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Direct Determination of Inhibitors in Polymers by Luminescence Techniques

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▶ **Inhibitors are usually determined by a time-consuming extraction from the polymer, followed by an infrared or ultraviolet spectrophotometric measurement on the extract. Most inhibitors are complex aromatic compounds which exhibit intense ultraviolet absorption and therefore should show luminescence in many cases. Several common inhibitors were found to have strong fluorescence and/or phosphorescence of possible quantitative use. Luminescence procedures for the direct determination of some selected inhibitors in polymer films were developed. Factors—e.g., film thickness, concentration quenching, background absorption, etc.—affecting the linearity of the analytical working curves and the precision of the measurements were investigated. Quantum efficiencies for the absorption-emission processes were determined by a comparative method using computer techniques for correction and conversion of the spectra to units of quanta per unit frequency interval vs. frequency.**

Inhibitors are often added to polymers to prevent oxidation and degradation which cause undesirable changes in polymer physical properties. Quantitative determination of inhibitors in polymers is difficult and in many cases the inhibitor must be extracted before the analysis can be made. Following extraction, the most common "finishing techniques" have been infrared and ultraviolet spectrophotometry. Extraction is time-consuming and degradation of the inhibitor can occur over such long periods of time. Extraction is not always complete and a correction factor may be required.

Many inhibitors, because of their complex aromatic structure, absorb ultraviolet radiation. For this reason, one of the most useful techniques involves extraction followed by ultraviolet spectrophotometric measurement of the inhibitor in the extract (*2*, *12*). Inhibitors have been determined directly on pressed films of the polymer by ultraviolet spectrophotometry in this laboratory. This direct technique may be used for both infrared and ultraviolet spectrophotometric measurement of inhibitor content, particularly if an inhibitor-free wedge-shaped polymer film is used differentially in the reference beam. However, the ultraviolet technique is not useful if the inhibitor has no distinct sharp bands or if other components of the polymer or other additives exhibit intense absorption. Basically, the infrared spectrophotometric approach is not too sensitive and large samples are required.

Luminescence techniques offer some advantages over absorption techniques from the viewpoint of sensitivity and specificity. The use of a spectrophotofluorometer for the determination of *N*-phenyl-1-naphthylamine and *N*-phenyl-2-naphthylamine in vulcanized rubber after extraction has been reported by Parker and Barnes (*8*). They emphasized that the pine tar and other additives in the rubber seriously interfered with the absorption spectrophotometric method but not with the fluorometric method. In more recent work, Parker and Hatchard (*9*) discuss the possibilities of phosphorescence measurements in chemical analysis and include one inhibitor (*N*-phenyl-2-naphthylamine) in their studies. A rather extensive list of elastomer additives (accelerators, antiagers, softeners, fillers, and other ingredients) have been studied by Provorov and Zaĭtsev (*11*) for possible analysis by fluorescence techniques.

The purpose of our study was to develop techniques for direct measurement of inhibitors in plastics by making use of fluorescence and phosphorescence phenomena. There is little information in the literature on the quantitative aspects of the direct examination of polymer films by luminescence techniques. Plitt and Toner (*10*) have surveyed the literature covering the fluorescence of fibers, rubber, cellulose, polymers, and plastics. They emphasize that the studies reported to date were frequently based on subjective observations of fluorescence in which a broad spectrum of ultraviolet activating energy was used. Plitt and Toner (*10*) used an Aminco-Bowman instrument and were among the first to capitalize on the selectivity provided by an excitation monochromator in the study of cellulosic polymers.

Some studies of luminescent materials in polymeric matrices have been reported, but these have not been quantitative. Wahl (*13*) constructed an apparatus for polarization of fluorescent emission and studied polymers containing —NH or —NH_2 groups with which 1 - dimethylaminonaphthalene - 5 - sulfonic acid chloride reacted. From variation of polarization with change in temperature he deduced the relaxation time of the rotational unit in the polymer. Melhuish and Hardwick (*6*) observed phosphorescence of anthracene in Lucite at room temperatures and found that the half life at 300° K. (13 msec.) was not much different than that at 80° K. (20 msec.). Anufrieva and Saitzera (*1*) found that the phosphorescence of dyes in poly(vinyl alcohol) can be observed

