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Environmental Factors and Mechanisms Controlling Degradation of Tb(III) Chelates: Development of Effective New Tb Phosphors for Postage Stamp Use

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U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
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Annual Report

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

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1.0 INTRODUCTION

The United States Postal Service (USPS) operates a modern, high speed mailhandling facer-canceller system by which nearly 30 billion stamps annually are faced and cancelled automatically. The system requires an effective, tagging phosphor. The tagged stamp coating, after excitation by UV light of a specific wavelength, must emit phosphorescence of a required wavelength with a minimum decay time of 1.5 milliseconds. A bright phosphor is cancelled automatically, and a stamp of low phosphorescence is rejected. Cancellation of a stamp diminishes its visible phosphorescence.

Thus, effective tagging phosphors, dissolved or dispersed in a varnish, and then applied to the surface of the stamp are the essential component of modern stamp coatings. Zinc orthosilicate doped with manganese (Zn_2SiO_4:Mn) is a typical inorganic phosphor, used in concentrations of 12 to 25 percent by weight (1) of the varnish formulation. This compound emits bright green phosphorescence (480-610 nm) after excitation by UV light of wavelength 254 nm, as shown by the location of the peak in Figure 1 both for a phosphorescent "Production Stamp" having a surface coating tagged with this phosphor, and the pure crystals cemented to a ceramic plate.

This inorganic phosphor is relatively inexpensive, at a cost of \$6.00 per pound, nontoxic, and resistant to humid air, to chemical or oxidative reactions, and to ultraviolet light (2). For all of these reasons, zinc orthosilicate doped with manganese is being used extensively as the principal tagging phosphor for current USPS facer-canceller systems, which represent an investment of \$14 billion.

Nevertheless, inorganic phosphors mixed with organic varnishes create problems. They are immiscible. Consequent susceptibility to abrasive removal may lead to diminished phosphorescence as well as excessive wear in processing and cancelling machinery. Losses in the amount of \$10 to \$12 million per year result, (a) because stamps rejected by the automatic canceller must be hand-cancelled, and (b) because processing machinery requires special cleaning. A miscible, nontoxic phosphor is needed that emits light in the desired region of the spectrum, with high brightness (or quantum efficiency).

Phosphorescent complexes of terbium(III) with certain organic ligands are attractive with respect both to luminescence wavelength and brightness. Examples of the peak maxima are displayed in Figures 1 and 2. The USPS has experimented extensively with such well characterized (2) terbium complexes as tris(acetylacetonato)terbium(III) [Tb(AcAc)3] because they are miscible with organic varnishes (2), resist abrasion, and emit green light. But even with a much lower phosphor concentration (1.44 percent), compared to zinc orthosilicate (20 percent), $Tb(AcAc)_3$ would be more costly in the quantities required for general use by USPS. The private contractor (Martin-Marietta Corp.) who studied this chelate, moreover, indicated susceptibility to rapid hydrolysis under accelerated aging conditions (2). At the request of USPS, the National Bureau of

Standards initiated an investigation of the decay mechanisms for known terbium phosphors as a partial basis for selecting or designing for synthesis efficient new tagging compounds (3).

The results of an automated literature search (Appendix 1) indicated the following important objectives in designing a successful phosphor:

1. Exclude water from the coordination sphere of terbium by molecular design to avoid intramolecular quenching.

2. Diminish or exclude intermolecular quenching by trace metals (such as cobalt) in the Tb coordination sphere

3. Increase brightness intensity (quantum efficiency) of the emitted light compared to current phosphors, by selecting chromogenic ligands.

4. Demonstrate the effectiveness and stability of the phosphor in actual stamp coating systems, including candidate varnishes.

1.1 scope of the data base for this report.

This report discusses synthesis of selected candidate phosphors showing more or less intense luminescence, with recipes for their preparation. These include at least one highly promising phosphor (the complex of terbium with dipicolinic acid). Additional syntheses are planned and discussed, along with the guiding molecular rationale.

Methods and results of phosphor evaluation are discussed, including accelerated aging under conditions of high humidity, temperature (91° F, 32° C) , illumination with ultraviolet light of high energy, and/or more natural conditions such as prolonged exposure to sunlight. The spectrum of processing varnishes includes: varnish composition, presence of ink or pigment, paper filler, backing, and phosphor concentrations in the coating varnishes. Detailed molecular characterization required for generating patents on the more useful new compounds will be reported in the second year of a two-year contract.

2.0 INSTRUMENTS AND METHODS

2.1 Materials

2.1.1 USPS candidate phosphors

Two candidate organoterbium chelates were supplied by USPS: tris(acetylacetonato)terbium(III) [Tb(AcAc)3]; and bis(anthranilato)acetatoterbium(III). The first is available commercially (Atlantic Chemicals,* P.O. Box 218, Nutley, NJ 07110)and a method for preparing the second has been reported to USPS (2).

2.1.2 Phosphors selected for synthesis.

2.1.2.1 Chelate of terbium(III) with pivaloyltrifluoroacetone (PTA) and trioctylphosphine oxide (TOPO) (4)**

Transfer 1.0 mL of a $TbCl_3$ solution (Alfa Research AAS standard 88110, containing 1095 microgram of Tb per mL; another pure source of Tb may be substituted) to a Teflon vial equipped with a Teflon cap. Bring the acid solution to pH 5 with aqueous 1.0 mol/L sodium hydroxide.

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* Certain suppliers of chemicals and equipment are identified by name in order to specify the experimental conditions adequately. This does not imply endorsement or recommendation by the National Bureau of Standards nor does it imply that the particular brands of chemicals and equipment named are necessarily the best for the purpose.

**This is based on Taketatsu's synthesis (4), modified by conditions suggested by Fisher and Winefordner (5)

Dilute to 10 mL with deionized water.

Transfer 3 mL of the terbium solution to a Teflon-capped, Teflon test tube. Add 3 mL of 0.01 mol/L TOPO in methylcyclohexane (MCH), and 3 mL of MCH solution containing 12 µL of PTA (1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione,PTA). Shake manually for about fifteen minutes and then allow the aqueous and organic phases to separate. Place a few drops of the organic phase on a microscope slide, observe by excitation with light of 254 nm; measure the intensity of emitted luminescence at 545 nm.

For comparison, examine the luminescence of complexes prepared either without TOPO or without PTA, as well as anhydrous and hydrated $TbCl_3$.

2.1.2.2 Terbium(III) complex with aurintricarboxylic acid (ATC) (6).

Dissolve 0.1940 g of ATC (4.6×10^{-4} Mole) in 10 mL of absolute ethanol and add, dropwise, 1.0 mL of a $TbCl_3$ solution containing 0.01824 g of $TbCl_3$ (6.86×10^{-5} mole) to precipitate the complex. Let stand for several days. Filter through coarse filter paper, wash with ethanol, and examine for luminescence after drying on a microscope slide.

2.1.2.3 Terbium(III) complex with trifluoro-1-phenyl-1,3-butanedione (TFPB) and TOPO.

Dissolve 0.1910 g (0.494 millimole) of TOPO in 3 mL of methylcyclohexane, and 0.1896 (0.878 millimole) of TFPB in 10 mL of methylcyclohexane. Mix the 3 mL solution of TOPO and 3 mL of TFPB (0.2639 millimole) with 1.0 mL of $TbCl_3$ solution containing 0.01854 g(6.86×10^{-5} mole) in a Teflon stoppered Teflon test tube, shaking 15 min. Measure, on a microscope slide, luminescence at 545 nm, with excitation by light of 254 nm.

2.1.2.4 Terbium(III) complex with 1,1,1,5,5,5-hexafluoroacetylacetone (HFA) and TOPO (5).

Dissolve 0.207 g of TOPO (0.535 millimole) in 3 mL of methylcyclohexane, and 0.2 mL (about 0.96 millimole) of HFA in 10 mL of the same solvent. Add 3 mL of each solution to 0.0686 millimole of $TbCl_3$ dissolved in 1 mL of water to give a molar ratio of HFA:$TbCl_3$ of about 5:1, with TOPO in large stoichiometric excess. Shake about fifteen minutes, and place a drop of the organic phase on a microscope slide to examine luminescence.

2.1.2.5 Complex of terbium(III) with benzo-15-crown-5 (7).

Dissolve 0.1354 g (0.5 millimole) of crown ether in 5 mL of acetone in a capped Teflon vial containing a magnetic bar coated with polyethylene. Add 0.0840 g (0.19 millimole) of $Tb(NO_3)5H_2O$ in 5 mL of benzene. Stir at room temperature 60 min. Let stand at 4° C for 73 hours.

In the absence of precipitate, evaporate about 7 mL of the solvent. Add a few drops of hexane and again permit the solution to stand at 4° C for a prolonged period of time (e.g., two weeks). Deposit a drop of the solution on a microscope slide to measure luminescence, verifying the absence of fluorescence under UV illumination at 254 nm.

2.1.2.6 Complex of terbium(III) with dipicolinic acid (DPA) in aqueous solution (8).

Dissolve 3.2 g (19 millimoles) of DPA (pyridine-2,6-dicarboxylic acid) in approximately 50 mL of 1.0 mol/L sodium hydroxide, aqueous. Dilute with deionized water to about 95 mL. Neutralize with dilute acetic acid (1:100 glacial acetic acid:deionized water) and finally dilute to 100 mL with deionized water, to prepare solution A.

Dissolve 2.05 g (4.75 millimoles) of $Tb(NO_3)_3 \cdot 5H_2O$, (hydrated terbium nitrate), in 50 mL of deionized water and dilute with 50 mL of deionized water to give solution B. Mix solutions A and B in equal proportions to obtain the phosphor $Tb(DPA)_n$. Check the pH of the solution and adjust with acid (HOAc or HNO_3) or base (NaOH) as necessary to a final pH between 6 and 8.

In this solution of complex, the concentration of terbium is about 0.375 percent (w/v). Mix this solution with a stamp varnish formulation in a ratio to be determined empirically to produce a coating with the desired phosphorescence intensity. For example, a ratio of 1:10 (solution:varnish) in varnish TG-2407-RV on multicolored stamp paper (USPS "Experimental" stamps) has been found to give a phosphorescence of about 100 PMU.

2.1.2.7 Preparation of $Tb(DPA)_n$ in organic media.

Add 3.2 g of DPA to 500 mL of tetrahydrofuran (THF), in which solvent the acid is almost insoluble. Add approximately 50 mL of deionized water with swirling to dissolve all but a trace of DPA within one half hour. Filter the solution through coarse sintered glass, washing twice with about 5.0 mL of wet THF (1:10 H_2O:THF). To the filtrate in an Erlenmeyer flask, add dropwise 2.05 g of $Tb(NO_3)_3$ $5H_2O$ dissolved in 5 to 10 mL of water. Let the mixture stand at least overnight to coagulate the colloidal suspension. Use a pipette to transfer the clear upper phase for filtration through a weighed, sintered glass crucible (medium porosity). When most of the clear solvent has been removed, wash the suspension with additional wet THF, mix the solvent and colloid, wait for separation and again remove the upper phase. Repeat three times to remove all excess DPA.

Finally, isolate the pure complex either by filtration on coarse sintered glass or by centrifugation, decanting supernatant fluids. For final drying, place the crucible in a desiccator and subject to partial vacuum overnight. The purpose of this treatment is to isolate a pure compound for characterization. Merely to prepare the phosphorescent compound for mixing with varnish does not necessarily require complete removal of solvent.

Although $Tb(DPA)_n$ and its components' are not believed to be toxic, normal handling precautions should be taken. Use plastic or rubber gloves to avoid skin contact with the raw materials or the finished phosphor. DPA may be a skin irritant. In large quantities it should be handled in a laboratory hood to the extent possible. Since THF is highly flammable and somewhat toxic, use this solvent only in a laboratory hood with proper ventilation, observing care to avoid sparks or fire. THF dissolves the materials from which most plastic gloves are made, including latex. Use Neoprene gloves in handling THF.

If THF is stored for long periods of time, check this solvent periodically for accumulation of potentially explosive peroxides (9).

2.2 Varnishes

Six coating varnishes were supplied to NBS by Mr. Joseph Y. Peng of USPS. The BEP designation and specified compositions of five of them are presented in Table 1. The sixth, SLV-4057, is a proprietary formulation requiring 20 percent zinc orthosilicate doped with manganese. Cobalt concentrations in the varnish were determined by NBS. Coatings prepared from the two formulations that have the highest cobalt concentration (TG-11-T and TG-8-T) were found to be nearly without fluorescence, after adding 1.44 percent (w/w) of $Tb(AcAc)_3$, and these varnishes consequently have not been studied in the detail devoted to varnishes TG-20-T and TG-2407-RV. Varnish TG-45-T, although lacking cobalt, also was essentially without phosphorescence after adding $Tb(AcAc)_3$. Study has only begun with phosphors added to varnish SLV-4057. However, mixtures of phosphor with this varnish are phosphorescent. This varnish is representative of coating materials destined for extensive use in the near future.

2.3 Stamp papers

Six types of stamp paper, provided by USPS for experimental application of phosphorescent coatings, are listed in Table 2.

2.3 Application of phosphor to paper

After mixing phosphors into varnishes, a small portion of each coating formulation was applied to one end of a test paper strip clamped by means of teflon clips to a glass plate. A metal drawdown bar (supplied by USPS) was used to draw the varnish uniformly over the paper surface in one continuous motion, in accord with the technique demonstrated for NBS by Ms. Barbara Kelley of USPS. Varnish thicknesses used on test papers usually were 0.0254 mm (1.0 mil). The drawdown bar and the glass plate were cleaned with acetone and methanol between varnish applications. In some experiments, the $Tb(DPA)_3$ phosphor in aqueous solution was applied directly to test papers by a similar drawdown technique, and no varnish was used.

After coating, test papers were dried at 66° C for 15-20 min, or until visibly and palpably dry.

2.5 Aging methods

Test stamp sheets clamped between teflon clips were suspended in test chambers. For dark, humid aging, stamp sheets were placed in a circulating, controlled temperature-humidity chamber (Hotpack, Philadelphia, PA) maintained at 31-32 C (88-90° F) and 90-94% relative humidity [monitored by dry and wet bulb chamber thermometer readings or by a humidity meter (Bacharach Instrument Co., Pittsburgh, PA)]. Dry aging was performed in a second laboratory oven at a relative humidity of ~17% at 31 °C. Humid and dry aging tests for stamp papers were also performed in the same laboratory ovens with continuous exposure to short-wave ultraviolet light (UV) illumination (General Electric 4T4-1 bulb) of intensity 600 $\mu W/cm^{-2}$ at the test paper surface (as measured with USPS meter #H-021028). Additionally, aging experiments using sunlight were performed by hanging test stamp sheets in an office window having a southern exposure and receiving several hours of direct sunlight daily with a measured illumination exceeding 4800 μwatt cm^{-2}. These experiments continued through summer, fall and winter months, during which the relative humidity in NBS buildings averages about 50%, but may occasionally range from 33-73% (10).

2.6 Luminescence measurements

2.6.1 Total luminescence (EMI)

Total luminescence of test stamps was measured using an epifluorescence microscope imaging (EMI) system (Fig. 3) consisting of a Zeiss Universal microscope equipped with quartz optics, an epiillumination system (HBO-100 lamp), an emission filter monochromator (Zeiss) and photometer (Zeiss model SF). The photometer signal was measured using an Apple II computer equipped with a multichannel analog-to-digital converter (Data Acquisition System AI13, Interactive Structures Inc.). Short wave (253.7 nm) UV from the microscope lamp was transmitted by a 253.7 nm bandpass exciter filter (G25-254-F, Corion Corp., Holliston, MA) and a 395 nm dichroic reflector (Zeiss) to the surface of the samples. Measurements were made using a 10X Zeiss ultraflaur quartz objective coupled with 10X oculars and a 1.25X optovar setting for a total magnification of 125X. A 2.5 mm pinhole stop below the photometer gave a 50 μm diameter field for luminescence intensity measurements.

The EMI system was calibrated daily using stable Tb-doped glass microspheres (11) , Mn-doped $ZnSiO_4$ ceramic plates (12) and current production stamps.

Photomicrographs were taken using a 35 mm camera system (Zeiss MC-63) which was mounted by replacement of the monochromator-photometer system.

2.6.2 Phosphorescence (PMU)

A USPS model 4A phosphormeter was used for green phosphorescence measurements. Zero adjustments and green phosphor calibrations were performed daily, prior to test stamp measurements. Data are expressed in phosphormeter units (PMU).

