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A NEW APPROACH TO PROTECTION AGAINST INTENSE LIGHT ENERGY

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INTRODUCTION Approximately one-third of the energy of a thermonuclear explosion is emitted in one minute or less in the form of light and heat rays. This electromagnetic energy is capable of causing skin burns and starting fires at considerable distances from the point of burst; hence, it is referred to as "thermal radiation". For a one megaton thermonuclear weapon, for example, the radii for first and second degree burns are about 15 and 11 miles, respectively, and the radius in which newspapers will ignite is about 9 miles (1).

This report is concerned with showing that certain polymers automatically generate a significant measure of thermal protection on exposure to intense thermal radiation by the following mechanism: 1. the polymer decomposes yielding a gas and compounds containing chromophoric groups; 2. the gas propels the compounds containing chromophoric groups into the region between the polymer and the source of the radiant energy; 3. the compounds containing chromophoric groups vaporize, intercept the thermal photons, and reradiate or dissipate the energy to the air as heat. This constitutes the new approach to protection against intense light energy.

THERMAL BEHAVIOR OF POLYVINYLIDENE FLUORIDE In the search for means of protection from the intense thermal energy of a thermonuclear explosion, it was established by Barnes and Yelland (2) that of the polymers listed in Table I, polyvinylidene fluoride, PVF_2, provided the best protection. This was determined by preparing 10 discs of each polymer, each containing 5 percent of a colored additive to make them all opaque, and each 0.060 inches thick. These discs were then exposed to a single-elliptical, carbon arc-image furnace at an irradiance level of 23 cal/cm^2 for one second. The temperature

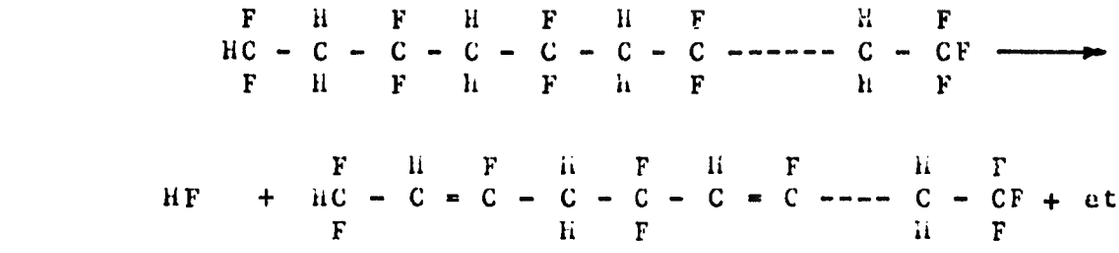
rise, ΔT (in degrees C), above ambient of a thermocouple placed on the rear surface of the disc was measured, the ten values were averaged, and the frequency of ignition of the decomposition products computed (2). This information is listed in Table I together with the polymer abbreviations to be used.

TABLE I

THE EFFECT OF HIGH-INTENSITY THERMAL RADIATION ON VARIOUS VINYL POLYMERS

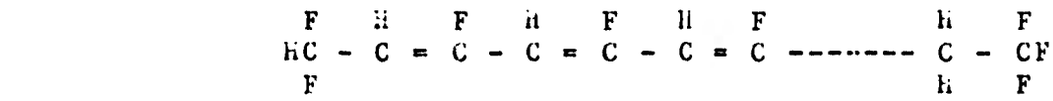
Polymer	Repeating Unit	Avg. ΔT (°C)	Frequency of Ignition (%)
Polyvinylchloride PVC	$-\mathrm{CH_2-CHCl}-$	22.3	100
Polychlorotrifluoroethylene, Kel-F	$-\mathrm{CF_2-CFCl}-$	13.0	0
Polyvinyl Fluoride PVF	$-\mathrm{CH_2-CHF}-$	16.8	100
Polyethylene PE	$-\mathrm{CH_2-CH_2}-$	19.2	100
Polytrifluoroethylene, PVF_3	$-\mathrm{CHF-CF_2}-$	11.3	0
Polyvinylidene Fluoride, PVF_2	$-\mathrm{CH_2-CF_2}-$	10.8	50
Teflon	$-\mathrm{CF_2-CF_2}-$	36.3	0