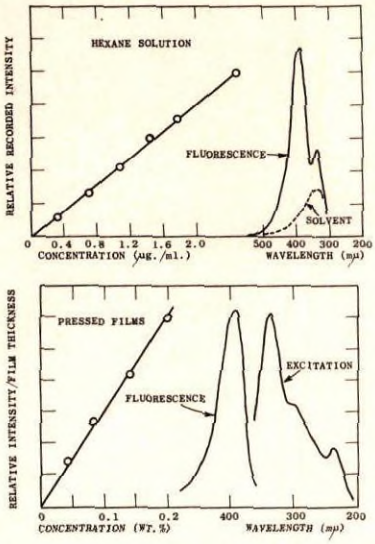


Figure 1. Fluorescence spectrum, excitation spectrum, and analytical working curve for Age Rite D in ethylene-propylene rubber

at room temperature without prior evacuation to remove oxygen which often quenches the emission in other systems.

Oster, Geacintov, and Khan (*7*) reported more extensive work on the luminescence of aromatic hydrocarbons in plastics, which serve as a better matrix than boric acid glasses, glucose glasses, or glycerol. They found that oxygen quenches the phosphorescence at room temperature but not at liquid nitrogen temperatures. Three methods of sample preparation were used by these workers: casting from a solvent, melting the polymer and studying the crystalline compound while pressure is being applied, and polymerization of a vinyl monomer in which the compound is dissolved.

Forster and Rickard (*5*) have indicated that work on phosphorescent plastics having long decay times at room temperature has been going on since 1957 in the laboratories of the General Post Office Engineering Research Station in England. These plastics were being developed for use in mail-coding applications. These authors found that the most effective activators contain one or more aromatic rings with substituent groups capable of reacting to form part of the resin molecule (usually cyanuric acid–formaldehyde resins). In all cases they found that $—SO_3H$ groups augmented the luminescence. These authors felt that the amino resins provided an environment which was particularly favorable to high phosphorescence efficiencies, even for dissolved species.

The work reported below covers a study of the luminescence of some selected inhibitors. Approaches to the direct determination of the inhibitor content of polymer films by fluorescence or phosphorescence are presented.

EXPERIMENTAL

Fluorescence and phosphorescence spectra were obtained with an Aminco-Kiers spectrophosphorimeter with fluorescence attachment. The excitation monochromator source was an Osram (xenon) lamp and the detector for the emission monochromator was a 1P28 phototube. Spectra were recorded with a Moseley Autograf X-Y recorder. The half life for phosphorescence was obtained by photographing the decay curve presented by a Hewlett-Packard oscilloscope with built-in time base.

For fluorescence measurements in solution, spectro grade hexane or isooctane (Matheson) was used. Phosphorescence spectra were obtained in a solid matrix at 77° K. prepared from a 1 to 1 (by volume) mixture of methylcyclopentane and methylcyclohexane (referred to as PH). These solvents were purified by percolation through a column of silica gel to remove aromatic impurities. Compounds which required a more polar solvent were dissolved in the more common EPA solvent (ether, isopentane, ethyl alcohol). Since all measurements were made at relatively high concentrations, background interference was small and it was not necessary to purify the EPA solvents further. Solutions were degassed with nitrogen and subsequently blanketed with nitrogen to prevent quenching by oxygen.

The inhibitors were used as supplied by the manufacturer without further purification.

An elastomer, ethylene-propylene rubber (EPR), was chosen for this study. Since the elastomer was soluble in aliphatic solvents, the inhibitor was added to the polymer dissolved in hexane and the solution was allowed to evaporate. Films were pressed from the inhibited polymer using a hydraulic press with heated and water-cooled platens. Heating was kept at minimum conditions (time and temperature) to prevent decomposition of the inhibitor. Flat mold plates were used and aluminum foil (Baker's, purified, 1-mil thickness) was used between the sample and the mold plates. The polymer film was stripped from the aluminum foil after immersion in liquid nitrogen. This procedure prevented stretching, which ordinarily caused the film to become partially opaque, interfering with quantitative measurement.

For fluorescence, the polymer films were mounted between two pieces of cardboard with a window cut to permit acceptance of the exciting radiation. The two pieces of cardboard were fastened (hinged) at the top and painted with dull black paint. The holder was designed to fit snugly into the 1-cm. square cuvette holder supplied by the manufacturer. The sample was placed in one of two possible diagonal orientations in the cell compartment so that either "frontal" or "inverse" excitation was achieved. In either case, the angle between the sample and the beam of exciting radiation was 45°.

