye will survive and provide protection; and since the temperature of the pyrolyzed surface is lower, less heat will be conducted to the thermocouple (substrate).

Finally, let us consider the effect of dyes on surface charring. The addition of dye to the control alters its pyrolysis behavior. The control is a carefully compounded system of Chlorowax, a colored, finely divided inorganic compound, and propellants. The concentration of the iron oxide is important. If the concentration is too high, the initial light energy of the arc is stopped in a very thin surface layer, causing this layer to char heavily and thus destroy the polyenes and impede propulsion by the water vapor and gases formed during decomposition. If the concentration is too low, radiant energy will reach the thermocouple. There is a concentration of iron oxide at which the Chlorowax decomposes so that the polyenes can be propelled from the surface, leaving a dirty brown surface and little, if any, char. Unfortunately, when the commercial dyes are added, they have the same effect as increasing the concentration of iron oxide, and excessive surface charring results. For each commercial dye, the proper level of dye and iron oxide concentrations would have to be determined. It is possible that in some cases no iron oxide will be needed. This is a desirable situation since it reduces the weight of the system.

In summary, then, comparison of the control with the control-dye combinations does not reflect the potential performance of the dyes because of complications brought about by the formation of polyenes from the Chlorowax, the elevated temperature at which the Chlorowax pyrolyzes, and the effect the dyes have on the component balance of the modified cream. Also, the dyes were tried singly.

Although the modified cream system leaves much to be desired, it has sufficed to prove the point, i.e., that small amounts of commercial dyes or other commercial compounds that absorb photons, when used according to the mechanism stated in the introduction, can provide substantial thermal protection against intense light energy.

### AMOUNTS OF DYES REQUIRED FOR THE PROTECTION OF THE SKIN, CLOTHES, AND HOUSES

Now that a mechanism is available whereby protection against intense light energy can be provided, we must now determine whether the weight of material required by this mechanism is feasible for actual use.

We shall assume that the skin, clothing, and real estate situated directly under a 10 MT thermonuclear weapon that explodes 3 miles above the ground are to be protected from the light energy released. (All computations are based on chapters VII and XI of Glasstone.<sup>13</sup>) The maximum radius of the fireball will be about 1.7 miles. Since 3.5 cal/cm<sup>2</sup> from this weapon at this distance delivered over the effective lifetime of the explosion (32 sec) will cause a first-degree burn on the skin, the total light penetrating<sup>13</sup> will be restricted to 3.2 cal/cm<sup>2</sup>. If this protection is provided to the exposed skin throughout the 32 sec, a first-degree burn should not result. A first-degree burn is a moderate sunburn with no blisters which heals without special treatment.<sup>15</sup>

The time at which the radiant power from the second pulse of a thermonuclear explosion is maximum,  $t_{\max}$ , is given by

$$t_{\max} = 0.032 \times W^{1/2} \text{ sec}$$

where  $W$  is the energy of the weapon in kilotons, in this case 10,000 kilotons. Therefore,

$$\begin{aligned} t_{\max} &= 0.032 \times (10,000)^{1/2} \\ &= 3.2 \text{ sec.} \end{aligned}$$

The effective duration of the explosion is  $10 \times t_{\max}$ , which is 32 sec. The maximum value of the thermal power,  $P_{\max}$ , corresponding to  $t_{\max}$  is given by

$$\begin{aligned} P_{\max} &= 4 \times W^{1/2} = 4 \times (10,000)^{1/2} \\ &= 400 \times 10^{12} \text{ cal/sec.} \end{aligned}$$

The area of a sphere 3 miles in radius is  $2.92 \times 10^{12} \text{ cm}^2$ . Consequently, the maximum power radiated is given by

$$\frac{P_{\max}}{\text{Area}} = \frac{400 \times 10^{12}}{2.92 \times 10^{12}} = 137 \text{ cal/cm}^2 \text{ sec.}$$

This intense irradiation peaks at 3.2 sec after the detonation of the explosion, and rises to and falls from this peak abruptly.