When pyrolyzed PVF_2 yields copious quantities of HF and a yellow to amber wax. A representative reaction is



gas yellow to amber, waxy fraction

Now, since the allylic position is relatively weak, under the intense heat more HF should split off so that the above reaction will proceed readily and some of the molecules with two double bonds should lose HF to produce



which is a molecule with three conjugated double bonds. This process can continue producing conjugation of longer wavelength anywhere in the degraded polymer chains (yellow wax).

Those molecules containing conjugated unsaturation together with the vast majority of molecules which undoubtedly do not, are propelled into the region between the polymer disc and the carbon arc-image furnace by the HF. Here the molecules with conjugated unsaturation intercept those light photons which lie within their absorption spectrum, go to a higher energy level, dissipate the energy via successive vibrational and rotational states while returning to the ground state, pick up a second light photon and continuously repeat the cycle provided they do not degrade or ignite. The half-life of the cycle will "generally vary down to 10^{-8} to 10^{-9} seconds" (3). Many chromophores consist of linear, conjugated unsaturation, called polyenes, and are quite efficient in intercepting thermal photons. As an example, consider the cyanogen bands of the carbon arc-image furnace (and peculiar thereto) at about 360, 390, and 420 mμ. The combined bands at 360 and 390 mμ are 40-50 percent more intense than any other span of equal width in the carbon arc emission spectrum. The molecule, $H-(CH=CH)_6-H$, a polyene, has a λ max at 364mμ and its absorption spectrum overlaps the two lower cyanogen bands. It has a molar absorbtivity (ε) of 138,000 (4). Assuming that $-(CH=CF)_6-$, a structure which could occur in the yellow, waxy fraction, also has these properties, the amount of material required to reduce the light intensity to 1/10,000 of its initial

value (an absorbance or optical density of 4) can be computed using the Lambert-Beer Law, $\log_{10}(Io/I) = ecb$ = absorbance = optical density, where Io is the initial light intensity, I is the intensity of transmitted light, e is the molar absorbtivity, c is the concentration in moles per liter, and b (= 1 cm) is the path length through the sample in cm.

$$\log_{10} (10,000/1) = 138,000 \times c \times 1$$
$$c = 2.9 \times 10^{-5} \text{ moles/liter}$$
$$c = 2.9 \times 10^{-8} \text{ moles/cc}$$

Since the molecular weight of H - $(CH = CF)_6$-F is 284 grams, the weight of this material required to block 99.99 percent of the light in the 364 mμ region and thereby protect 1.0 cm^2 of the polymer disc from light in that region is

$$2.9 \times 10^{-8} \times 284 = 8.22 \times 10^{-6} \text{ grams}$$
$$= 8.22 \text{ micrograms.}$$

Since the weight of the yellow, waxy fraction produced during a one second exposure to the arc is about 26 mg (5), it is entirely possible for such a small quantity of polyene linkages to arise, and even more probable that shorter polyene segments also will be produced and in greater amounts. Consequently, once the waxy fraction appears in the region between the PVF_2 disc and the light source, practically all of the energy below about 400 mu and about 1/3 of the light energy above 400 mu is intercepted and reradiated or dissipated to the air. Curves showing the carbon arc emission spectrum and the percent transmission of a 5 percent solution of the waxy fraction in spectroscope grade p-dioxane are shown in Fig. 1.

From Fig. 1. it is apparent that the energy of the combined cyanogen bands at 360 and 390 mu is less than 10% of the energy emitted by the arc, or, for one second, less than 2.3 cal. The amount of energy penetrating the 2, 4, 6, 8, 10, 12, 12 heptafluorododeca- 1, 3, 5, 7, 9, 11 hexaene, H-$(CH=CF)_6$-F, is therefore less than 0.00023 cal. On a bright day the intensity of sunlight is about 0.02 cal/cm^2 sec.