Mounting film samples for phosphorescence was more difficult than

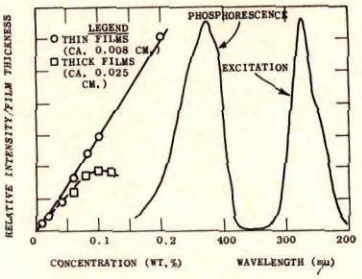


Figure 2. Phosphorescence spectrum, excitation spectrum, and analytical working curves for Santonox in EPR films

for fluorescence. Samples were immersed directly in liquid nitrogen contained in quartz Dewar flasks provided by Aminco. The holder was fashioned from a strip of aluminum folded double with a window cut to provide acceptance of the exciting radiation. The sample assembly was held by a slotted cork, which was also used to cover the top of the Dewar flask. In use, the film was usually oriented near 45° with respect to the exciting radiation. Final adjustments were made by moving the assembly (using the cork stopper) until maximum emission intensity was obtained. Adjustment was made not by rotating the holder (the 45° incident angle was maintained) but by lateral displacement in the direction of 90° with respect to the plane of the film. Positioning the film in this manner aligned the excited portion of the film with the entrance slits of the emission monochromator. Immersion of the polymer film and holder in the liquid nitrogen caused extended bubbling, but this was reduced or eliminated by careful filtering of the liquid nitrogen, before use, to remove ice crystals.

Recorded spectra were corrected and quantum efficiencies were calculated by procedures described in a previous publication (*4*).

DISCUSSION OF RESULTS

Age Rite D. Age Rite D, a polymeric form of trimethyldihydroquinoline, does not exhibit any well defined ultraviolet absorption band for spectrophotometric measurement in the presence of interfering background absorption. However, its fluorescence is intense and the excitation wavelength (340 mμ at higher concentrations) is high enough to be outside the region where most interfering substances would be excited to fluoresce.

Age Rite D may be determined directly in polymer cement before evaporation of the diluent. The concentration of inhibitor in the polymer cement is normally near 0.01 weight % at a polymer concentration of 5 weight %. Fluorescence intensity becomes linear with Age Rite D concentration below 2 to 5 p.p.m. when measured in a square 1-cm. cuvette. Therefore, samples were

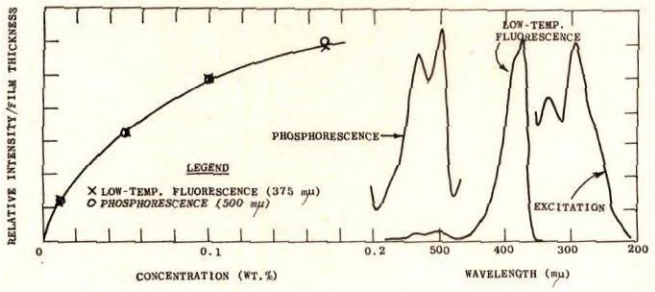


Figure 3. Phosphorescence, low-temperature fluorescence, and excitation spectra and analytical working curve for phenyl 2-naphthylamine in EPR films

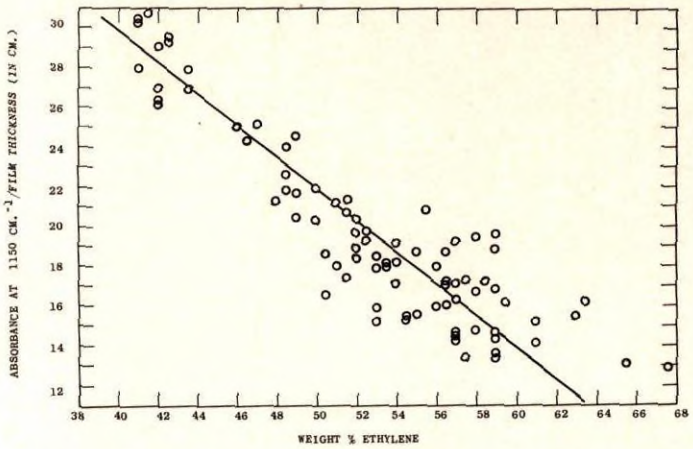


Figure 4. Correlation among infrared band intensity, composition, and thickness of EPR films

Used for determination of film thickness

diluted prior to direct measurement of the inhibitor by fluorescence. A typical spectrum and an analytical working curve are shown in Figure 1.

For the measurement of Age Rite D directly in pressed polymer films containing 0.1 to 0.2 weight % it was necessary to keep the films very thin (less than 0.01 cm.) in order to prevent concentration quenching. Intensities were placed on an equivalent basis by dividing the recorded intensity by the film thickness (path length). Typical spectra and a working curve for direct measurement of Age Rite D in polymer films are included in Figure 1. For these measurements an inverse type of excitation was used.