2.7 Cobalt in varnish measurements

The cobalt content of five USPS varnishes (TG-20-T, TG-11-T, TG-8-T, TG-5-T, TG-2407-RV) was determined by graphite furnace atomic absorption spectrophotometry (GFAA). Aliquots (0.2-0.4g) of varnishes were transferred with a teflon spatula to tared glass vials (7 mL) and weighed. The varnishes were then dissolved in tetrahydrofuran (THF, 2-5 mL) and analyzed for cobalt using a Perkin-Elmer model 460 dual-beam AA spectrophotometer with deuterium lamp background correction and a model 2100 graphite furnace atomizer. GFAA conditions were: lamp, Co hollow cathode (Perkin-Elmer) operated at 30 mA; wavelength, 240.7 nm; drying time, 20 s at 100° C; char, 10 s at 500° C; atomization, 8 s at 2700° C; slit width 0.2 alt; purge gas, argon, 30 mL min^{-1}, interrupt mode; integration time 8 sec. Aliquots (20 uL) of THF solutions of varnish were introduced into the graphite furnace with a Perkin-Elmer AS-1 autosampler. Atomic absorption data were collected using a Shimadzu C-RIA integrator printer.

A Co calibration curve was prepared by dissolving $Co(NO_3)_2.6H_2O$ in deionized water. Five replicate determinations were made for each sample dilution, typically with standard errors below 2.5%. The detection limit calculated (13) for Co was 6 ng mL^{-1}.

Cobalt concentrations in varnishes were determined by the method of additions. Dilutions of varnish (1:10 to 1:5000, depending on the varnish) in THF were spiked with Co (in THF) to give 0, 0.044, 0.08, and 0.16 µg mL^{-1} Co. The negative x-intercepts of the linear regression lines ($r>0.987$) were taken as the amount of Co in the samples (Table 1).

2.8 Elemental analysis

Total element analysis was performed on $Tb(DPA)_n$ samples by Schwarzkopf Microanalytical Laboratory, Inc. (Woodside, NY 11377).

2.9 Infrared Spectroscopy

Fourier Transformer Infrared spectra (absorbance and reflectance) was obtained by Analtech Laboratory.

2.10 Luminescence lifetime, for phosphors including $Tb(DPA)_3$ were measured by R. Snider of USPS.

3.0 RESULTS AND DISCUSSION

3.1 Molecular design

An automated computer search (appendix 1) was designed to collate references to rare earth chelates capable of emitting light in the required green region of the spectrum (500 - 550 nm) and to correlate structural characteristics with emission brightness (quantum efficiency) and phosphorescence stability. Of rare earth chelates, only terbium emits green light (545 nm) of high intensity, owing to the $^5F_4 \rightarrow {}^7F_5$ electronic transition. Enhancement of luminescence occurs by radiationless transfer of photons from excited ligands to terbium. The intensity of the light emitted by the central terbium atom varies with ligands. Enhancements in luminescence, compared to that of Tb(III) in water, range from hundreds for $Tb(DPA)_3$ and certain peptides, (14,15) to thousands (16), for porcine pancreatic elastase.

3.1.1

Quenching by coordinated water

Molecules of water coordinated with the central metal atom quench excited terbium by radiationless deexcitation (17). Horrocks and Studnick (17) replaced bound water with deuterium oxide in chelates of terbium with proteins with enhancement of luminescence owing to substitution of -OD for -OH groups. Attempts to dehydrate completely the luminescent complex of tris(acetylacetonato)terbium(III) [Tb(AcAc)3] resulted instead in removal of only two molecules of water to give the monohydrate. With additional heating the compound decomposed (18) or polymerized (19).

The effects of water on the luminescence of terbium complexes indeed can be profound, as our data in Table 3 demonstrate. The luminescence of anhydrous crystals of $TbCl_3$ exceeds that of hydrated crystals by nearly two orders of magnitude. Similarly, the luminescence of the complex of terbium with pivaloyltrifluoracetate (PTA) is negligible without the large synergistic trioctylphosphine oxide (TOPO) moiety, possibly indicating that the hydrophobic chains of TOPO enhance luminescence by excluding water from the coordination sphere of terbium by "encapsulation" (20). Lacking chromogenicity, TOPO alone fails to impart luminescence energy to terbium.

The data in Table 4 represent an example of changes in luminescence, due to environmental moisture, in a coating material tagged with $Tb(AcAc)_3$. The phosphor was mixed into varnish TG-20-T (Table I) in the approximate concentration of 1.44 percent (w/w). Sample No. 1, after twenty-four hours in a humid oven (93 percent relative humidity (RH), 31 °C) showed a decrease in luminescence that was partially recovered when the sample was removed from the oven and kept under ambient conditions for an additional twenty four hours. Increases in the luminescence of samples 2, 3, and 4 show that illumination under office fluorescent lamps was not harmful. The observed <u>increases</u> in luminescence [$Tb(AcAc)_3$, ambient; Figure 4] may be a result of increasing phosphor concentration owing to evaporation of volatile components of the varnish at 66° C.

Sample No. 5 (Table 4), on the other hand, with continuous exposure to the humid atmosphere, lost three-fourths of its initial luminescence within three days, with little additional change during 164 hours of additional exposure. These data are definite evidence that coatings incorporating the $Tb(AcAc)_3$ luminiphor in varnish are sensitive to moisture, the conclusion previously reached by Martin-Marietta (2). We make one important reservation: the residual luminescence is not completely quenched by water compared, for example, to the much lower luminescence of hydrated terbium chloride, and remains apparently stable on prolonged aging.

Subsequent tests of phosphorescent coatings on stamp papers therefore were continued by NBS for much longer periods of time than those employed by the Martin-Marietta laboratories (2).

3.1.2

Luminescence quenching by metal ions.

Certain metals, including cobalt and nickel (21), are capable of radiationless quenching of terbium chelates, an intermolecular process of potential importance since varnish formulations in the past have contained relatively large amounts of cobalt driers (Table 1). Reportedly, such varnish formulations have become almost obsolete (22), so that quenching of phosphors by cobalt itself may not be a future problem. The potential interaction of cobalt and terbium illustrates, nevertheless, the value of encapsulating the central terbium, preferably by molecular design (20).

3.3 Relative luminescence of selected complexes

3.3.1 Total luminescence

Table 5 summarizes the total luminescence of selected terbium phosphors. $Tb(AcAc)_3$ consists of one terbium atom bonded through six carbonyl groups to three unsubstituted pentyl chains, with three coordinated molecules of water (18,19). The luminescence intensity at 545 nm of the material studied by NBS exceeds that of anhydrous terbium chloride, even though it must be assumed that the organoterbium phosphor is fully hydrated; i.e., this complex had been stored for months at room temperature, and was not heated prior to use. Bis(anthranilato)acetatoterbium(III) (23) is the complex formed between the terbium(III)acetate and anthranilic acid (2-amino-benzoic acid), with potential bonding between the metal and either carboxylic oxygen or amino nitrogen electron donors. Its luminescence intensity, despite the aromatic chromophore, is much less than that of $Tb(AcAc)_3$. Characterization of the structure has not been reported in the detail known for $Tb(AcAc)_3$. Pivaloyltrifluoroacetone (1,1,1-trifluoro-5,5-dimethyl-2,4-pentanedione) complexes with terbium require a synergistic Lewis base (24) to produce enhanced luminescence. The preparation in water here proves to be only half as bright as that prepared in methylcyclohexane, indicating that the aqueous preparation is probably more hydrated. The terbium complex with hexafluoroacetoacetonate (1,1,1,5,5,5-hexafluoro-2,4-pentanedione) produces only weak luminescence, even in the presence of TOPO. The complex of terbium with aurintricarboxylic acid (ATC; formula given in Appendix 2) precipitated overnight from aqueous solution but displayed no luminescence despite the aromaticity and bulkiness of the ligands.

The complex of terbium with dipicolinic acid (DPA; 2,6-pyridinedicarboxylic acid, Figure 5) prepared in an aqueous medium (14) produced by far the highest luminescence intensity of all of the phosphors so far examined (Table 5).

3.3.2 Relative phosphorescence of tagged varnishes

Table 6 summarizes the measured phosphorescence intensities of coating systems consisting of varnishes tagged with either Tb(AcAc)$_3$, Tb-PTA-TOPO, or Tb(DPA)$_3$. The bright phosphorescence of Tb(DPA)$_3$, consistent with the total luminescence (Table 5) makes this a highly attractive candidate tagging phosphor.

Table 7 includes projected materials consumption and costs if Tb(AcAc)$_3$ were substituted by USPS for the current inorganic phosphors, with terbium concentrations of 0.44 percent by weight of varnish; or if Tb(DPA)$_3$ were the phosphor, with a terbium concentration of 0.026 for varnish TG-2407-RV, or 0.075 percent for varnish TG-20-TG. Basing calculations on a 1982 quotation for Tb_4O_7 in 99.9 percent purity (Appendix 3), it is evident (Table 7) that Tb(DPA)$_3$ prepared from DPA and Tb_4O_7 could be used at lower net cost than zinc orthosilicate at $6.00 per pound; Tb(AcAc)$_3$ could not be. Moreover, the estimated quantity of terbium required to make Tb(DPA)$_3$ in adequate bulk would still be a reasonably small fraction of the total annual U.S. production, whereas Tb(AcAc)$_3$ would be required in quantities exceeding 50 percent of U.S. annual production.

3.2. Stability and Effectiveness of $Tb(AcAc)_3$-tagged Coatings.

3.2.1 Stability

$Tb(AcAc)_3$, was mixed into each of two varnishes (TG-2407-RV and TG-20-T) and coated to a depth of 0.0254 mm (1.0 mil) on six different experimental stamp papers (papers I - VI, Table 2), with a terbium concentration of 0.44 percent (w/w). Phosphorescence readings in PMU, and total luminescence in EMI units were taken periodically as aging progressed over a period of time exceeding 400 hours of exposure to air at 94 percent RH, in the dark or with illumination by UV light (254 nm, 600 μwatts/cm^2). The aging data are summarized in Tables 8 and 9, and in Figure 6.

Martin-Marietta reported that a varnish coating tagged with $Tb(AcAc)_3$ lost about sixty percent of its initial phosphorescence after ten hours of exposure to the elevated temperature of 155 °F at 90 percent relative humidity (2); more extended aging was not reported. In the present experiments, we usually observe very substantial decrease in luminescence within two hours of accelerated aging, but the initial losses consistently are followed by prolonged increases, usually continuing for at least 240 hours.

For example, sample III (Table 8), at first displays the initial, somewhat low phosphorescence of 11 PMU, dropping in fifteen minutes to 3 PMU but increasing thereafter to 35 PMU after 400 hours. It is highly probable that matrix changes, possibly involving chemical reactions with the phosphor, are partly responsible for both phenomena; e.g. quenching by kinetically rapid hydration might be followed by intramolecular rearrangements to generate a thermodynamically more stable and also a more efficient phosphor. To investigate such hypotheses requires a method of inspection in situ - for example, with reflectance FTIR spectroscopy to follow the disappearance and appearance of specific bands.

For different papers and varnishes, differences appear both in the intensity of the initial phosphoresence and its changes during the course of aging. Thus, unfilled paper No.I coated with doped varnish TG-2407-RV shows an initial phosphorescence of 26 PMU compared to 80 PMU for clay-filled paper No. V. The low viscosity of this varnish is consistent with rapid absorption of both phosphor and varnish for the unfilled but apparently not the filled paper. Within one hour, paper no. V loses one-third of its initial phosphorescence, while paper I experiences no loss.

With the much more viscous varnish TG-20-T, the phosphorescence data for samples I and V are nearly the same for the first 280 hours of aging. Presumably, they are not affected by differences in paper because the phosphor is immobilized at the surface by the viscous coating material, and does not migrate so rapidly inward.

Aging beyond 280 hours reveals additional differences between sample I, which retains its phosphorescence, and V, which decays to about 10 percent of the maximum. Inferentially, phosphor decay is a result of interactions between each phosphorescent coating system and its environment including gummed backing on stamp papers. Thus, the more stable sample VI differs materially from sample V only in that sample VI has gum but sample V does not. Thus, the gum appears to stabilize the phospher. To do so, it would have to migrate through the paper to the opposite surface, there possibly to participate in some sort of encapsulation process.

There is evidence for such migration. The data in Tables 10 and 11 indicate that the course of aging in a dark humid atmosphere is ultimately perturbed by fungal growth on both sides of all papers having a gummed backing. Since gums are a source of food to the fungi, their appearance on both sides is positive evidence that gums do in fact migrate through the paper.

In contrast with the favorable stability of $Tb(AcAc)_3$ must be noted its low quantum efficiency or brightness in varnish TG-2407-RV requiring about 0.44 percent terbium (1.44 percent chelate) to develop 70-40 PMU of initial phosphorescence. Although the concentration is considerably lower than the 12 percent to 25 percent concentrations of zinc orthosilicate required for comparable intensities, it is economically unfavorable, as indicated in Table 7, because the terbium complex is much more expensive.

3.2.2 Long-term aging of $Tb(AcAc)_3$-doped coated papers under ambient conditions.

Accelerated aging methods (UV light of high intensity, elevated temperature, high atmospheric pressures and humidities, etc.) are of value for comparing systems that differ in some well controlled characteristic. Their disadvantage is that accelerated aging can not readily be extrapolated to "natural" aging conditions unless similar chemical or physical molecular processes as bond formation and bond breaking or migration are known to occur under both accelated and natural conditions, under controlled relative rates. To simulate plausible conditions in service, we initiated long term aging experiments with coated papers suspended in a south-facing office window to receive several hours of sunlight per day.

Figures 7 to 12 illustrate sunlit aging of stamp surfaces coated with $Tb(AcAc)_3$-tagged varnishes for a prolonged period including late Summer and Fall days. The intensity of the incident light, filtered through an office window, exceeded 4800 microwatts/cm^2, the upper detectable limit. The aging system is reasonably "natural", though harsh; e.g., it is consistent with storing a sheet of stamps near a sunlit window for an extended period.

The aging results are similar to the results empirically observed under UV illumination, though much slower. In sunlight, a coating of varnish TG-2407-RV typically loses 30 to 50 percent of its initial phosphorescence in 36 hours, but then regains 50 to 100 percent within 80 days. A coating of varnish TG-20-T typically starts with a much lower measured phosphorescence and then experiences increasing phosphorescence for at least 80 days.

The differences in changes occurring on the first day again may be due to absorption of varnish and phosphor in the case of varnish TG-2407-RV, but not the more viscous varnish TG-20-T. At present, we must infer that reactions between the complex and its matrix are responsible for the continuing increases in phosphorescence in both varnishes. Decreases in the number of coordinated water molecules might have the observed effects. To determine whether new bonds form will require reliable surface analysis.

Of immediate importance is the empirical observation that phosphor $Tb(AcAc)_3$ does not experience a net loss of phosphorescence over long periods of exposure to sunlight filtered through an office window.

3.3 Long-term aging of $Tb(DPA)_3$-doped coated stamp paper

3.3.1 Accelerated Aging

Figures 13 through 18 show the effects of high humidity (94 percent RH at 31 °C) and intense ultraviolet illumination (600 microwatt/cm^2, 254 nm) on the luminescence of phosphor tagged varnish TG-20-T on the six experimental stamp papers (Table 2). UV light is much more damaging to the phosphorescence of this complex than to $Tb(AcAc)_3$. Reflectance FTIR again is a particularly promising tool for studying the decay mechanism. Alsaado et al. showed, for example, that complexes of terbium with DPA may bind either one, two, or three ligands to the central metal (25). Copeland and Brittain (26) demonstrated that luminescence increases when the number of coordinated ligands goes from one to two DPA units. Our data (Table 12) show increasing phosphorescence with initial proportions of 1:2, 1:3, and 1:4. Partial decomposition of $Tb(DPA)_3$ to $Tb(DPA)_2$ and $Tb(DPA)_1$, with increasing hydration is a plausible mechanism for the decreasing luminescence. Proof of actual changes in the bonding structure await sensitive surface analysis.

Three additional points need to be made: (1) the residual brightness is much greater than that of $Tb(AcAc)_3$ extrapolated to the same concentration; and (2) synergistic reactions including an organic acid or Lewis base might prevent hydration and should be explored further; but (3) UV aging is not necessarily a good criterion of stability.

3.3.2 Long term sunlight aging

$Tb(DPA)_3$ in alkaline solution is intensely phosphorescent (166 PMU) at a terbium concentration of only 0.066 percent (w/w) (Figure 19); this is more than twice as bright as $Tb(AcAc)_3$ used in a terbium concentration seven times greater (0.44 percent). A relatively rapid decrease in phosphorescence characterizes the first twenty four days of exposure to sunlight in a south-facing office window. For the next 120 days, the rate of loss is slower and nearly constant, and the phosphorescence decrease to 85 PMU. At this point, the rate slows again so that the next sixty days of exposure results in an additional decrease of only 5 PMU. Projecting this rate of loss, the system would retain about 20 PMU after a total of three years in sunlight. We are continuing the experiment for the longest practical time because of the obvious value of "natural" vis-a-vis artificial, accelerated aging systems.

To eliminate the effects of the varnish itself on the decay mechanism, $Tb(DPA)_3$, in neutral aqueous solution, was applied directly to six papers for sunlight exposure. Table 13 summarizes the results. The type of paper strongly affects its initial phosphorescence, as well as its resistance to decay. Sunlight causes no diminution of phosphorescene for papers I, II, and III relative to control samples prepared at the same time and stored in a desk drawer (Table 13, Figure 20). This is conclusive evidence that the phosphor itself resists quenching (or degradation) in this harsh, sunlit environment.