EXPERIMENTAL RESULTS There is considerable evidence for the presence of unsaturation in the pyrolysis products of PVF_2. Mass spectroscopy of the gaseous pyrolysis products of PVF_2 indicated the presence of

$$CH_2F - CH = CF - CH = CH - CF = CH - CF = CH_2$$

Note the presence of four conjugated double bonds. Also, practically all of the gaseous decomposition products contained unsaturation (9).

Examination of the yellow, waxy fraction showed:

1. Assuming the formation of one double bond for every 10 carbon atoms, the elemental analyses calculated and found are:

	C%	F%	H%
Calculated	40.0	57.0	3.0
Found	39.5	57.5	3.02
Found	40.7	56.1	3.17

Since there is about one multiple bond for 10 carbon atoms, there is a good chance for a small amount of conjugation.

2. IR absorption in the 1590 and 1600 cm^{-1} region which is characteristic of conjugated unsaturation (11) is strong.

3. UV transmission, Fig. 1. shows less than 1 percent transmission from 200 to 400 mu and then the transmission rises rather rapidly. Polyenes (hydrocarbon) show intense absorption up to 370 mu and then the absorption falls off rapidly (12). Thus the behavior of the amber waxy fraction in the UV conforms to what would be expected.

4. As stated earlier, as the number of conjugated double bonds in the polyene decreases the relative amounts of that polyene should increase, ie., there should be more polyenes containing 3 double bonds than there are containing 6 double bonds. Hence, the UV absorbance curve should peak where butadiene peaks, 217 mu (13), and it does.

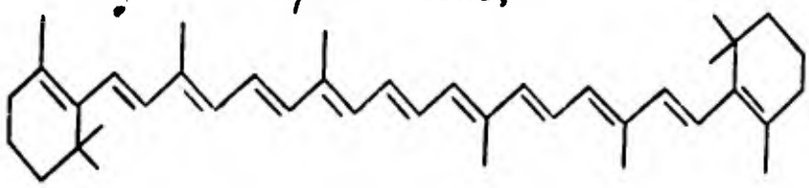
5. Since the wax is yellow it must absorb blue light, and, consequently, chromophores, which could contain conjugated unsaturation, must be present.

6. On standing for a period of time the wax hardens, just as paint hardens or "dries" when exposed to air. However, since paint "dries" by oxidation at double bonds, this implies the presence of double bonds in the waxy fraction.

For a given concentration of the polyene groups there is some thickness of the waxy fraction at which 99.9 percent of the thermal energy that lies within the absorption spectra of the polyene groups is intercepted.

Increasing the thickness so that absorption in the same region is 99.999 percent will not change the amount of light transmitted very much. The point is that above some thickness the light transmitted will be substantially independent of thickness. The approximate amount of light that should be transmitted by a "thick" layer of the amber, waxy fraction can be estimated from the curves of Fig. 1. At each point on the abscissa the product of the percent transmission and emission at that point on the abscissa can be plotted. The area under the resulting curve is a measure of the energy transmitted and amounts to about 50%. Since the concentrations of the various polyenes in the amber, waxy fraction is unknown, one cannot be any more specific. In any case, if one is to accept that the polyenes in the amber waxy fraction are responsible for most of the thermal protection afforded, a "thick" layer of the fraction should intercept a reasonable portion of the incident light based on the known behavior of polyenes (see para. 3, Experimental Results, above). When tested, using a thickness which should provide absorption above the 99.9 percent level (approximately 0.040 inches), 55 percent of the light from the arc was absorbed. Thus the yellow, waxy fraction absorbs a significant portion of the thermal energy and conjugated unsaturation is therefore a major factor in the thermal behavior of PVF_2.

As a check of this concept a saturated solution of a diphenyl polyene, β-carotene,



in a polyacrylate containing a solvent was prepared. The solvent was evaporated leaving an amber disc about 1/16" thick and 2" in diameter containing about 2.4 mg solute. β- carotene absorbs strongly from about 390 to 500 mμ (14), and weakly at bordering wavelengths. The wavelength at which maximum absorption occurs (λmax.) is 460 mμ, and the molar absorbtivity (e max.) at the wavelength of maximum absorption is 150,000. From Fig. 1, one would estimate that less than 50% of the light should be absorbed. On testing, using a clear control, about 40% of the light of the carbon arc was absorbed. There is then no question but that a polyene, protected from oxidation and dispersed as molecules, will absorb a significant fraction of the light energy of the arc.