The light spectrum from the explosion extends from about 200 to 1400  $\mu$ . The atmosphere cuts off the light radiation outside this range. For the purpose of computation, it will be assumed that 15% of the light energy of a thermonuclear explosion is in the UV, 70% is in the visible, and 15% is in the near-IR. This is probably not too far from reality. Even if too much energy is allotted to the UV, the error is on the safe side, since the UV is much more damaging biologically than are visible and infrared rays,<sup>16-20</sup> and the UV will be screened the strongest.

Eventually, it may be possible to choose just two dyes which have combined molar absorptivities at various wavelengths that conform to the actual spectrum of light from a thermonuclear explosion. At present, several dyes will be required. Certainly, four dyes should cover this range well; one for the UV, two for the visible spectrum, and one for the near-IR. Since this is in part a feasibility study, three commercially available dyes and one proprietary dye were chosen. Their behavior when combined with a carrier and subjected to intense light energy is not known. They were selected because their molecular weights and molar absorptivities appeared to be representative, and because their absorption spectra covered the range of wavelengths required. At this time, no attempt will be made by the author to meet all the criteria for the dyes and carrier stated in the introduction because of the magnitude of the task. The four dyes chosen and their properties are given in Table IV. For the present, it will



TABLE IV  
Dyes and Their Properties Needed for the Calculations

|                       | Range covered | Energy allotted, % | MW    | MW used | $\epsilon_{\max}$ | $\epsilon_{\text{used}}$ | $\lambda_{\max}$ , $m\mu$ |
|-----------------------|---------------|--------------------|-------|---------|-------------------|--------------------------|---------------------------|
| Pentacene             | UV            | 15                 | 278   | 278     | 125,000           | 30,000                   | 310                       |
| Methyl violet         | visible       | 35                 | 394   | 394     | 73,000            | 50,000                   | 584                       |
| Malachite green       | visible       | 35                 | 364   | 364     | 68,000            | 50,000                   | 620                       |
| Proprietary Dye H-126 | near-IR       | 15                 | <2000 | 2000    | 50,000–100,000    | 50,000                   | —                         |

be assumed that the molar absorptivities of dye vapors are essentially the same as those found for dye solutions.

The combination of methyl violet and malachite green produces a black color ( $\epsilon$  is the molar absorptivity of the dye,  $\lambda_{\max}$  is the wavelength of maximum absorption). The proprietary dye, H-126, is an organic compound<sup>21</sup>; its actual molecular weight and physical properties are not available. It is used in absorptive and reflective lenses for goggles and helmet visors and necessarily has a window in the visible, a special feature not needed for this application. It is the only material known to the author with such a high molar absorptivity in the near-IR.

The computations for pentacene<sup>27</sup> will be carried out in some detail. Since the computations for the other three dyes are quite similar, only the results will be given.

Since the sunburn region (280–320  $m\mu$ ) is in the UV, very little energy in this region should be allowed to reach the skin. By trial and error, it was found that a concentration,  $c$ , of  $2.44 \times 10^{-5}$  g/cm<sup>3</sup> =  $8.7 \times 10^{-5}$  M/l. for a pathlength,  $b$ , 1 cm (in all cases) was enough to reduce the UV energy which penetrates to the substrate to 0.35 cal. This is shown by the following calculations. The average incident energy for each 1-sec interval from 0 to 32 sec was obtained from the scaled power-versus-scaled time curve given on p. 359 of Glasstone<sup>13</sup> referenced earlier. Each value was then multiplied by 15% to give  $I_0$  for the UV dye (by 35% for the dyes for the visible range and by 15% for the proprietary dye covering the near-IR). For each second, the energy transmitted,  $I$ , can be computed from the Lambert-Beer law:

$$\log I_0/I = \epsilon cb$$

$$\log I_0/I = 3 \times 10^4 \times 8.7 \times 10^{-5} \times 1 = 2.62$$

$$\log I_0/I = \log 410.$$

Hence  $I_0/I = 410$ ,  $I = I_0/410$ .