However, inks and pigments may also participate in quenching mechanisms. Papers I - III are unfilled, and IV - VI are clay-filled; No. III has a pigmented multicolored surface and No. IV is partially inked (cf. Table 2). The differences between filled and unfilled papers in initial phosphorescence are due undoubtedly to differences in the rate of water adsorption. This was demonstrated by simple paper chromatography. Strips of sample I (unfilled, non-gummed) and sample V (clay-filled, non-gummed) 2.54 cm in width were first spotted with a drop of solution containing phosphor, and then suspended over two separate reservoirs of deionized water, with initial contact one cm distant from the spot. In one hour, water had migrated upward through sample V, carrying and dispersing the phosphor, which remained brightly phosphorescent. There was no measureable migration of water through the unfilled paper. Thus in the absence of varnish the initial differences in phosphorescence shown in Table 13 are due for a given paper to adsorption of solution in filled but not unfilled paper.

Additional effects depend on surface treatments for pigmented and inked papers. Some of these probably are due to the chemistry of $Tb(DPA)_3$; either degradation to lower complexes, or hydration, or both. However, intermolecular quenching by metals or dyes cannot be ruled out. Evidence of changes in bonding await microscopic FTIR, expected to be in place and operating at NBS within the next two months.

3.4 Synthesis and characterization of Tb(DPA)$_n$

3.4.1 Effects of pH and stoichiometry on luminescence.

Figure 6 is the structural formula of dipicolinic acid (2,6-pyridinedicarboxylic acid). Figure 21 is a schematic diagram for the characterization of this important complex, both in solution and in pure crystalline form. Proton NMR on products of mixtures in the Tb:DPA ratio of 1:0.5, 1:2, and 1:4 shows distinctly different spectra, attributed to 1:1, 1:2, and 1:3 complexes, respectively (25). In addition to showing that phosphorescence as well as total luminescence both are affected by stoichiometry, our data in Table 12 demonstrate a pH effect. When the pH of the reaction medium lies between pH 6 and pH 9, no pH effect is evident. Lower phosphorescence is evident at pH 4.5, suggesting degradation of the complexes to a lower DPA ligand number under acid conditions.

3.4.2 Effects of processing variable

3.4.2.1 Within our measurement purposes, there is constancy in major emission peak wavelength. Figures 22 and 23 represent measurements taken at discrete intervals between 470 nm and 610 nm on phosphor excited by light of wavelength 254 nm. The specimen consisted of the non-colored area of a multicolored "experimental" stamp paper having small disconnected hexagons of individual color: pink, red,green, blue, brown, and yellow. The varnishes are of low viscosity (TG-2407-RV) and high viscosity (TG-20-T).

The three scanned peaks are attributable to three electronic transitions, decreasing in energy with increasing wavelength. The major peak is near 545 nm in either varnish. The various colored areas affect relative peak intensities but not the location of the peak maximum (Figures 24 and 25). The same comments apply to clear and inked areas (the darkest inked areas observed) on USPS stamps designated "For Experimental Purposes Only" (Figures 26 and 27).

3.4.2.2 Correlations of phosphor concentration and total luminescence.

In Figures 28 and 29, the luminescence intensities are correlated with six concentrations of $Tb(DPA)_n$ (Tables 14 and 15), for seven distinct areas on multicolored stamps. A yellow stamp, for example, would require only about 30 percent as much phosphor to attain a given phosphorescence as a blue or pink stamp, while for a given color in varnish TG-2407-RV, somewhat less phosphor is required to achieve a given luminescence than in TG-20-T. Reduction of luminescence by ink (Figure 30) exceeds 50 percent of the luminescence of a non-colored area on the inked stamp.

3.4.2.3 Correlations of phosphor concentration and phosphorescence.

Pigment or ink reduce by 40 percent and 50 percent, respectively, the phosphorescence of varnish-coated (TG-2407-RV) (Figures 31 and 32) stamp paper tagged with $Tb(DPA)_3$ compared to plain paper. Varnish TG-2407-RV requires a lower concentration of dopant than TG-20-T to achieve the same phosphorescence: e.g., 0.026 percent of terbium in TG-2407-RV, or 0.077 percent in TG-20-T, provides 80 pmu, comparable to 0.44 percent of terbium as $Tb(AcAc)_3$ (see Table 7 and Figure 33).

3.4.3 Preparation of pure crystals.

3.4.3.1 Precipitation from tetrahydrofuran (THF)

Solutions of DPA in wet THF (1:10 H_2O:THF) form a colloidal precipitate instantly when terbium is added dropwise from aqueous solution as $Tb(NO_3)_3.5H_2O$. With terbium and DPA in the molar ratio of 1:4, excess DPA is dissolved into wet THF. Elemental analysis (Table 16) indicates the condensed formula $Tb(DPA)_3.2H_2O$. The colloid may be a polymer, in view of the low coordination implied by this stoichiometry. Also, individual crystals are not visible under the microscope at a magnification of 250 (Figure 34). This preparation is highly interesting because the 1:1 ratio of metal to DPA ligand is formed under conditions (excess DPA) that favor a 1:3 complex in water. It is not recommended for large scale production of the phosphor because the stoichiometry does not favor maximum phosphorescence; purification of a colloid is awkward; and THF is a fire hazard.

3.4.3.2 Complex of $Tb(DPA)_3$ in aqueous solution.

A 1:4 ratio of Tb to DPA in alkaline solution gives a complex believed to be predominantly of the formula $Tb(DPA)_3.XH_2O$, on the basis of data given in 3.4.3.3. below. In addition to the complex, excess DPA, sodium and nitrate ions remain in solution. A few drops of this solution, containing 0.37 percent (w/v) of terbium was dried on a glass slide and then photographed under a magnification of 250 (Figure 35) showing hexagonal crystals and dendritic fibers. The fibers readily removed by washing with wet THF (see below), probably consist of excess DPA.

3.4.3.3 Precipitation by acid from alkaline solution.

Nitric acid, added dropwise to alkaline solutions of terbium and DPA (1:4) precipitates very bright crystals. The crystals were centrifuged, separated by decanting fluid, and washed with wet THF. Elemental analysis (Table 17) indicates the condensed formula $Tb(DPA)_3 \cdot 2H_2O$. Microscopic examination (Figure 36) shows discrete crystals free of the DPA dendritic structures visible in samples of the unpurified alkaline solution (Figure 35).

3.4.3.4 Direct precipitation from alkaline solution.

When terbium(III) in water is added dropwise to a solution of 0.4 M DPA in a solution of pH 11 to pH 13, phosphor crystals precipitate slowly. Overnight storage at 4 °C of a solution approximately 0.1 mol/L in terbium gave large crops of well-formed crystals (Figure 37) that luminesce about six times more brightly that terbium acetylacetone (Table 5), or anhydrous terbium chloride. The crystals were readily purified to a white powder by centrifuging, decanting supernatant fluids, washing twice with ethanol, and finally drying under nitrogen at 57° C. The yield exceeds 87 percent, assuming the formula $Tb(DPA)_3.2H_2O$, to be verified by elemental analysis. The supernatant liquid also contained minute hexagonal crystals in suspension, isolated by drying off a drop of fluid on a microscope slide (Figure 38).

Pending additional analytical data, this will be the recommended method for preparing pure crystals of terbium(tris)dipicolinate.

3.4.3.5 Solubility of $Tb(DPA)_3 \cdot 2H_2O$

This phosphor is insoluble in water and in acid, but dissolves in alkaline solutions of pH 11 or higher.

Hexane, methylcyclohexane, isopropanol, ethanol, methanol, acetonitrile, pyridine, tetrahydrofuran, and toluene all failed to dissolve the crystals. Formamide dissolves the crystals at least in the ratio of 1:10 (weight of crystals to volume of solvent), and dimethylformamide in trace quantities. However, 10 percent solutions in formamide were diluted with three parts of methanol to one of solvent without reprecipitating crystals. The difference in solubility between the crystals and the solvated phosphor is potentially important in two areas: introduction of nonaqueous solutions of the phosphor may be required for varnishes that are not miscible with water; and chromatographic separation of pure crystals may require a nonaqueous moving phase that must not precipitate crystals on the column packing.

3.4.3.6. Surface Structure of phosphorylated stamps

We have noted that inorganic phosphors are readily removed by abrasion from stamp surfaces. Reduction of abrasive removal is one of the major advantages sought with organic phosphors. Figure 39 is the photomicrograph of a current stamp (magnification 125) showing many surface crystals. Abrasion removes the crystals because they are not strongly bonded to the carrier varnish.

Figure 40 shows the distribution of $Tb(AcAc)_3$ in a varnish with a concentration only about ten percent of that of inorganic phosphor. Again the many visible crystals indicate that the phosphor is not well dissolved.

Figure 41 shows microcrystalline $Tb(DPA)_3$ dispersed in varnish TG-20-T, at a phosphor concentration of about 0.12 percent (or one-tenth that of $Tb(AcAc)_3$ in Figure 40), and the particles are extremely small.

Figure 42 shows $Tb(DPA)_3$ in varnish TG-2407-RV at 0.12 percent (w/w), a homogeneous distribution with essentially no particulate matter. Figure 43 is the picture of a stamp paper on which an aqueous solution of $Tb(DPA)_3$ was applied directly to give a strongly phosphorescent surface (90 PMU), with no evidence of crystals.

Just as $Tb(AcAc)_3$ strongly resists abrasive removal(2), the absence of crystals in Figures 41 to 43 suggests that $Tb(DPA)_3$ also will resist abrasive removal because of equally strong or stronger intermolecular bonding with varnishes and/or paper.

3.4.3.7 Fortran Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy is a uniquely valuable tool for fingerprinting organic compounds, because it is sensitive to differences in vibrational frequencies characteristic of chemical bonds and functional groups; and for following changes due to bond breaking, formation, or bond rearrangement. FTIR magnifies the sensitivity of absorption IR by multiple scanning, spectrum addition, and incrementing IR spectra.

We have applied FTIR for preliminary analysis of $Tb(DPA)_3$ in each varnish: TG-2407-RV, and TG-20-T. Figures 44 and 45 are FTIR spectra of TG-2407-RV, and of the same varnish containing the phosphor. The spectra are essentially identical, indicating little or no chemical reaction between components of the varnish, and the phosphor. Figures 46 and 47 are FTIR spectra of TG-20-T with and without phosphor. Here we see a pronounced increase in absorbance at about 1650 cm-1, and a relative decrease in absorbance near 1720 cm-1 upon adding phosphor. These differences are attributed tentatively to chemical changes affecting a component of varnish having carbonyl groups. Of equal importance are two correlations: that crystals are found in tagged TG-20-T, but not in TG-2407-RV (Figures 40 and 41); and that coatings in varnish TG-20-T display lower phosphorescence. Both phenomena suggest modifications in the terbium complex in TG-20-T but not in TG-2407-RV. Installation at NBS of micro-FTIR equipment in the near future will permit more definitive analysis of the suspected changes in bonding.

3.4.3.8 X-ray spectroscopy

Pure crystals of $Tb(DPA)_3$ have been prepared only recently and consequently are now available for the first time for X-ray analysis. Albertsson (27) prepared impure crystals of several lanthanide dipicolinates (not including terbium) by drying off aqueous solutions and observed the hexagonal crystal habit that may be clearly seen in Figures 37 and 40. On the basis of X-ray spectra, he suggested a structure consisting of an infinite chain of lanthanoid units. Unfortunately, it is unclear how his samples were prepared, their elemental composition, or their purity. Our data will be free of these disadvantages.

3.5 Time Constants in Phosphorescence Decay

Table 18 summarizes the measured decay time constants of inorganic (zinc and europium) and organoterbium ($Tb(DPA)_3$) phosphors. The decay curves are shown in Figure 48-53. Phosphorescence was measured during 10 ms following illumination for 20 ms (254 nm). Both green (500 - 550 nm) and green-red [red = (600-630)mm] phosphorescence measurements are obtained by cancellation detectors in the field (28), and consequently both measurements are of interest here. Inorganic or organic europium chelates characteristically luminesce in the red region. Though not directly related to the development of a green phosphor, the subject of this report, europium phosphors represent another rare earth complex of current and future impact in USPS research.

Zinc orthosilicate doped with manganese (Figure 48) displays much longer green and green-red time constants (3.4 and 3.2 msec) than $Tb(DPA)_3$ coated directly on paper (Figure 49, Table 18). $Tb(DPA)_3$ in varnish TG-2407-RV, however, shows relatively long decay times (Figure 50) of 2.0 ms (green) and 1.47 ms (green-red). These differences are consistent with the somewhat lower phosphorescences measured in SVD-4057: we have found that 0.48 percent of $Tb(DPA)_3$ in SVD-4057 (0.11 percent terbium) gave a phosphorescence of 60 PMU compared to over 200 PMU in TG-2407-RV. These preliminary data indicate probably different stereochemical modifications of the phosphor due to two varnishes; i.e., one varnish interacts more extensively with the phosphor than the second, changing the efficiency of transfer of light energy from ligands to the central terbium atom. Figure 52 is a comparison of the effects of two varnishes on decay time. Papers, whether clay-filled or non-filled, may exert additional effects. Accurate diagnoses of any structural differences in the coating situations are needed to rationalize better encryptation techniques and to identify the varnish component that causes problems.

Figures 53 and 54 are decay surves for $Tb(AcAc)_3$ in varnishes TG-2407-RV and TG-20-T on a clay-filled paper (0.44 percent terbium, w/w), after exposure for about six months to sunlight through a south-facing office window. Figure 55 is the curve-obtained for $Tb(DPA)_3$ in varnish

TG-2407-RV (terbium 0.066 percent, w/w) similarly exposed to sunlight for six months. Figures 56 and 57 are curves obtrained with $Tb(DPA)_3$ directly applied to unfilled paper from aqueous solution, and aged in sunlight or in the dark (a desk drawer) for at least three months. The time constants calculated from these curves are summarized in Table 18.

Several important conclusions emerge. Sunlight exposure does somewhat shorten the decay time constant of $Tb(DPA)_3$ in varnish TG-2407-RV applied to a clay-filled paper, but not the phosphor directly applied to the unfilled paper. This may indicate that photochemical degradation of the varnish itself in turn modified the molecular structure of the phosphor through intermediate chemical reactions. An additional possibility is that the varnish becomes opaque with time and diminishes the quantity of light emitted by the coating. Thus it will also be necessary to examine varnishes in the absence of phosphor.

$Tb(AcAc)_3$ (0.44 percent terbium, w/w) in varnish TG-2407-RV shows a slightly higher decay constant than $Tb(DPA)_3$ at 0.066 percent terbium but it is now known whether terbium concentration effects the constant. Both $Tb(AcAc)_3$ and $TB(DPA)_3$ are affected by varnish. For $Tb(DPA)_3$, the decay time is much lower in TG-20-T than in TG-2407-RV. For $Tb(DPA)_3$, the decay time is higher in TG-2407-RV than in SVD-4057. Data for unaged $Tb(AcAc)_3$ unfortunately are not available but will be obtained in the near future.

The lower decay time constant of europium oxide (red and red-green both give 1.01 ms constants) is probably acceptable for the anticipated use of this phosphor (Figure 58). Luminescence will be read during the "on" period of the excitation and emission cycle. However, greater brightness and longer decay times may be characteristic of certain europium chelates that would permit using lower amounts of europium with savings in materials costs.

3.6 Rationale for Development of Next Generation Phosphors

In Table 5, it is shown that the luminescence of $Tb(AcAc)_3$ is enhanced by a factor of 80, over hydrated $TbCl_3 \cdot 6H_2O$; for $Tb(DPA)_3 \cdot 2H_2O$ the enhancement factor is 365, exceeding $Tb(AcAc)_3$ by a factor of 4.6. Data in Table 7 show that the phosphorescence of $Tb(DPA)_3$ in varnish equals in brightness that of $Tb(AcAc)_3$ in 6 to 17 times greater concentration. However, reported enhancements as high as 20,000 at 543 nm (16) [or even 100,000 at the emission wavelength of 545 nm (29)] indicate that still greater quantum efficiences may be attainable with specific organoterbium phosphors. Among the more attractive candidates are terbium complexes with polypyrazolylborates (30; appendix 4), with 15-crown-5 ethers bearing aromatic substituents (31); with selected peptides (15,16); and possibly terbium complexes with both DPA and a synergistic dicarboxylic acid that would form outer-sphere bonds, unlike the inner sphere coordination that characterizes DPA (14).

These modifications hold promise for enhanced phosphorescence and/or stability in coating systems. $Tb(DPA)_3$ itself shows remarkable stability during the key experiment in which it is exposed to sunlight (Figure 21). In a varnish however, it is not completely impervious to its chemical environment (Figure 19). Hence the possibility arises that a co-ligand will enhance stability.

Critical for ultimate selection of proposed phosphors will be field tests conducted by USPS on bulk quantities suitable for coating millions of stamps. Prototype bulk synthesis intended for $Tb(DPA)_3$ will be planned to allow for later synthesis of additional phosphors.