DISCUSSION For PVF_2, the manner in which polyenes can be generated, their existence in the decomposition products, and their presence there in an amount sufficient to absorb a significant fraction of the incident light energy has now been established. It will now be shown, where applicable, that the energy attenuation by chromophoric groups (primarily polyenes) operating according to the mechanism postulated is the controlling factor determining the relative Δ T values occurring in Table I.

Since PVF_2 produces the most HF and, therefore, probably the greatest quantity of molecules containing conjugated unsaturation of all the hydrofluoropolymers, and of course PE and Teflon, and if such molecules are a major factor in energy dissipation, then PVF_2 should have the lowest Δ T value and it does. The fact that the Δ T value was the lowest despite the fact that the frequency of ignition was 50%, strongly indicates that the conjugated sequences survived the flames.

Turning now to PVF_3, it is apparent that HF can also split off in the same manner as for PVF_2. Consequently PVF_3 should have a low Δ T and it does. After removal of HF the conjugated sequences consist solely of carbon and fluorine. These should not ignite; the frequency of ignition should be low, and it is.

When HF splits off from PVF, unsaturated hydrocarbon segments are formed which should ignite readily destroying the conjugation, and generate a lot of smoke. Consequently the ΔT for PVF should be above that for PVF_2 and PVF_3, the frequency of ignition should be high, and a lot of smoke should be produced, all of which occur.

Thermal protective creams containing halogenated chemicals compounded at the U.S. Army Natick Laboratories have shown excellent thermal protection when exposed to the highest intensity of the electric arc for periods up to 6 seconds (15). Copious quantities of decomposition products were generated which expanded towards the light source. It was felt at the time that there might be some connection between thermal protection and these gaseous decomposition products (15). One of the ingredients of these creams is polychlorotrifluoroethylene, Kel-F (20). On pyrolysis, Kel-F, yields the same yellow-amber, waxy fraction (6) as does PVF_2, PVF_3 and PVF (7) which indicates the presence of chromophoric groups and a gas, monomeric trifluorochloroethylene (6). Since fluorine decolorizes the waxy fraction (6) the chromophoric groups

probably consist of conjugated unsaturation. With a zero frequency of ignition, the ΔT value should be below that of PVF and it is.

Since PE, on pyrolysis, would not yield significant amounts of conjugated unsaturation compared to PVF_2 and PVF_3 its ΔT value should be higher and it is. In this case the usual energy sinks such as endothermic decomposition, loss of high temperature material, etc. are the controlling factors.

It is known that PVC loses HCl very readily on pyrolysis (much more readily than PVF_2 loses HF). The amount of conjugated unsaturation produced should be much larger (8) and its ΔT value the very lowest of the group. There is a fundamental difference between the pyrolysis behavior of the two polymers, however. In the case of PVC the HCl comes off so readily (9) that relatively few carbon-carbon bonds are broken. Thus most of the conjugated sequences remain on the surface of the disc absorbing the thermal energy very efficiently which results in a high ΔT value. Here again the conjugated sequences are hydrocarbons so even if any are ejected in front of the disc they will provide little protection because they will be destroyed by the flames as in the case of PVF.

The surface of a Teflon disc after arc pyrolysis is brown to black. Chromophores are therefore present on the surface of the disc and the energy of the arc will be absorbed efficiently. Since the extent of decomposition is quite low, energy attenuation or dissipation by endothermic decomposition etc. is not available. The main factor here is probably reflection (only 9 percent because of the colored additive (5)) until the surface discolors. The ΔT value should be high and it is.

Since the halogen gases are colored in those cases where they are formed they will contribute to thermal protection (a low ΔT) just as the polyenes do.