Rayleigh scattering becomes a greater problem in measurement of Age Rite D in polymer films than in solution. The excitation and emission wavelengths are not separated sufficiently to reduce the Rayleigh scattering in film measurements and large background corrections are required which reduce the precision of the film *vs.* the solution technique.

Santonox. Santonox, 2,2′-dimethyl-5,5′-di-*tert*-butyl-4,4′-dihydroxydiphenyl sulfide, has no sharp absorption bands and has only very weak fluorescence which may be exploited analytically. Its phosphorescence, however, is as intense as that of the parent compound diphenyl sulfide. Excitation and phosphorescence spectra and working curves are reproduced in Figure 2. For these measurements a frontal type of excitation was used. The film thicknesses were measured with a micrometer which introduces 5 to 10% imprecision, particularly for the thinner films. Some evidence of concentration quenching was indicated for the series of thicker films by the nonlinearity of the curve at higher inhibitor contents (see Figure 2).

Phenyl-2-naphthylamine. Phenyl-2-naphthylamine (PBN) is easily measured by ultraviolet spectrophotometry, as it has an intense sharp band at a wavelength high enough to reduce interference from background absorption caused by other additives or impurities. However, PBN exhibits rather intense phosphorescence and low-temperature fluorescence which may be used to advantage when other additives interfere in the absorption method. Typical phosphorescence spectra, low-temperature fluorescence spectra, excitation spectra, and working curves are included in Figure 3. A frontal excitation was used. The low-temperature spectra were obtained with the phosphorescence attachments but with the rotating can shutter removed. The nonlinearity of the analytical curve in Figure 3 indicates a strong concentration quenching effect even at the 0 to 0.05 weight % level. Thus, at a level of about 0.2% PBN, quantitative analysis would be difficult except for very thin films because of the observed "inner-filter" effect.

Measurement of Film Thickness. One of the most convenient methods of measuring polymer film thickness is by means of a mechanical thickness gauge or micrometer. Films thicker than about 0.02 cm. may be measured with an accuracy of about ±5% relative. However, to reduce inner-filter effects in the luminescence measurements, films should usually be less than 0.02 cm. (ca. 0.01 cm.) thick. At levels near 0.01 cm. the accuracy is probably not much better than ±10% relative. Under such conditions the measurement of film thickness is likely to be less reliable than measurement of the actual luminescence intensity.

A more precise method of measuring film thickness involves the use of infrared spectrophotometry. In the case of EPR, a correlation was established among infrared band intensity, composition, and micrometer film thickness from measurement of a large number of samples (see Figure 4). The composition of the copolymer was determined by use of the calibration data presented previously (*3*). In using the infrared procedure, the film was masked so that the infrared radiation passed through essentially the portion of the film used in the luminescence measurement. The results obtained by the infrared procedure and the thickness determined by the mechanical thickness gauge are compared in Table I.

Effect of Film Thickness on Results. Several factors were found to be responsible for variation in lumines-

Table I. Comparison of Film Thickness from Gauge and from Infrared Band Intensity

Thickness, cm.			
Thickness gauge	Infrared method	Thickness gauge	Infrared method
0.0135	0.0136	0.0074	0.0068
0.0115	0.0103	0.0146	0.0141
0.0123	0.0113	0.0112	0.0115
0.0097	0.0100	0.0081	0.0082
0.0137	0.0122	0.0149	0.0136
0.0136	0.0126	0.0133	0.0130
0.0078	0.0076	0.0122	0.0114
0.0121	0.0122		

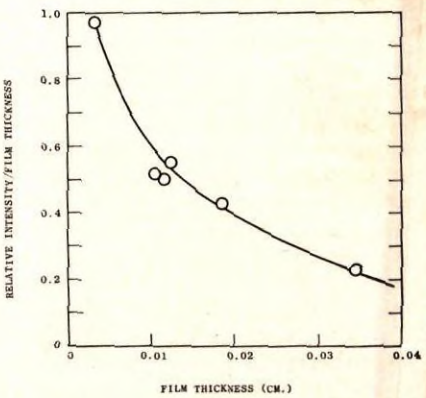
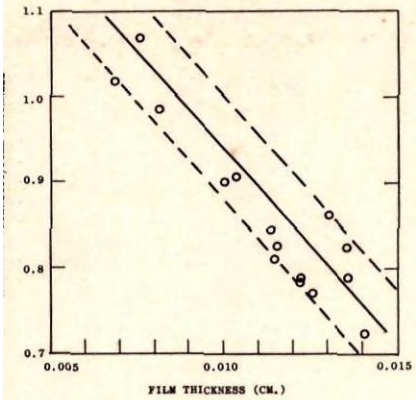