Finally, an improved red organophosphor is urgently needed. Organoeuropium complexes emitting red luminescence (615 nm) can be synthesized by methods similar or identical to those for terbium phosphors. Although synthesis of europium complexes was not included in plans for current NBS programs, the technology for terbium complexes will be transferrable to europium in significant part. Another potential rare earth candidate is samarium. Its oxide manifests light emission at 600 nm. The chelate emission maxima may or may not lie sufficiently within the useful range of 600-630 nm. It merits research because it is a much less costly substance then either europium or terbium (Appendix 3a).

4.0 CONCLUSIONS

Figure 59 is the summary work schedule originally contracted by NBS with USPS and dicussed in this report. Phase I and Phase II have proceeded concurrently.

The first year's efforts on the evaluation and synthesis of novel phosphorescent organoterbium complexes has featured two major developments: proof (Phase I) that $Tb(AcAc)_3$ is a much more stable phosphor than previously believed; but (Phase II) that the quantum efficiency of $Tb(DPA)_3$ is about twenty times higher than that of $Tb(AcAc)_3$. $Tb(DPA)_3$, furthermore, appears to be more miscible. The cost of using $Tb(AcAc)_3$ as a replacement for current inorganic phosphors would be prohibitive because of its low quantum efficiency. That objection does not apply to $Tb(DPA)_3$. For these reasons, $Tb(DPA)_3$ is a much more promising phosphor.

For $Tb(DPA)_3$, production feasibility, including cost and availability of raw materials, processibility, cost of synthesis, and compatibility with existing systems, presents no major technical barriers. Longevity, the second major criterion of a useful phosphor, also has been well demonstrated for $Tb(DPA)_3$ under this contract in several months of continuous exposure to sunlight in a south-facing office window. Contract deliverables for the second year (Figure 59) included 5-10 g of the best NBS phosphors, and several one to two g samples of $Tb(DPA)_3$ already have been delivered to USPS.

$Tb(DPA)_3$ is less resistant than $Tb(AcAc)_3$ to prolonged UV exposure at high intensity and energy -e.g., for one hundred hours or more - at 254 nm and 600 $\mu w\ cm^{-2}$. A criterion requiring prolonged resistance to UV light would, however, be of questionable relevance to the more important requirement of stability under service conditions. A stamp is not likely to be exposed to UV light of high intensity and energy for long periods of time except during artificial tests of stability.

The new phosphor exhibits good resistance to decay in humid air [94 percent RH at 91 °F (32 °C)], an imporant property for this compounds, but not surprising since it is synthesized in water. However, in examining such properties as heat stability, resistance to oxidation and resistance to fungal attack and high humidity, further effort is needed and will be undertaken during the second year of research. A fundamental problem in this effort will be to distinguish between the chemistry of the phosphor and of its matrix, primarily using reflectance FT-IR to follow the course of changes in bonding at the surface. This is especially important when organic varnishes are used to entrain the phosphor. Direct application of the phosphor to paper, in its aqueous matrix, will be further pursued as a technique for isolating effects of matrix variables due to either the varnishes, the paper, or inks.

The discovery that aqueous solutions of the phosphor can be applied directly to one type of paper suggests a revolutionary stamp technology. A process eliminating the varnish matrix for applying phosphor would be useful for many practical reasons. Such an investigation was not part of the original NBS contract, but relevant data have been and will be noted with care.

This report presents a compelling rationale to expand production of $Tb(DPA)_3$ as a candidate USPS phosphor, subject the material to actual field tests, and complete all of the details of characterization needed for a protective patent. Consequently, NBS and USPS have negotiated an add-on contract to expand phosphor porudction for the originally contracted 10 g to a 50 gallon volume of aqueous $Tb(DPA)_3$ solution in the concentration needed to prepare stamp coatings of the desired brightness. In addition, chromatographic methods of isolation and analysis will be developed according to the terms of the contract, and micro Fourier transform infrared spectra will be obtained, especially in the reflectance mode, to study more closely changes in bonding that occur when the phosphor is mixed and/or aged in different matrices.

The premise inherent in $Tb(DPA)_3$ as a highly effective organoterbium tagging phosphor, is due to the physical chemistry of the ligand groups. They are are strongly chromophoric, hydrophobic, and sterically large. These molecular properties are consistent with our original objective to prepare an "encapsulated" chromogenic phosphor. Additional candidate phosphors merit synthesis and evaluation as potentially more stable or more efficient phosphors. Examples are polypyrazolylborates, protein-terbium macromolecules, and possibly synergistic combinations of ligands including DPA and either aliphatic carboxylic acids or Lewis bases. These syntheses will be pursued intensively, and completed in FY85.

We expect that the technology developed for terbium chelates will remain largely applicable to both europium, and samarium, in subsequent development of red phosphors for USPS applications. This concept will be subordinated to terbium research in FY85, but a limited effort will be started in anticipation of more intensive work in FY86 on europium and samarium chelates.

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TABLE 1

Description of Varnishes

BEP Designation	Ingredients (BEP)		Cobalt content (NBS) µg/g	Application
	Wt. %	Compound		
TG-20-T	8.4	Acryloid Polymer	.018	Cottrell press
	39.2	Butyl carbitol		
	24.0	Hexylene glycol		
	15.0	Green phosphor		
	5.0	Santocel C		
	8.4	Ethyl cellulose		
TG-2407-RV	24	Acrylic Polymer	0.00	Intaglio, Rotogravure press
	18	Isopropanol		
	23	Water		
	15	Denatured Alcohol		
	20	Zinc silicate		
TG-11-T	72.68	Heat-Set varnish	2.17	Offset press
	0.52	Cobalt drier		
	1.03	Lecithin		
	5.15	Thixcin E		
	20.62	Green Phosphor		
TG-8-T	66.5	Varnish formula 2395A	2.19	Offset press
	5.0	Thixcin E		
	0.5	Cobalt drier		
	28	Phosphor		
TG-45-T	60	Varnish formula UV 8	0.00	-
	30	Green phosphor		
	5	Lo-Val 27		
	5	Hexylene glycol		

TABLE 2

Designation of USPS Papers Used in Accelerated Aging and Luminescence Studies

I - Non filled, non-gummed, plain.
II - Non clayed, 50:50 tapioca:polyvinyl alcohol gum, plain
III - Multicolored with six color hexagons ("Experimental")
IV - Printed with black ink ("For Testing Purposes Only")
V - Clay-filled, non-gummed, plain
VI - Clay-filled, 100% tapioca gum, plain

TABLE 3

Effect of Coordinated Water

Phosphor	Luminescence, EMI units	
	Avg	s*
$TbCl_3$ (anhydrous)	2810	42
$TbCl_3 \cdot 6H_2O$	42	9
Tb-PTA**	56	48
Tb-PTA-TOPO***	1400	13
Tb-TOPO	150	13

* standard deviation from the mean of six measurements

** PTA = pivaloyltrifluoroacetone

*** TOPO = Trioctylphosphine oxide

TABLE 4

Changes with Time and Treatment in the Luminescence of $Tb(AcAc)_3$ Dispersed in Varnish

TIME (Hours)	1*	2**	3***	4****	5*****
0	2980	2740	2770	2700	3200
24	1830	4090	3920	3780	1910
48	2710	5900	3370	3580	900
70	2940	6580	6080	6030	870
94	2680	4880	4280	4860	760
118	3080	5500	5020	6040	330
164	3760	6770	6480	7480	800

* Aged at 93% relative humidity and 31° C for twenty-four hours, then in ambient air

** Aged in darkness, ambient

*** Aged under fluorescent lights, ambient

**** Aged in a desiccator over Drierite

***** Aged at 93% relative humidity and at 31° C for the whole period

TABLE 5

Relative Total Luminescence of Selected Terbium Phosphors

Phosphor	Luminescence (EMI units)	Standard
Tb(AcAc)$_3$	3300	200*
Tb(An$_2$Ac)	1860	200*
TbCl$_3$(anhydrous)	2810	200*
TbCl$_3$·6H$_2$O	42	200*
Tb-PTA-TOPO**	1400	200*
Tb-PTA-TOPO***	700	200*
Tb-PTA	56 (14)**	800* (200)**
Tb-TOPO	150 (22)**	1350* (200)**
Tb-HFA-TOPO	930 (91)**	2050* (200)**
Tb-ATC	220 (34)**	1310* (200)**
Tb(DPA)$_3$	1740 (15,350)**	374*** (200)**

* A selected cluster of microbeads doped with Terbium oxide

** Data normalized for comparison

*** EMI scale modified to be able to read the luminescence of Tb(DPA)$_3$·2H$_2$O, requiring use of Tb(AcAc)$_3$ as standard

TABLE 6

Phosphorescence of Tagged Coatings on Stamp Papers (PMU)

Paper	Varnish	Phosphor $Tb(AcAc)_3$ (0.44)*	 Tb-PTA-TOPO (0.57)*	 $Tb(DPA)_3$ (0.066)*
I	TG-2407-RV	26	11	168
II	TG-2407-RV	41		200
III	TG-2407-RV	45	16	148
IV	TG-2407-RV	42	8	108
V	TG-2407-RV	80	20	164
VI	TG-2407-RV	79	16	200
I	TG-20-T	44		70
II	TG-20-T	52		71
III	TG-20-T	11		22
IV	TG-20-T	18		34
V	TG-20-T	45		66
VI	TG-20-T	28		64

* Percent (w/w) of terbium in varnish

TABLE 7

Relative phosphorescence intensity of $Tb(AcAc)_3$ in varnish applied to unfilled paper

Phosphor	Tb (%)	PMU	Estimated terbium consumption* pounds/year	Estimated terbium consumption* Percent of US Production	Cost** ($/year)
			Varnish TG-2407-RV		
$Tb(AcAc)_3$	0.44	79	7940	52.2	5.6 M
$Tb(DPA)_n$	0.026	75	464	3.1	0.33 M
			Varnish TG-20-T		
$Tb(DPA)_n$	0.075	80	1350	9.0	0.95 M

* Estimated for fifty billion stamps coated to a depth of 0.0254 cm(1.0 mil), with surface dimensions 2.54 by 3.81 cm (1.0 by 1.5 inch).

** For comparison, the current inorganic phosphor, zinc orthosilicate, at the cost of $6.00 per pound, would cost an estimated $1.3 M to $2.7 M for coatings containing 12 to 25 percent of phosphor.

Table 8

Luminescence of Stamp Papers Coated with Varnish TG-20-T, with $Tb(AcAc)_3$ Dopant. Accelerated Aging, Humid, Ultraviolet Light Illumination*

	Paper**					
	I	II	III	IV	V	VI
Time (hours)	Phosphorescence***					
0.00	44	52	11	18	45	28
0.25	31	23	3	16	33	15
1.00	24	22	5	14	28	13
2.00	24	22	6	15	27	14
22.00	28	25	13	23	32	28
67.00	38	31	19	25	42	37
185.00	46	54	21	16	50	35
235.00	55	66	30	17	70	31
283.00	55	66	32	16	64	27
403.00	55	54	35	13	20	20
475.00	55	41	32	13	7	20
	Luminescence****					
0.00	310	410	180	290	380	230
0.25	240	250	110	240	320	170
1.00	210	250	140	240	290	160
2.00	260	260	170	240	290	190
22.00	300	270	290	330	360	270
67.00	300	330	300	330	370	330
283.00	470	530	390	160	610	290
403.00	510	590	380	280	150	340

---

* 600 μw cm^{-2}, 254 nm

** See Table 2

*** Postal Meter Units (PMU)

**** Epifluorescence Microscopic Imagery (EMI) units (mv)

Table 9

Luminescence of Stamp Papers Coated with Varnish TG-2407-RV, with Tb(AcAc)$_3$ Dopant. Accelerated Aging, Humid (94%, 88 °F), Ultraviolet Light Illumination*

Paper**

TIME (hours)	I	II	III	IV	V	VI
Phosphorescence***						
0.00	26	41	45	42	80	79
0.25	29	42	34	31	64	66
1.00	26	39	23	30	55	51
2.00	23	37	29	28	53	49
22.00	27	42	26	32	47	45
67.00	30	48	33	34	55	55
185.00	32	51	44	34	60	42
235.00	35	54	60	31	60	46
283.00	33	50	56	27	58	46
403.00	28	45	43	22	54	40
475.00	37	44	42	14	54	35
Total Luminescence****						
0.00	210	360	370	750	720	760
0.25	290	450	390	620	610	540
1.00	280	410	370	570	530	530
2.00	280	380	310	490	490	490
22.00	230	340	340	410	370	370
67.00	230	300	390	420	430	430
283.00	260	410	570	410	450	420
403.00	310	470	370	160	470	450

---

* 600 μw cm^{-2}, 254 nm

** See Table 2

*** Postal meter units (PMU)

**** Epifluorescence Microscopic Imagery Units, mV

TABLE 10

Phosphorescence (PMU) of Stamp Papers Coated with Varnish TG-2407-RV, Doped with Phosphor $Tb(Acc)_3$ or $Tb(DPA)_3$. Window Aging

Time	Paper						
(Day)	I*	II*	III*	IV*	V		VI*
					A*	B*	
0	29	48	29	41	71	164	70
1	--	--	--	--	--	165	--
4	26	50	37	35	68	--	64
5	--	--	--	--	--	164	--
8	24	42	27	27	50	--	52
9	--	--	--	--	--	163	--
15	21	36	31	25	41	--	44
16	--	--	--	--	--	152	--
22	22	37	29	24	39	--	40
23	--	--	--	--	--	140	--
27	--	--	--	--	--	139	--
29	23	40	35	27	39	--	40
30	--	--	--	--	--	132	--
34	--	--	--	--	--	130	--
36	23	39	36	25	39	--	38
37	--	--	--	--	--	125	--
41	--	--	--	--	--	125	--
42	22	39	33	25	39	--	38
44	--	--	--	--	--	124	--
46	24	43	39	27	44	--	43
48	--	--	--	--	--	123	--
49	24	42	39	28	44	--	40
51	--	--	--	--	--	123	--
53	23	41	38	29	44	--	41
55	--	--	--	--	--	124	--
57	24	43	41	29	46	--	42
59	--	--	--	--	--	120	--
60	26	46	44	32	49	--	48
61	--	--	--	--	--	119	--
65	--	--	--	--	--	116	--
68	24	44	39	30	47	--	44
69	--	--	--	--	--	108	--

* $Tb(AcAc)_3$: 1.44% chelate, 0.44% Tb(w/w)

** $Tb(DPA)_3$: 0.28% chelate, 0.066% Tb(w/w)

TABLE 11

Phosphorescence (PMU) of Stamp Papers Coated with Varnish TG-20-T, with $Tb(AcAc)_3$ Dopant. Window Aging .

Time	Paper*					
(Days)	I	II	III	IV	V	VI
0	11	12	12	10	16	14
4	14	16	15	13	20	18
8	15	18	17	13	20	18
15	15	19	16	14	21	20
22	17	21	19	15	23	21
29	19	24	24	17	25	25
36	20	25	24	18	27	25
42	21	26	24	18	28	26
46	23	28	28	20	31	28
49	23	28	28	20	31	30
53	23	28	27	21	31	30
57	24	30	30	22	33	31
60	26	33	32	25	37	33
68	26	32	33	23	34	32

* See Table 2

TABLE 12

Phosphorescence of Tb(DPA)$_n$ as a Function of pH and Tb/DPA Ratio in Aqueous Solution

Tb:DPA*

1:2		1:3		1:4	
pH	PMU	pH	PMU	pH	PMU
4.5	28	4.6	23	4.6	61
5.8	43	5.8	54	6.0	71
6.8	41	7.3	54	6.9	70
8.1	39	8.0	52	7.8	65
9.1	42	9.3	54	9.2	71

* Aqueous drawdowns applied to stamp paper; Terbium concentration 0.034 percent (w/v).

TABLE 13

Window aging of $Tb(DPA)_3$ added directly* to papers I-VI (PMU)

	I**		II**		III**	
Time (Days)	Light	Dark	Light	Dark	Light	Dark
0	110	100	52	48	31	23
1	102	95	37	44	26	21
7	120	90	48	42	33	20
13	116	88	47	40	31	16.5
26	119	89	51	44	33	19
35	124	93	56	47	28	17.5
44	124	94	57	49	34.5	21
61	121	90	55	43	31.5	19
70	124	92	56	48	32	18
89	120	93	53	47	28	20

	IV**		V**		VI**	
Time (Days)	Light	Dark	Light	Dark	Light	Dark
0	7	8	14	14	13.5	13.5
1	7	8	13	14	13.5	13.5
7	6.5	7.5	13	13	13.5	14
13	6.5	7.0	12	13.5	12.5	13
26	6	7.5	10	13.5	11	13
35	5.5	7.5	9	13.5	10.5	13
44	5.5	8.0	8.5	14	9	14
61	6.0	7.5	7	13	7.5	12.5
70	4.5	7.0	7	13	7.5	12.5
89	4.5	7.5	7	14	7	13

* Terbium concentration 0.037 percent in aqueous solution.