Other channels which the incident thermal energy might take are: 1. reflection, 2. absorption causing a rise in temperature, 3. endothermic decomposition, 4. a change in phase, 5. loss of high temperature material, 6. conduction to the surroundings, 7. re-radiation, and 8. scattering by particulate matter (smoke). Although these various channels can and do serve as energy sinks for a considerable portion of the incident energy, none,

when considered individually, could explain the data of Table I. There is no doubt that energy attenuation by the mechanism described is the dominant factor in these experiments.

It is interesting to note that although blisters were raised on the surface of the plastic containing the β carotene by the energy absorbed, no char was formed. This indicates that thermal protection is not necessarily a function of char formation. This conclusion is supported by the fact that PVC, PE, Kel-F, PVF, PVF_2, and PVF_3 all show charred surfaces after pyrolysis on the carbon arc-ima-ge furnace but widely different Δ T values. The temperature reached by the material which actually absorbs the light photons is probably so high that the composition of this material for each polymer is practically the same, 90% carbon or better. Since char formation probably takes place in a fraction of a second in all cases, if it were a dominating factor in these experiments the behavior toward the impinging light energy should be substantially the same resulting in Δ T values which are close together. This is not the case. There are two other polymers which show extensive char formation on pyrolysis. These are the phenolic and the epoxy polymers. The phenolics yield xanthene (16), which on oxidation gives xanthone (17). Xanthone is stable up to 860 degrees centigrade and when it decomposes dibenzofuran results (18). All three compounds absorb strongly in the UV and dibenzofuran fluoresces (19). An epoxy was pyrolyzed at the U.S. Army Natick Laboratories and its UV spectrum is very close to the one for PVF_2 shown in Fig. 1. Hence, in addition to the char both polymers yield compounds containing chromophoric groups. Both polymers have been used in nose cones and motors of rockets. Also, it appears that even when the life of the motor is exhausted, the char remains. It is suggested that one of the reasons for the good performance of these polymers is that the decomposition products contain chromophoric groups which act as a "heat shield".

Polyenes transmit much of the light of wavelength greater than 500 $m\mu$. To block this energy and simultaneously reduce the system to its essentials one therefore needs a carrier and several pure compounds containing chromophoric groups which will together efficiently absorb thermal radiation of injurious wavelengths. When intense thermal radiation strikes this system it will be absorbed by the compounds containing chromophoric groups vaporizing them and decomposing the carrier mainly

into gases. The gases will propel the compounds into the region between the target and light source where they will absorb energy as described earlier.

A rough estimate of the amount of material required per square centimeter for actual use can be computed. Earlier it was calculated that 8.22×10^{-6} gms/cm^2 = 2.42×10^{-3} oz/yd^2 was required to block out the cyanogen bands. Allowing for a carrier and compounds containing chromophoric groups which will absorb outside of the cyanogen bands, the amount required for substantial protection should not exceed 0.2 oz/yd^2 (2 oz/yd^2 is considered a light coating on fabrics). This small weight of material required constitutes an important advantage of this approach. In fact on a protection afforded per gram of material ratio basis, it is difficult to even conceive of an alternate system that is better.

CONCLUSIONS The thermal protective mechanism deduced from the pyrolysis behavior of the polymers tested appears to be correct, and, used intelligently, should lead to optimum protection against the intense light energy from a thermonuclear burst or any other source.

In general, any combination of compounds containing chromophoric groups or which will react to provide such groups, dissolved or dispersed in a carrier which will generate or provide a propelling gas when exposed to thermal evergy should act as a "heat shield", ie, provide a measure of thermal protection.

The degree of protection depends on the temperature of decomposition or vaporization of the carrier, the amount of propellant produced by the carrier (conversion should be close to 100% to avoid char formation which absorbs energy efficiently), the volatility of the compounds containing chromophoric groups, the thermal stability of these compounds, their concentration in the carrier (the higher the concentration the more heat generated in a given layer of carrier and the sooner the compounds containing chromophoric groups are released), and the extent to which the absorption spectrum of the dyes covers the range of injurious thermal radiation.