For the first second (0–1):

$$I_0 = 2.05 \text{ cal and } I = 0.005 \text{ cal}$$

For the second second (1-2):

$$I_0 = 14.4 \text{ cal and } I = 0.035 \text{ cal}$$

For the third second (2-3):

$$I_0 = 18.5 \text{ cal and } I = 0.045 \text{ cal}$$

For the fourth second (3-4):

$$I_0 = 20.5 \text{ cal and } I = 0.050 \text{ cal}$$

For the fifth second (4-5):

$$I_0 = 13.5 \text{ cal and } I = 0.033 \text{ cal}$$

These computations are carried out for the 32 sec. The values of  $I$ , when summed, equal  $0.35 \text{ cal/cm}^2$  total UV energy transmitted in 32 sec. These results and results from similar calculations for the other three dyes are listed in Table V.

Assuming that the area of the clothed body and the exposed skin is 2 square meters =  $2 \times 10^4 \text{ cm}^2$ , the total weight of dye required is  $2 \times 10^4 \text{ cm}^2 \times 16.56 \times 10^{-5} \text{ g/cm}^2 = 3.3 \text{ g}$ . Further, assuming that the weight of the carrier will be about the weight of the dyes, the weight of the dye-carrier system amounts to 6.6 g; allowing for a margin of safety of 100%, this amounts to 13.2 g (about the weight of three 25¢ pieces). Obviously, this is not a tiring amount for a person to carry. In the case where the vapor pressure of the dye is high at a temperature which is not injurious to the substrate, it may be possible to reduce the amount of carrier substantially or even, perhaps, to eliminate it.

The amount of dyes required for the protection of homes and buildings will vary with the wall and roof areas. The concentration of  $16.56 \times 10^{-5} \text{ g/cm}^2$  corresponds to  $3.4 \times 10^{-4} \text{ lb/sq ft}$ , and allowing a margin of safety of 100%, the concentration would then be  $6.8 \times 10^{-4} \text{ lb/sq ft}$ . To protect an area of 10,000 sq ft would therefore require 6.8 lb. (It might be possible to incorporate the dye concentration required to provide  $6.8 \times 10^{-4} \text{ lb/sq ft}$  in a commercial house paint.) To protect 10,000 sq ft of land (about  $1/4$  acre), 6.8 lb of the above dyes would have to be deployed above the

TABLE V  
Light Energy Penetrating the Four Dyes

|                 | Energy transmitted<br>over 32 sec,<br>$\text{cal/cm}^2$ | Concn. of<br>dye, ( $\text{g/cm}^2$ )<br>$\times 10^{-5}$ |
|-----------------|---|---|
| Pentacene       | 0.35  | 2.44  |
| Methyl violet   | 1.25  | 1.91  |
| Malachite green | 1.25  | 1.77  |
| Proprietary dye | 0.35  | 10.44   |
| Total           | 3.2   | 16.56   |

land just prior to the explosion. It would appear that there is not much point in protecting homes and buildings directly under a thermonuclear explosion from the intense light rays when they will be damaged, possibly crushed, by the shock wave. However, it does appear possible to mitigate all the destructive effects of a thermonuclear explosion by use of dyes.

So far, we have assumed that it is not a windy day. If a strong wind is blowing, the protective screen of dyes would have to be replaced as fast as it is blown away, and this will require considerably more of the dye-carrier system. At least some protection will be provided until military personnel realize what is happening (especially if they have been forewarned) and take some measure of evasive action such as turning around, lying down, or taking cover where possible. The wind would blow any dye dispersed in the air above land and property away quite quickly. One can only hope that all of one's neighbors had also decided to protect their land and property similarly.