** For paper designation, see Table 2.

TABLE 14

Luminescence as a function of terbium ($Tb(DPA)_3$) concentration on varnish TG-20-T coated on multicolored stamp paper

	Color Area Tested						
Terbium (%, w/w)	Blue	Pink	Brown	Red	Yellow	Green	Clear
0.000	71	70	74	63	130	98	117
0.023	169	133	152	133	480	416	587
0.047	295	207	420	495	637	743	766
0.070	341	316	334	357	734	593	950
0.094	431	587	514	815	1796	844	1276
0.117	678	586	839	902	1436	1483	2160
slope	4708	4930	5880	7325	12990	9813	15270
95% Confidence Interval	1560	1910	2989	4107	8063	5690	8020
Intercept	55	41	45	25	114	122	90
r^2	0.946	0.959	0.882	0.893	0.821	0.850	0.914

TABLE 15

Luminescence as a function of terbium ($Tb(DPA)_3$) concentration in varnish TG-2407-RV coated on multicolored "Experimental" stamp paper

	Color Area Tested						
Terbium (%, w/w)	Blue	Pink	Brown	Red	Yellow	Green	Clear
0.0000	66	85	77	48	129	102	115
0.0129	99	108	106	102	298	265	376
0.0258	172	165	174	135	565	594	713
0.0386	211	255	219	156	889	890	1264
0.0516	422	456	328	150	1205	1072	1454
0.0644	473	459	429	175	1588	1238	1995
slope	6768	6666	5550	1728	22950	18640	29315
95% Confidence Interval	2600	2790	998	1140	3656	2526	4280
Intercept	23	40	46	71	41	93	44
r^2	0.925	0.915	0.960	0.863	0.988	0.986	0.986

TABLE 16

Elemental analysis of reaction product of Tb and DPA in 1:10 H_2O:THF

	Found (%)	Theory (%)
Carbon	27.0	23.1
Hydrogen	3.1	2.5
Nitrogen	4.4	3.9
Terbium	36.3	41.5
Oxygen	29.0	26.5

Empirical formula: $C_7H_9NTbO_6$

Corresponds to $Tb(DPA) \cdot 2H_2O$

TABLE 17

Elemental analysis of $Tb(DPA)_n$ prepared in alkaline water, precipitated with acid, and washed with 1:10 H_2O:THF

	Theory		Found
	$Tb(DPA)_3 \cdot H_2O$	$Tb(DPA)_3 \cdot 2H_2O$	
H	2.02	2.31	2.26
N	6.22	6.06	6.07
C	37.30	36.33	36.10
Tb	23.56	22.95	22.95
O**	30.90	32.29	32.62**

* Schwartzkopf Microanalytical Laboratory

** Oxygen estimated by difference, not measured

Table 18

Figure	Material	e^{-kt}	time constant* (ms)
48	Zinc orthosilicate	Green	3.36
	(no varnish)	Green-red	3.19
49	Tb(DPA)	Green	1.41
	(no varnish)	Green-red	1.18
50	$Tb(DPA_3 \cdot 2H_2O$	Green	1.42
	(in TG-2407-RV)	Green-red	1.47
51	$Tb(DPA)_3 \cdot 2H_2O$	Green	1.42
	(in SVD-4057)	Green-red	1.30
52	$Tb(DPA)_3 \cdot 2H_2O$:		
	(in TG-2407-RV)	Green-red	1.59
	(in SVD-4057)	Green-red	1.32
53	$Tb(AcAc)_3$**	Green	1.58
	(TG-2407-RV)	Green-red	1.45
54	$Tb(AcAc)_3$**	Green	1.45
	(TG-2407-RV)	Green-red	1.24
56	$Tb(DPA)_3$***	Green	1.60
	(No varnish)	Green-red	1.48
57	Tb(DPA)****	Green	1.65
	(No varnish)	Green-red	1.45
58	Eu_2O_3	Red	1.01
	(ceramic)	Red-green	1.01

* Preliminary test data on systems not yet completely defined.

** Following six months' exposure to sunlight in a south-facing office window.

*** Following three months' exposure to sunlight in a south-facing office window.

**** Following three months' storage in a desk drawer.

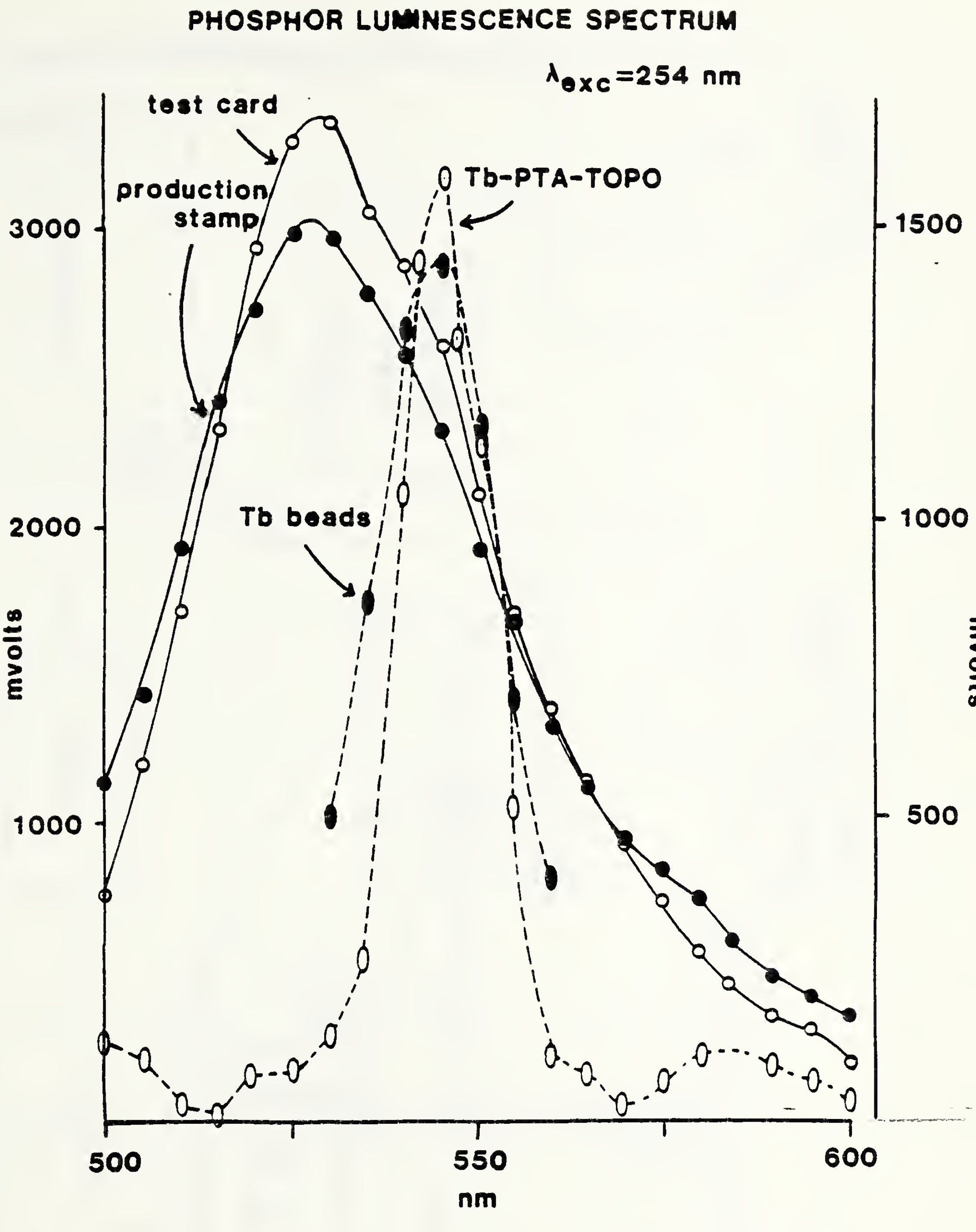


Figure 1 Luminescence spectrum of phosphor materials with 254 nm excitation. Solid lines show inorganic phosphor emission in a current USPS production stamp (entitled Science and Technology) (o) and incorporated into a ceramic test card (o). Dotted lines show emission of inorganic Tb phosphors in glass microbeads (0) and in an NBS synthesized complex of Tb with pivaloyltrifluoracetate (PTA) and trioctylphosphine oxide (TOPO) in varnish TG-2407-RV (0) applied with a 1.0 mil drawdown bar to plain, non-clayed paper. Data were taken using the EMI system and are reported in mV.

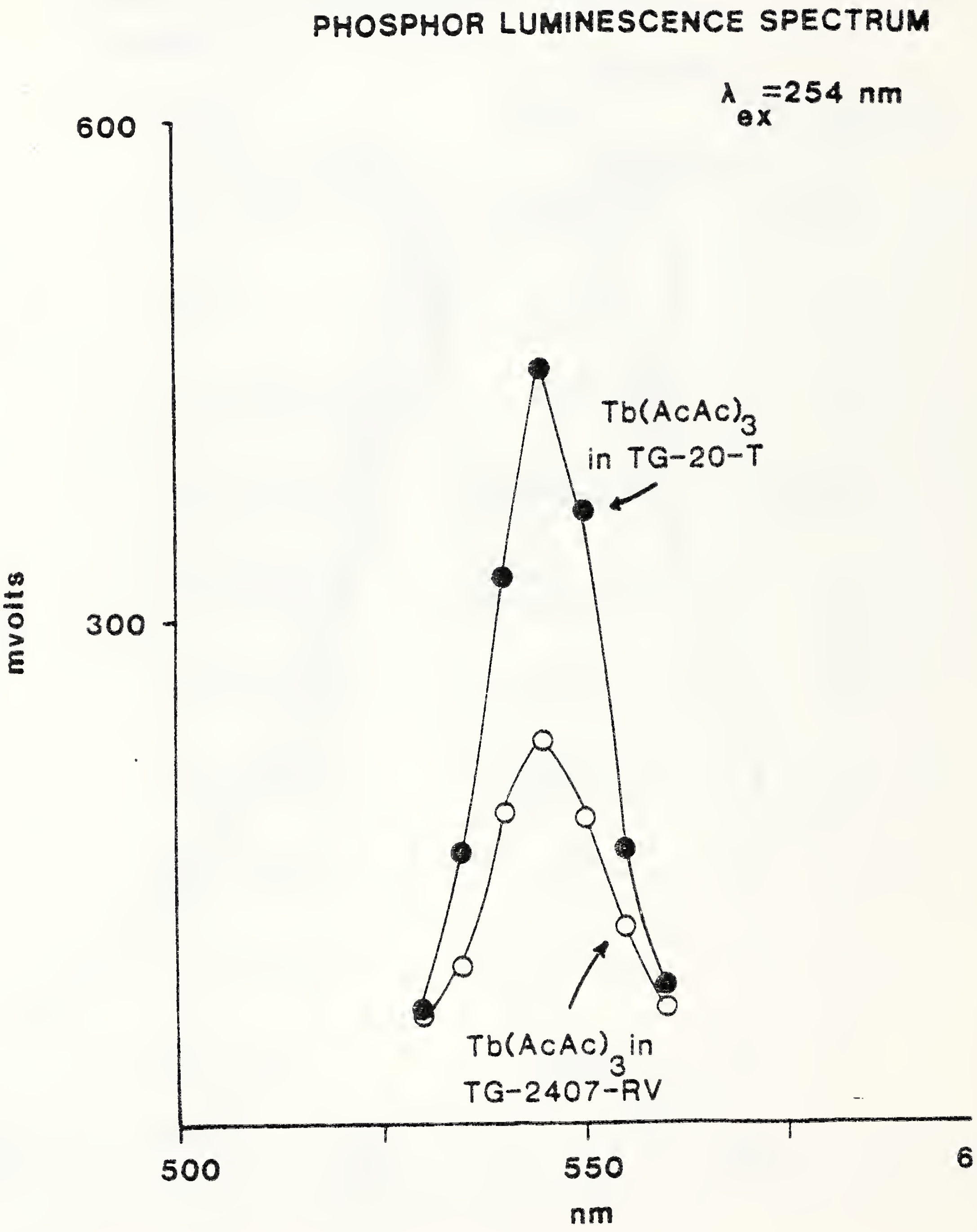
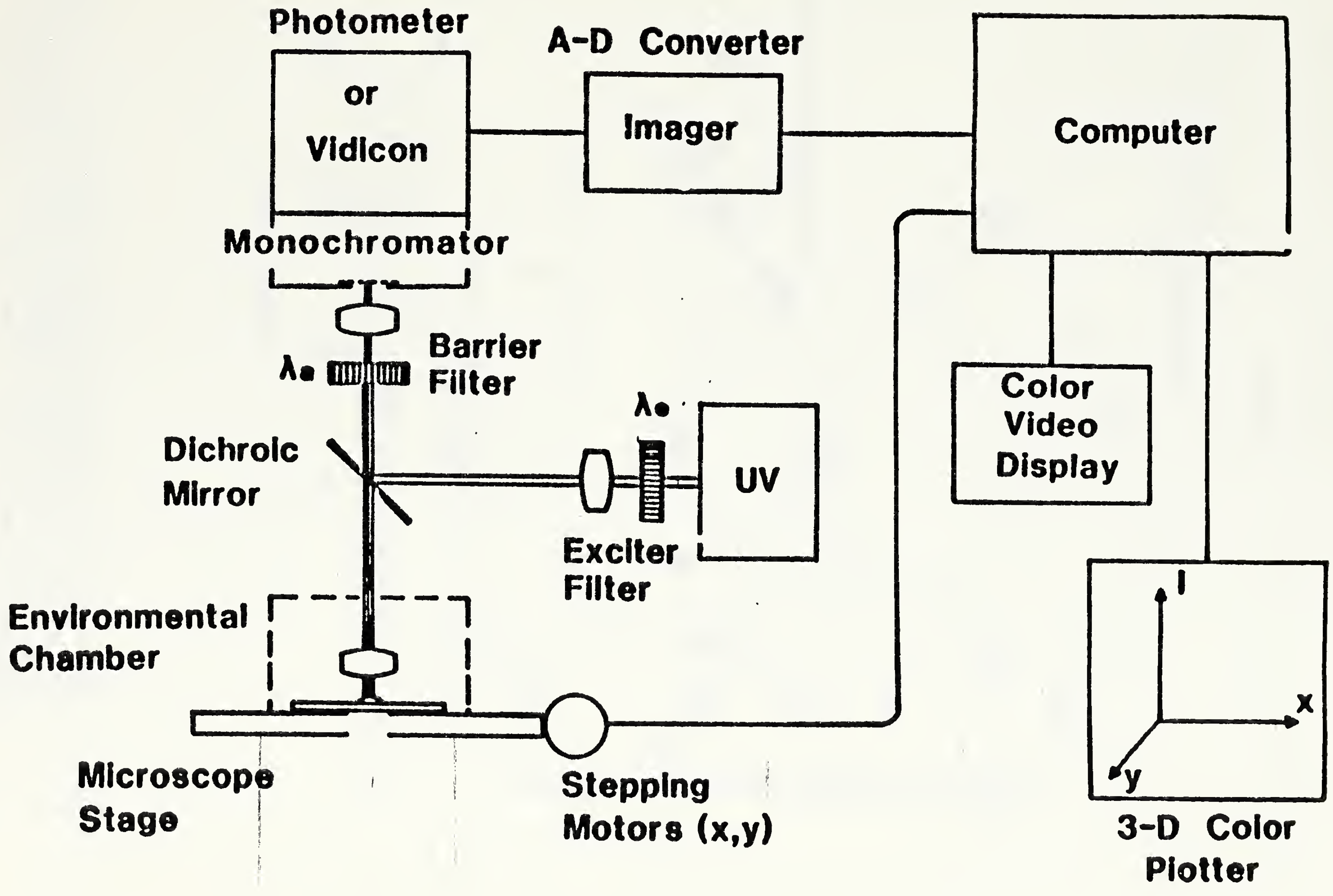


Figure 2 Luminescence spectrum of Tb acetylacetonate in varnish Tg-20-T (o) and TG-2407-RV (o) (0.44 w/w) applied with a 1.0 mil drawdown bar to plain non-filled paper. Data were taken using the EMI system and are reported in mV.

Figure 3



Epifluorescence Microscope Imaging (EMI) system diagram.