Figure 5. Effect of film thickness upon fluorescence intensity

Self-quenching evident (0.0612 wt. % PBN in EPR)



igure 6. Effect of film thickness upon hosphorescence intensity

General background absorption high (0.1 t. % Santonox in EPR)

ence intensity/unit film thickness vhen the film thickness was changed ver a wide range. An inhibitor with high absorptivity such as PBN vill show deviation from linearity at igh concentrations (see Figure 3). This inner-filter effect is caused by a lecrease in the per cent transmittance f the sample film at higher PBN con-entrations. Thus, a fewer number of nolecules are excited at the back than t the front of the film where the exciting adiation first strikes the sample. Like-vise, at the same PBN concentration, s film thickness is increased the same nner-filter effect is observed because he per cent transmittance is again lecreased (see Figure 5). Therefore, or quantitative measurement of PBN n polymer films it becomes necessary o control film thickness within narrow olerances. From Figure 5 it was esti-nated that a variation from 0.010 to 0.014 cm. in film thickness resulted in change from 0.60 to 0.50 in relative luorescence intensity.

Santonox, on the other hand, has a ow absorptivity and does not show any 'concentration quenching." However, ince its excitation wavelength is lower han that of PBN, a higher background bsorption is usually encountered be-ause of residual catalyst components nd other impurities found in the EPR. This background absorption, which is ignificant compared to the absorption by the Santonox, thus accounts for a neasurable variation (inner-filter effect) vith film thickness (see Figure 6). Limits of deviation of about 6% in elative phosphorescence intensity were drawn in Figure 6. Essentially all of he points fall within these limits. From the curve in Figure 6 it was esti-nated that to obtain results with a precision ±7 or 8% at a film thickness ear 0.010 cm. it would be necessary to control film thickness within ±10%.

Precision. The effects of film thick-ness make selection of conditions for letermination of precision somewhat difficult. The determination of Santonox by phosphorescence was chosen for the calculation, since it did not show concentration quenching at lower concentrations (ca. 0.1 weight %). Using the phosphorescence intensities from films ranging from 0.011 to 0.014 cm., the precision (95% confidence limits) was calculated to be 8 8% relative (see Table II).

Quantum Efficiencies. Efficiencies for the absorption-emission processes for the inhibitors were determined

Table II. Precision of Spectrophosphorimetric Determination of Santonox in EPR

Film thickness from 0.011 to 0.014 cm.

Wt. % Santonox found		
0.0811	0.790	0.0770
0.0862	0.0822	0.0787
0.0845	0.0830	0.0786

Av. 0.0811

95% confidence limits ±0.0071 (or 8.8% relative)

Table III. Quantum Efficiencies for Inhibitors Determined by Comparative Method (4)

Quinine sulfate used as reference standard, $\phi = 0.55$

Compound	Solvent	Concn., μg./ml.	Absorptivity at exc. max., liters/g. cm.	Maxima, mμ Exc.	Maxima, mμ Emis.	Quantum efficiency ϕF	Quantum efficiency ϕP
Age Rite D	2,2,4-Trimethylpentane	10.0	5.7	245	395	0.35	...
Santonox	EPA	1.0	26.4[a]	245	420	...	0.22
Phenyl-2-naphthylamine							
Room temp.	2,2,4-Trimethylpentane	1.0	87.3	260 295	395	0.25	...
Low temp. (77° K.)	EPA	100	157[a]	260 295	372 285 495 527 570	0.27[b]	... ... 0.018[b]

[a] Determined at 77° K.
[b] Values determined by Parker and Hatchard (9) were $\phi F = 0.26$; $\phi P = 0.44$.