Of course, there is no guarantee that the weapon will be 10 MT and detonate at a height of 3 miles. If the weapon is smaller or explodes at a greater distance, the above amounts of dye and carrier should suffice. If the weapon is larger than 10 MT and/or detonates closer than 3 miles, more dye and carrier will be needed. To get some idea of just how much more of the dye-carrier combination will be needed, assume for computational purposes that the weapon is 50 MT and that it also explodes at a distance of 3 miles above the ground. The maximum radius of the fireball will be about 2.9 miles. The scaled plot of power versus time will be similar to the prior one, but this time  $t_{\max}$  and  $P_{\max}$  are

$$\begin{aligned} t_{\max} &= 0.032 \times W^{1/2} = 0.032 \times (50,000)^{1/2} \\ &= 0.032 \times 225 = 7.2 \text{ sec} \\ P_{\max} &= 4 W^{1/2} = 4 \times 225 \\ &= 900 \times 10^{12} \text{ cal/sec} \end{aligned}$$

and the maximum power per square centimeter at a distance of 3 miles is given by

$$\frac{900 \times 10^{12}}{2.92 \times 10^{12}} = 308 \text{ cal/cm}^2\text{sec.}$$

Since the effective duration of a 50 MT explosion is  $10 t_{\max} = 10 \times 7.2 = 72$  sec, the energy transmitted per second must be reduced so that the total energy transmitted is less than about 4 cal to prevent a first-degree burn. The amount of dye required to attenuate the incoming energy in the UV, visible, and near-IR to a total of 4 cal/cm<sup>2</sup> over the 72 sec is about  $20.06 \times 10^{-5}$  g/cm<sup>2</sup>. This amounts to an increase of  $(20.06 - 16.56) / 16.56 = 3.50 / 16.56 = 22\%$ . Consequently, insofar as the Lambert-Beer law holds, it appears that somewhat larger weapons or closer distances external to the fireball still will not involve excessive weights of dye and carrier.

Because of the lack of spectra (molar absorptivity versus wavelength from 2000 to 14,000 Å) for the methyl violet, malachite green, and proprietary dye, there is no assurance that the effective molar absorptivity in the visible and near-IR does not dip below the value used in the calculations, namely 50,000. Compensating for this is the fact that pentacene has a molar absorptivity of 10,000 at 5800 Å (in the visible), methyl violet and malachite green absorb in the UV, and the proprietary dye absorbs in the visible and UV.<sup>21</sup> Also, we have assumed the atmosphere to be perfectly transparent, which is not true; that the molecular weight of the proprietary dye is 2000, which is probably too high; and we have ignored the fact that human skin reflects 15% or more of the light<sup>22</sup> and that flesh is relatively transparent in the near-IR.<sup>23,24</sup> Energy in the sunburn region of the UV is stopped by the epidermis,<sup>23</sup> which is only 0.1 mm thick except for the palms of the hands and soles of the feet.<sup>25</sup> However, energy in the near-IR penetrates from 5 mm to 25 mm into the flesh.<sup>20,26</sup> Hence, energy in the near-IR is distributed over a volume of flesh at least 50 times larger and the risk of a burn is correspondingly reduced. It is, therefore, doubtful that the concentration of proprietary dye listed in Table V,  $10.44 \times 10^{-5}$  g/cm<sup>2</sup>, is really necessary. Further research should substantially reduce the weight of dye(s) required.

### CONCLUSIONS

In the two prior articles,<sup>1,28</sup> it has been indicated or shown that the unusually good thermal protection offered by some materials when exposed to the carbon arc-image furnace cannot be attributed primarily to any one of the usual modes of energy attenuation, and that the simultaneous formation of dyes and gases can account for this improved performance. In this article, it has been demonstrated that small amounts of dyes added to a carrier are capable of providing enhanced thermal protection. It is therefore felt that the three-step mechanisms postulated in the introduction are valid. It is also felt that of the hundreds of dyes are carriers available or synthesizable, suitable dye-carrier pairs can be found for each substrate, which will provide substantial, perhaps adequate, thermal protection against a thermonuclear explosion via the mechanism described in the introduction, without using an excessive weight of material.

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