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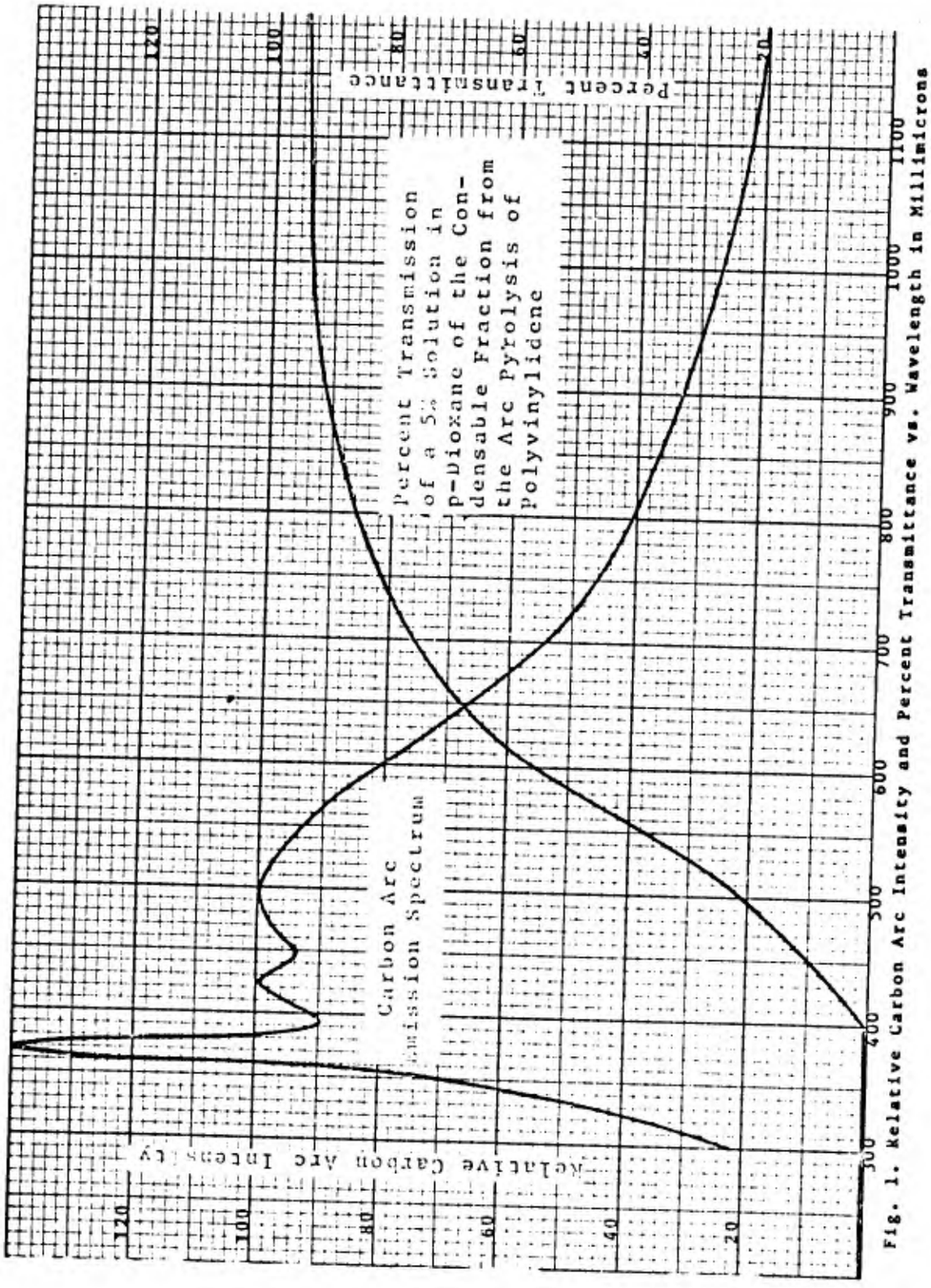

Fig. 1. Relative Carbon Arc Intensity and Percent Transmittance vs. Wavelength in Millimicrons