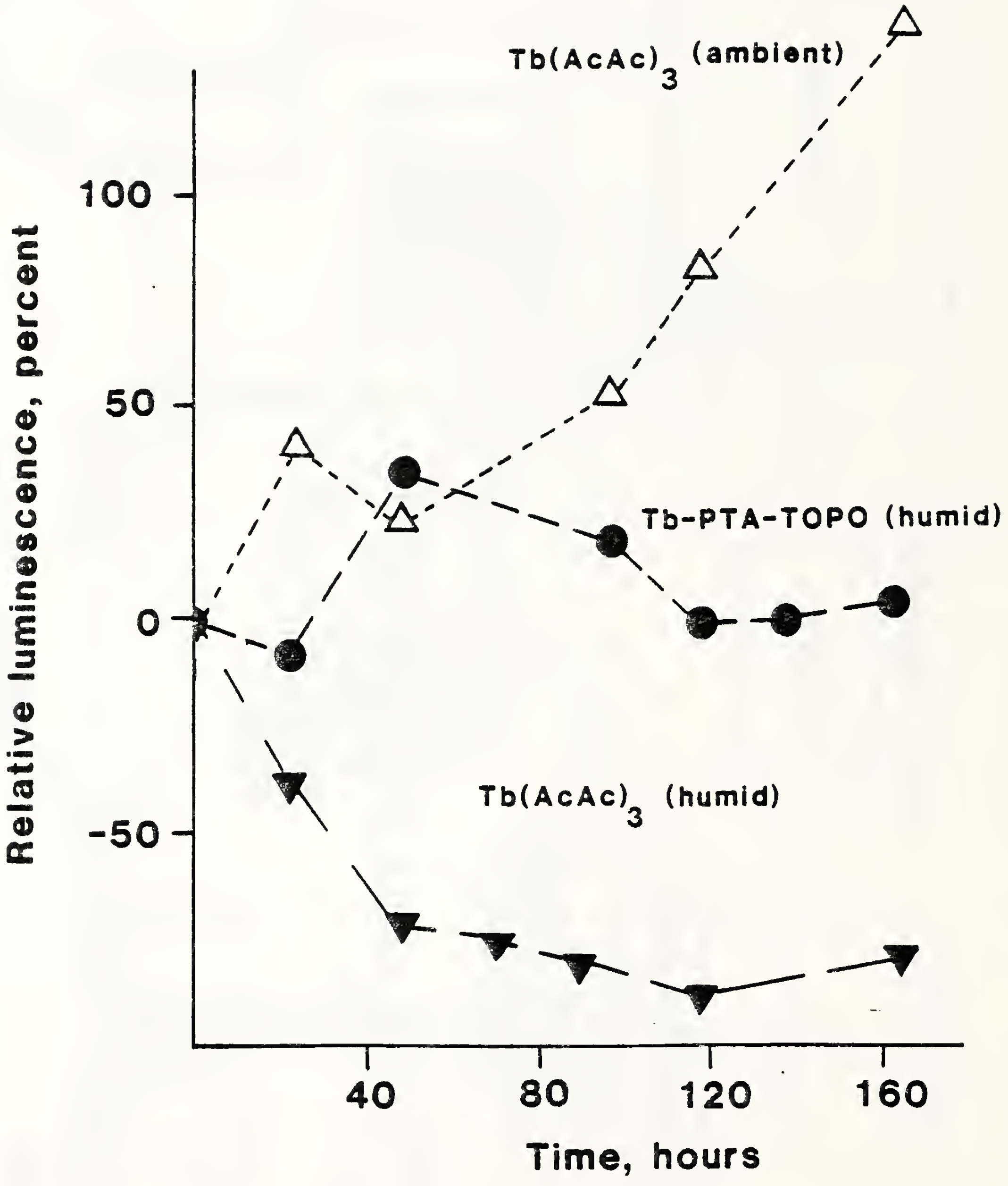
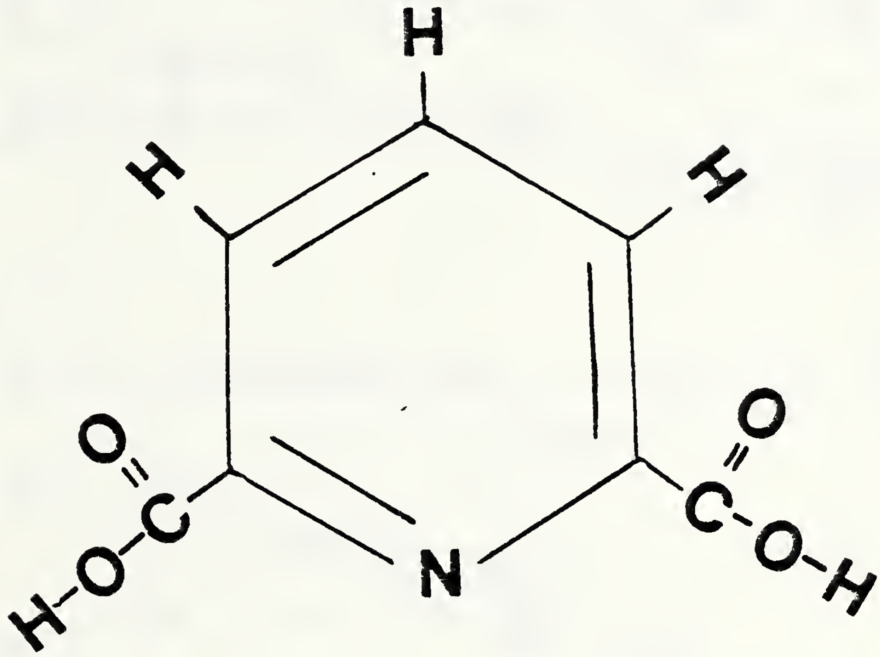


Figure 4 Luminescence of stamp papers coated with varnishes TG-2407-RV and TG-20-T, with Tb(AcAc) dopant (0.44% Tb w/w). Accelerated aging, humid (94% relative humidity, 88° F), ultraviolet light exposure (254 nm, 3 w/cm^2). See Table 2 for stamp paper designations.

Figure 5



Dipicolinic acid (DPA)

2,6-pyridine-dicarboxylic acid

Tb AcAc 94% RH-UV exposure

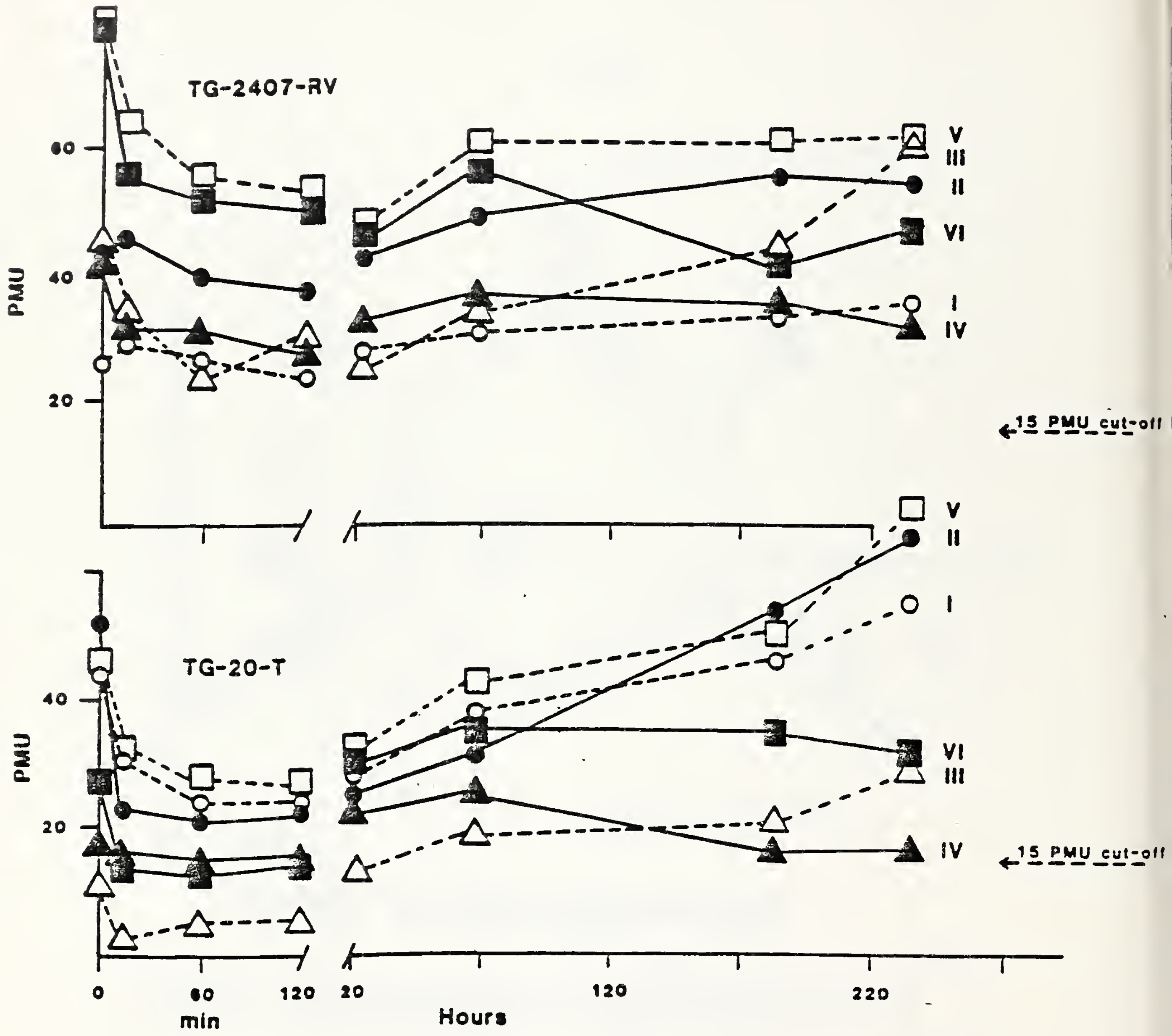
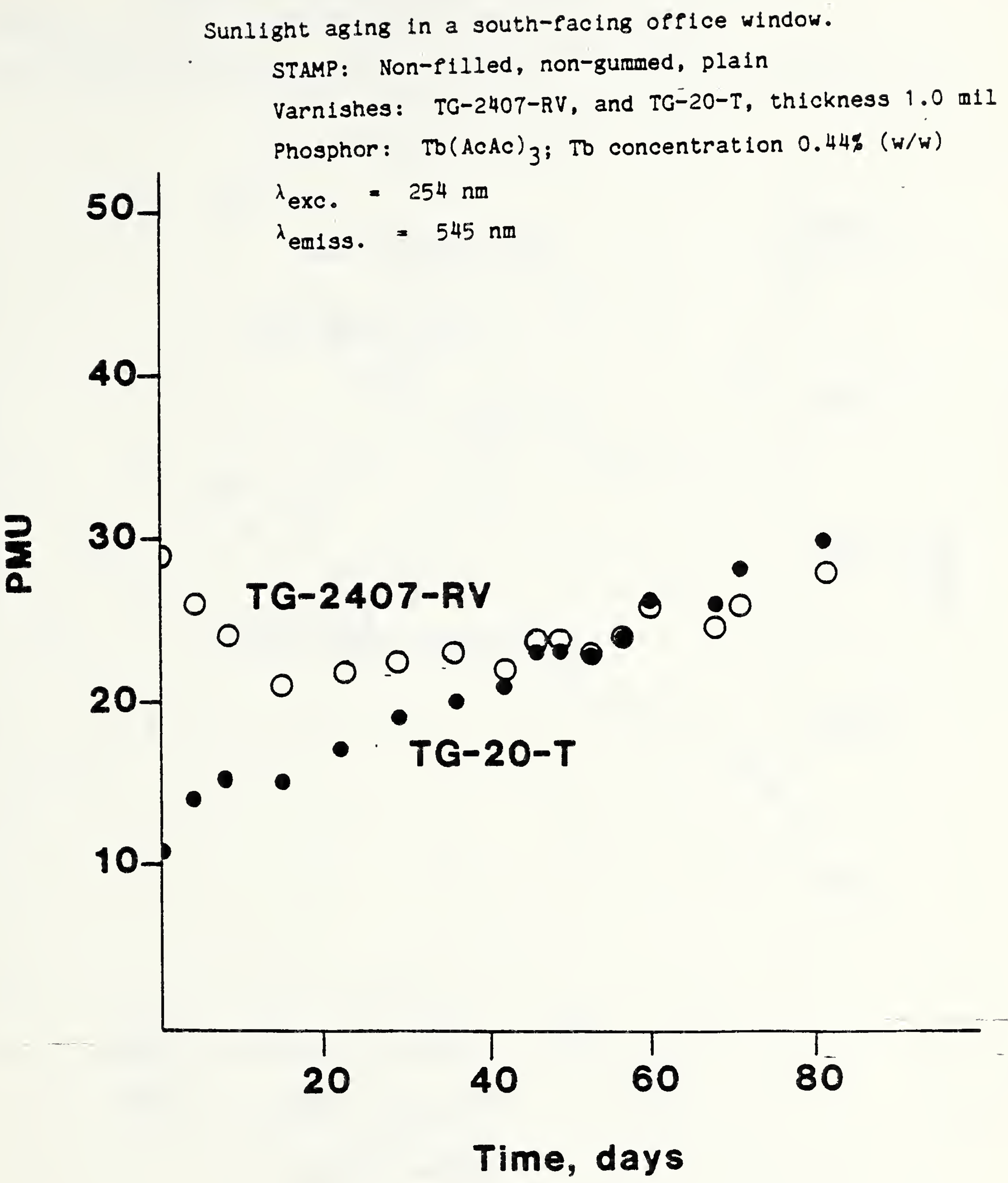


Figure. 6 Luminescence of stamp papers coated with varnishes TG-2407-RV and TG-20-T, with $Tb(AcAc)_3$ dopant (0.44 % Tb, w/w). Accelerated aging, humid (94 % relative humidity, 88 °F), ultraviolet light illumination (600 µwatt/cm^2). See Table 2 for description of stamp papers.



Sunlight aging in a south-facing office window.

STAMP: Non-filled, non-gummed, plain

Varnishes: TG-2407-RV, and TG-20-T, thickness 1.0 mil

Phosphor: $Tb(AcAc)_3$; Tb concentration 0.44% (w/w)

$\lambda_{exc.}$ = 254 nm

$\lambda_{emiss.}$ = 545 nm

Figure 7 Natural aging of coated stamp paper exposed to sunlight in a south-facing window for a prolonged period of time. Doped varnishes ($Tb(AcAc)_3$), 1.0 mil in thickness, coated on paper No. 1, plain, non-filled, non-gummed.

Sunlight aging in a south-facing office window.

STAMP: Non-filled, gummed, plain

Varnishes: TG-2407-RV and TG-20-T, thickness 1.0 mil

Phosphor: $Tb(AcAc)_3$; Tb concentration 0.44% (w/w)

$\lambda_{exc.}$ = 254 nm

$\lambda_{emiss.}$ = 545 nm

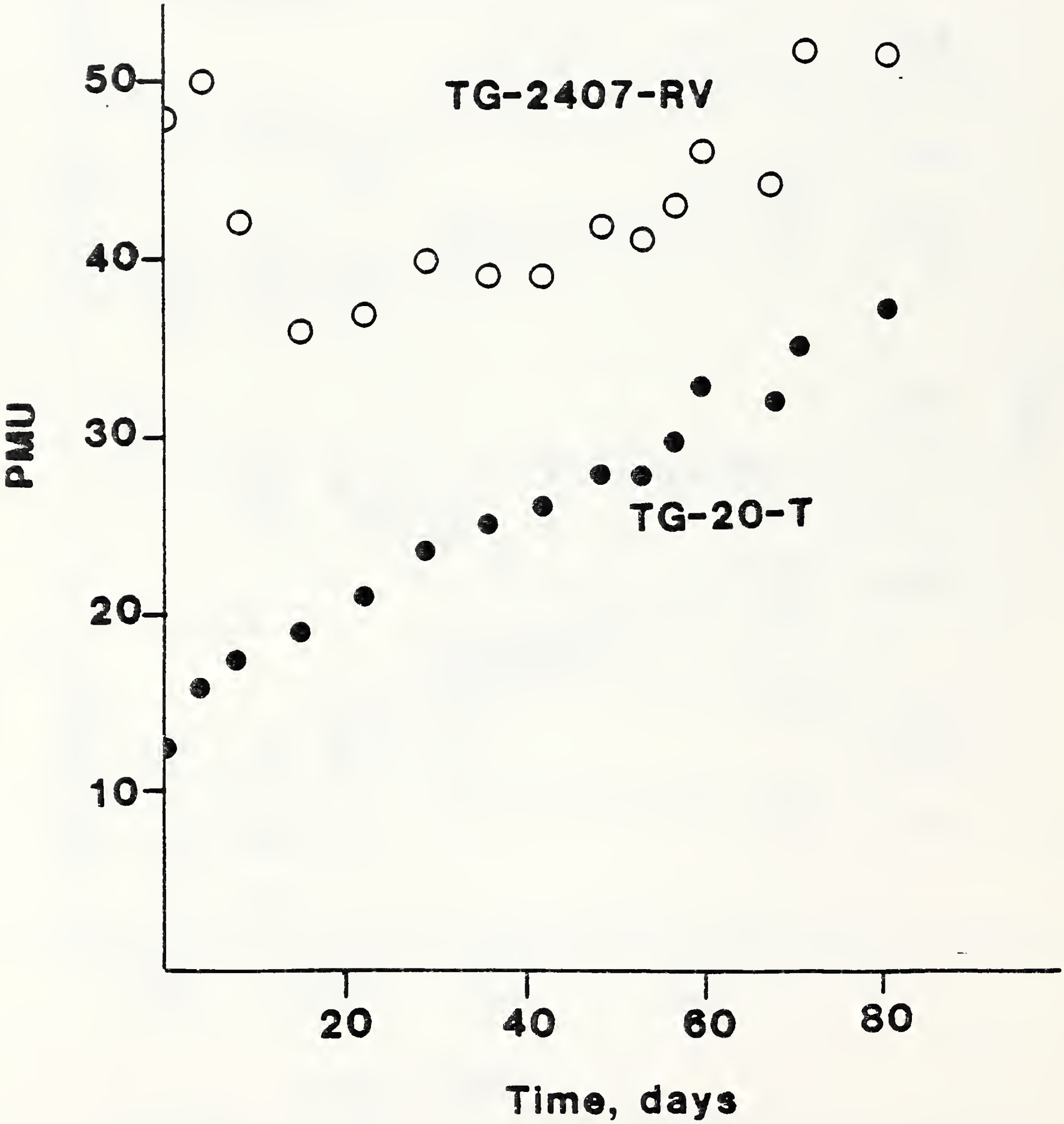


Figure 8 Natural aging of coated stamp paper exposed to sunlight in an south-facing window for a prolonger period of time. Doped varnishes ($Tb(AcAc)_3$), 1.0 mil in thickness, coated on paper No.2, plain, non-filled, gummed.