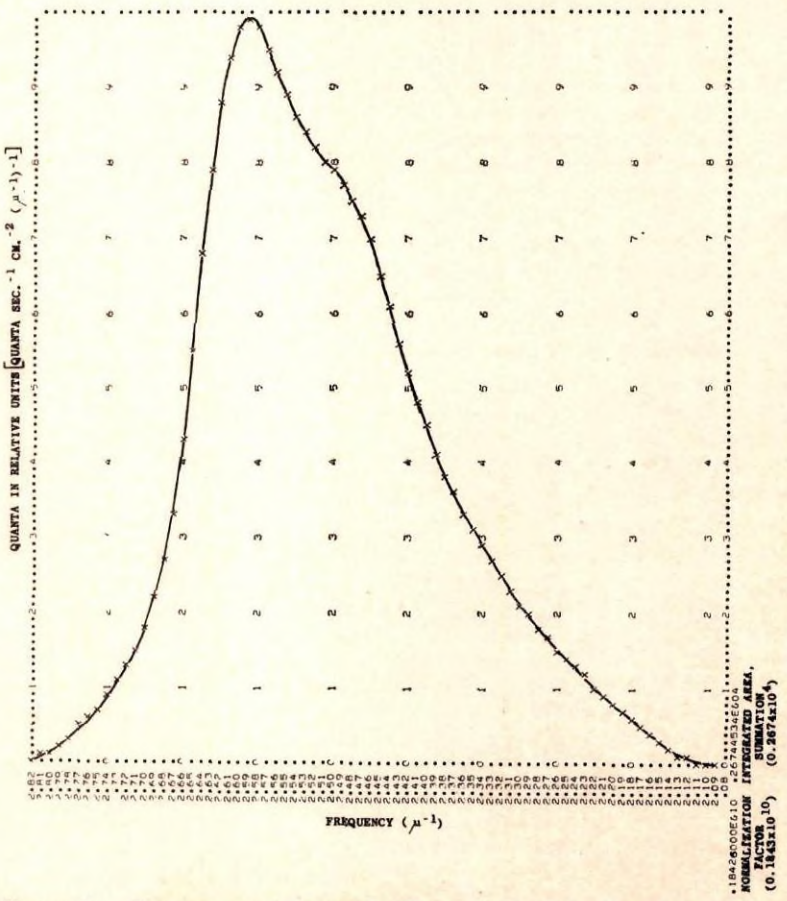


Figure 7. Computer-corrected low-temperature fluorescence spectrum of phenyl 2-naphthylamine in EPR film

by the comparative method previously described (*4*), in which the relative luminescence intensity is compared to that for a compound of known quantum efficiency. Quinine sulfate was selected as the reference standard for these measurements. The luminescence intensity was obtained by integration of the computer-corrected spectrum expressing the spectrum in units of relative quanta per unit frequency interval *vs.* frequency. An example of the computer-corrected low-temperature fluorescence spectrum of PBN is shown in Figure 7. The integrated area and the normalization factor (to convert the peak intensity to 1.0) from the computer program are shown in the lower right-hand corner of the printed spectrum. Since the excitation wavelengths were different for each of the inhibitors and the reference standard, the ratio of excitation intensities (in relative quanta) was included in the calculations. The equation expressing these relationships is:

$$\phi_2 = \phi_1 \frac{F_2 A_1 E_1}{F_1 A_2 E_2}$$

where

- ϕ = quantum efficiency
- F = fluorescence intensity in quanta (integrated area)
- A = absorbance at the wavelength of excitation representative of the solution used for the luminescence intensity measurement
- E = intensity of exciting radiation in quanta.

Subscript 1 refers to the reference standard and subscript 2 refers to the compound being studied.

Some results of quantum efficiency calculations for the inhibitors studied are listed in Table III.

The quantum efficiencies for Age Rite D and PBN at room temperature were determined in square 1-cm. cuvettes using quinine sulfate as the reference standard. The value for PBN at 77° K. was obtained by use of the phosphorescence attachment with and without the liquid nitrogen in the quartz Dewar flask. Absorptivities and integrated emission intensities were determined at room temperature and at liquid nitrogen temperatures (77° K.). Knowing ϕ at room temperature, the value at 77° K. was calculated by direct ratio. The quantum efficiency for phosphorescence of PBN was calculated by direct ratio with the value for low-temperature fluorescence. Likewise, the quantum efficiency for phosphorescence of Santonox was calculated using the quantum efficiency for low-temperature fluorescence of PBN as the reference standard.

Quantum efficiencies for PBN have been determined by Parker and Hatchard (*9*). Their value for fluorescence agrees very well with the data reported in Table III, but the value for phosphorescence is much different. The low phosphorescence efficiency shown in Table III is not understood, but is probably related to the nature of the solvent, impurities, etc. The value for Santonox was determined using the rotating shutter, as this compound was observed to "saturate," yielding high values when the measurement was made without the shutter.

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