Sunlight Aging in a south-facing office window.

STAMP: Multicolored, "Experimental"

Varnishes: TG-2407-RV, and TG-20-T, thickness 1.0 mil

Phosphor: $Tb(AcAc)_3$; Tb concentration 0.44% (w/w)

$\lambda_{exc.}$ = 254 nm

$\lambda_{emiss.}$ = 545 nm

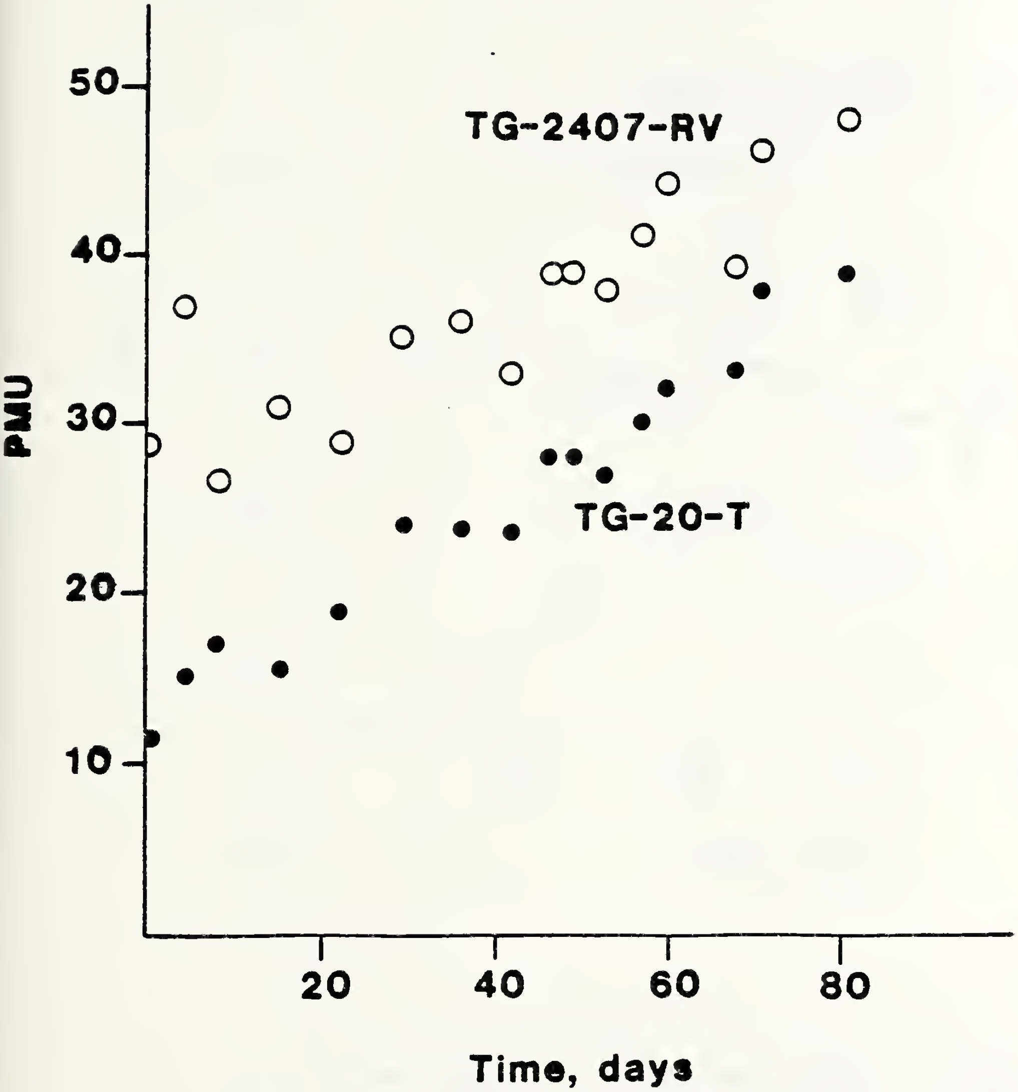
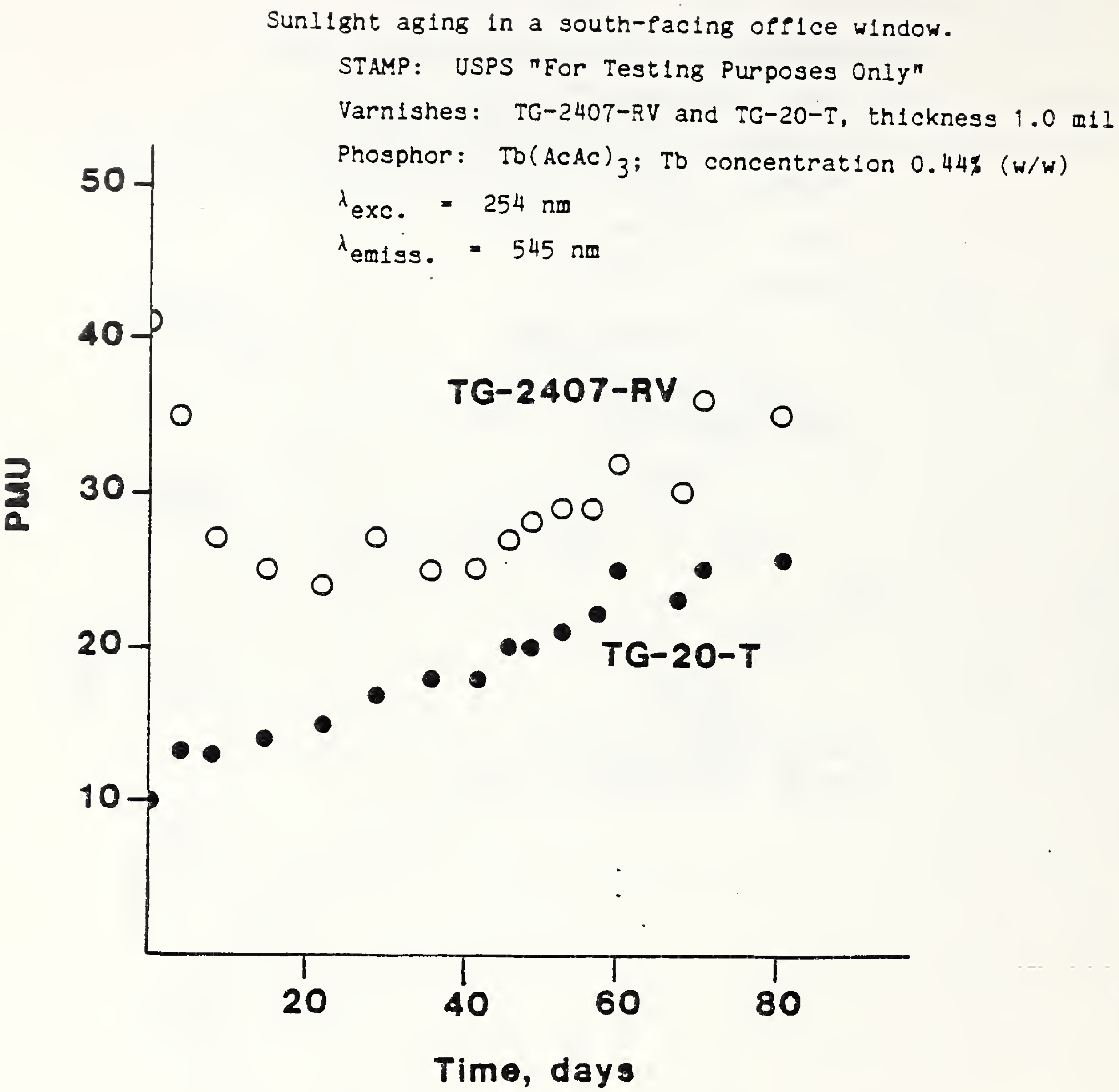


Figure 9 Natural aging of coated stamp papers exposed to sunlight in a south-facing office window for a prolonged period of time. Doped varnishes ($Tb(AcAc)_3$, 1.0 mil in thickness, coated on paper No. 3, USPS "Experimental" multicolored sheet.



Sunlight aging in a south-facing office window.

STAMP: USPS "For Testing Purposes Only"

Varnishes: TG-2407-RV and TG-20-T, thickness 1.0 mil

Phosphor: $Tb(AcAc)_3$; Tb concentration 0.44% (w/w)

$\lambda_{exc.}$ = 254 nm

$\lambda_{emiss.}$ = 545 nm

Figure 10 Natural aging of coated stamp paper exposed to sunlight in a south-facing window for a prolonged period of time. Doped varnishes ($Tb(AcAc)_3$), 1.0 mil thickness, coated on paper No. 4, USPS sheet labeled "For Testing Purposes Only."

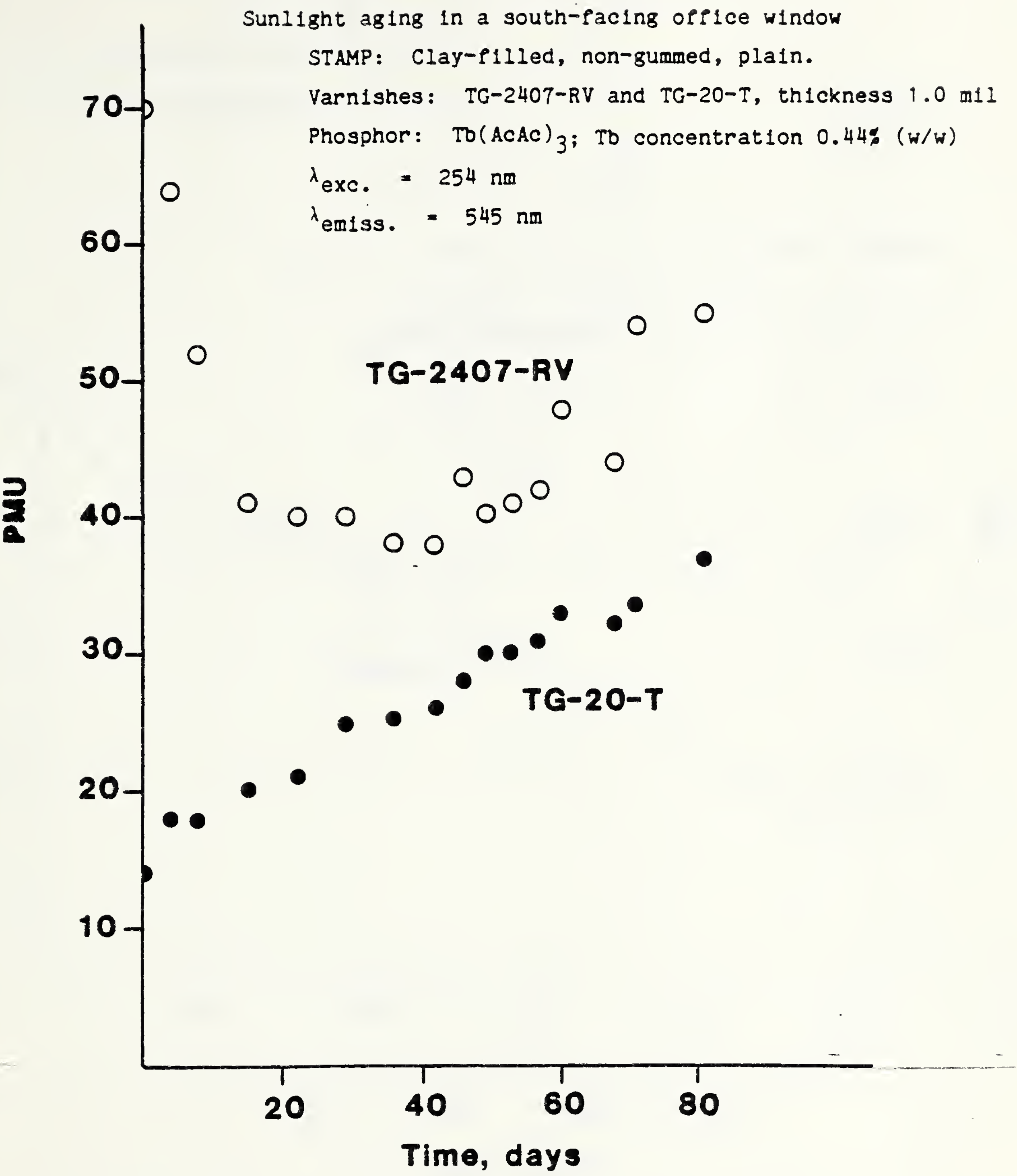


Figure 11 Natural aging of coated stamp paper exposed to sunlight in a south-facing window for a prolonged period of time. Doped varnishes (Tb(AcAc)$_3$), 1.0 mil in thickness, coated on paper No. 5, plain, clay-filled, non-gummed.

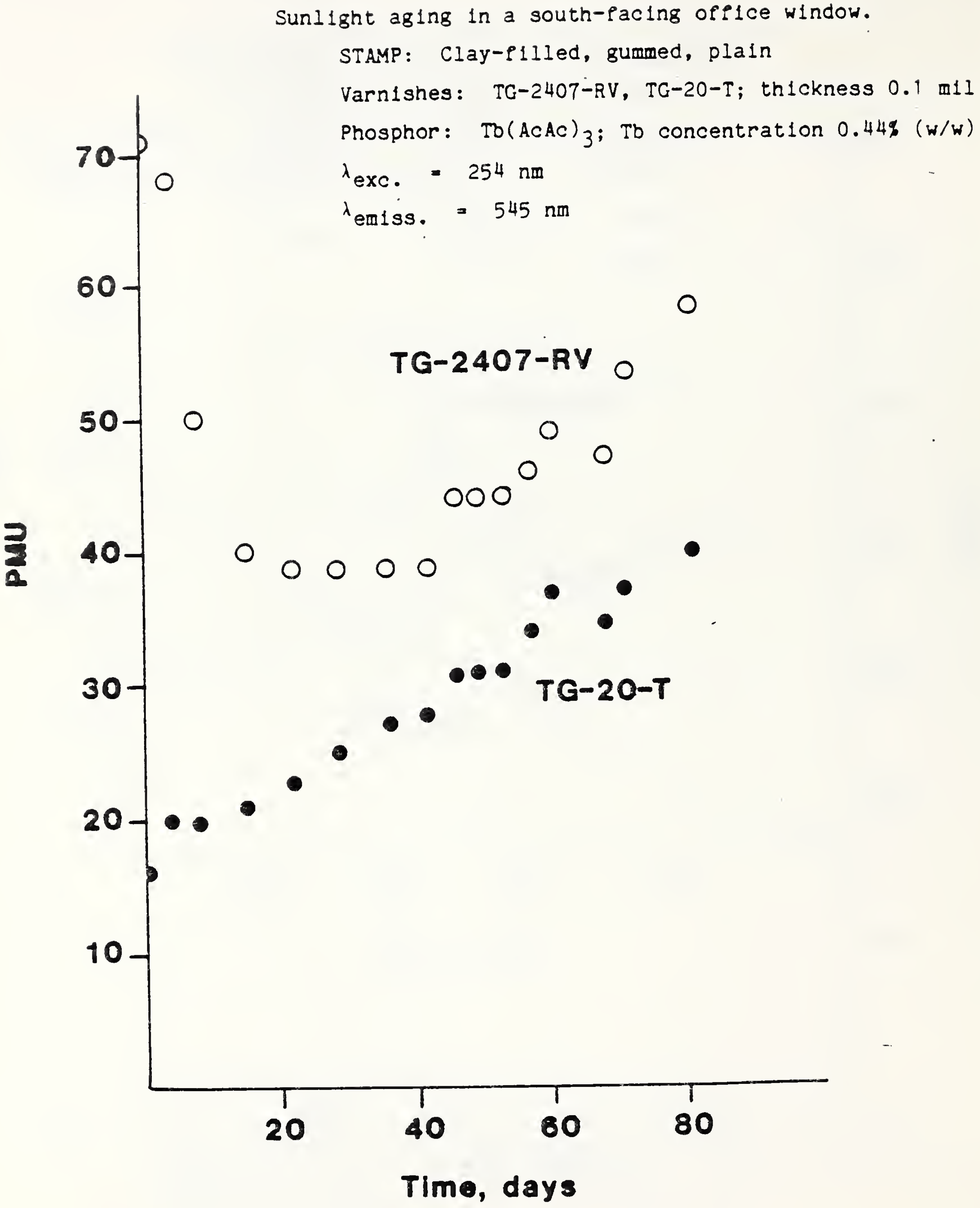


Figure 12 Natural aging of coated stamp paper exposed to sunlight in a south-facing window for a prolonged period of time. Doped varnishes ($Tb(AcAc)_3$), 1.0 mil in thickness, coated on paper No. 6, plain, clay-filled, gummed.

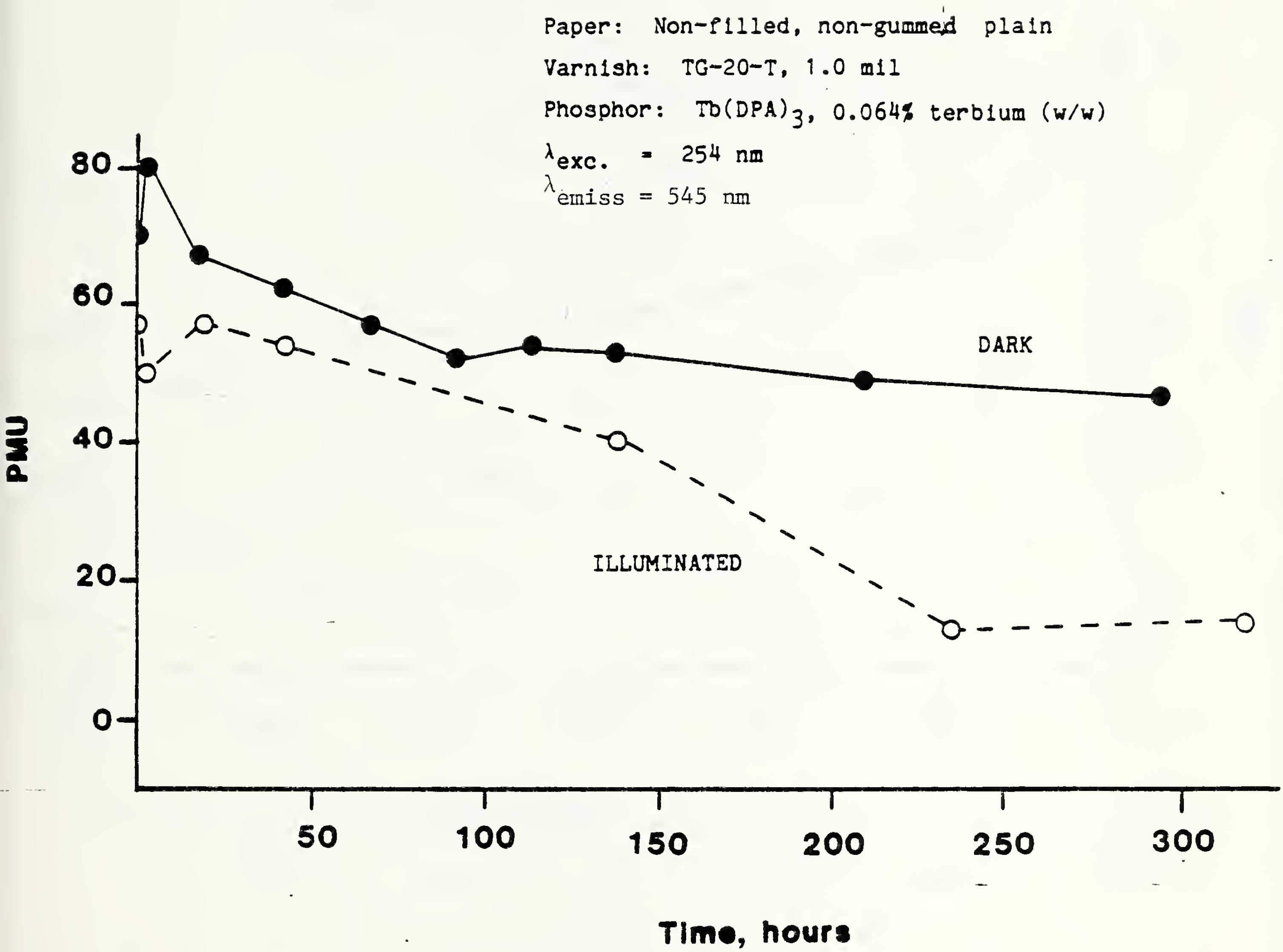


Figure 13 Phosphorescence decay during humid aging (94% RH, 91° F) of coated stamp paper (Varnish TG-20-T, 1.0 mil; phosphor $Tb(DPA)_3$, 0.064% terbium (w/w).

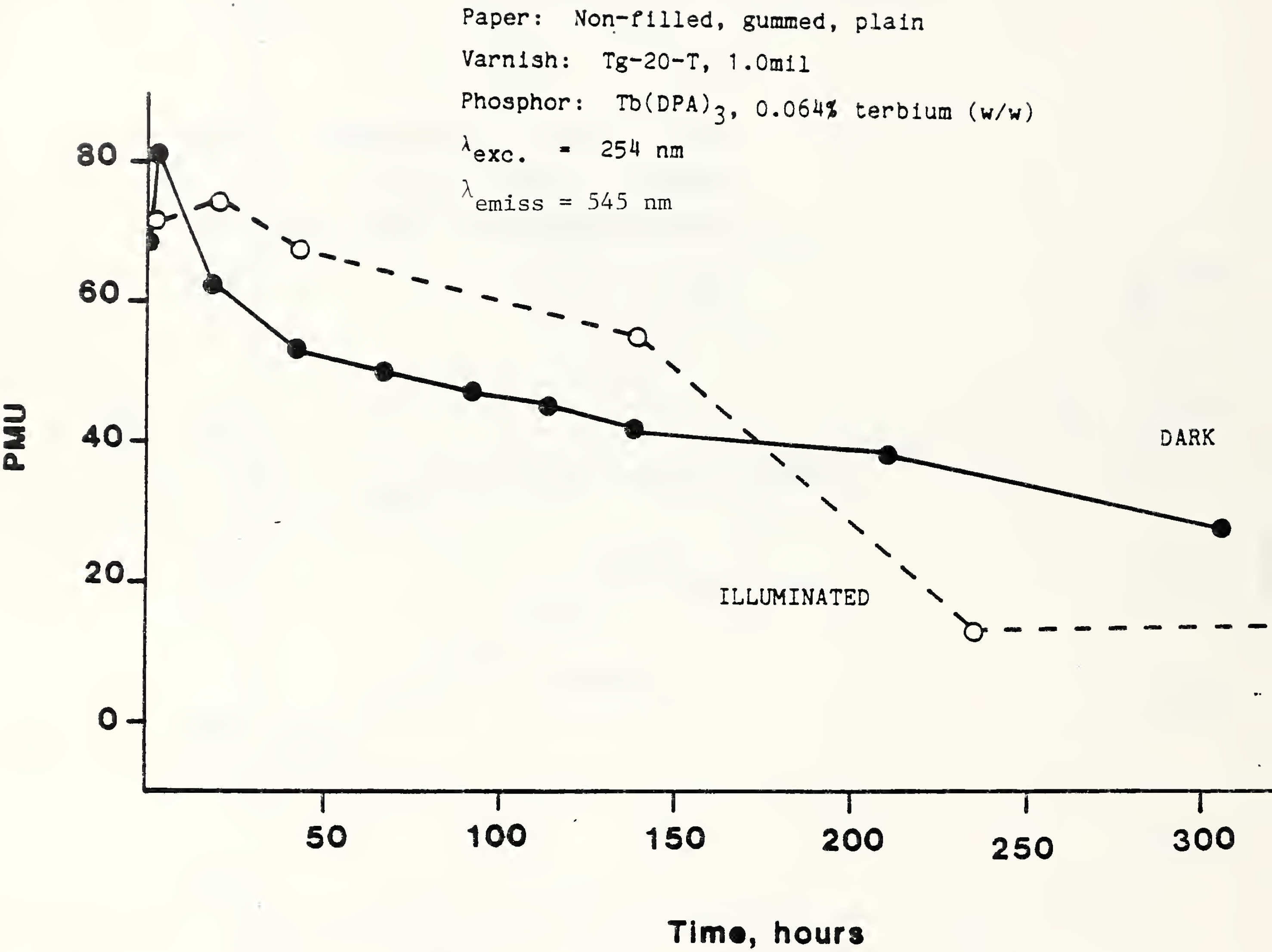


Figure 14 Phosphorescence decay during humid aging (94% RH, 91° F) of coated stamp paper (Varnish TG-20-T, 1.0 mil; phosphor TB(DPA)$_3$, 0.064% terbium (w/w).

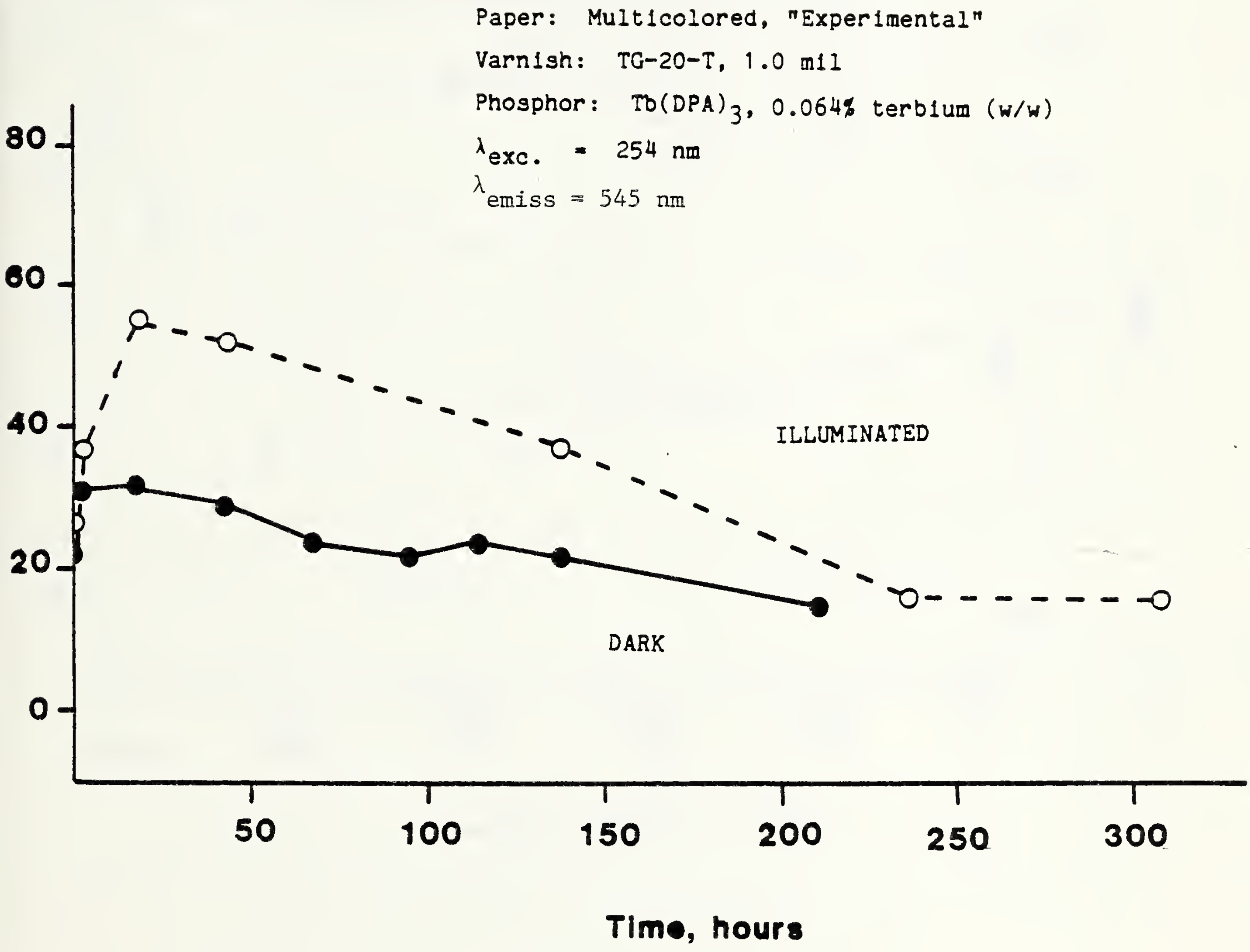


Figure 15 Phosphorescence decay during humid aging (94% RH, 91° F) of coated stamp paper (Varnish TG-20-T, 1.0 mil; phosphor $Tb(DPA)_3$, 0.064% terbium (w/w).

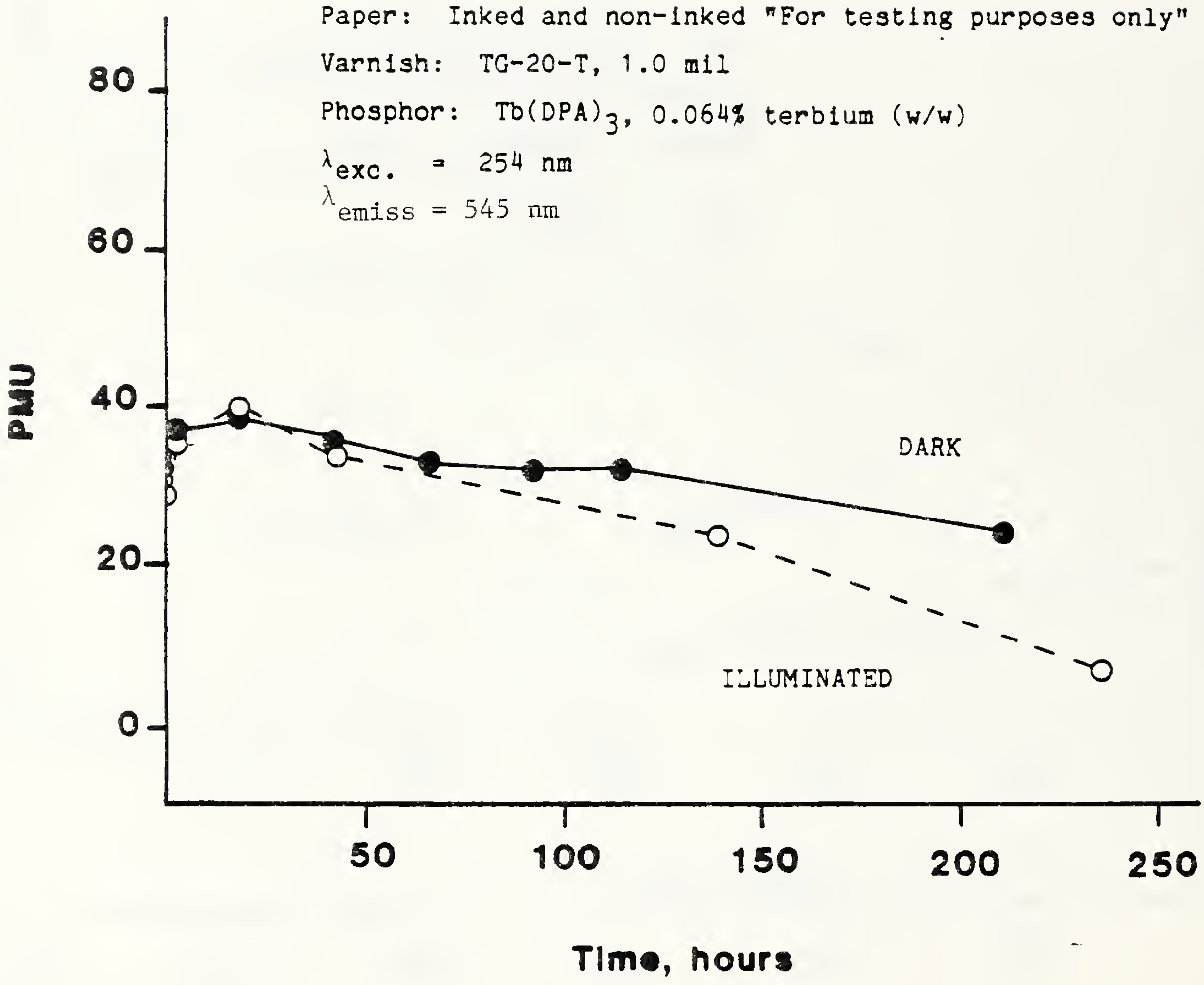


Figure 16 Phosphorescence decay during humid aging (94% RH, 91° F) of coated stamp paper (Varnish TG-20-T, 1.0 mil; phosphor Tb(DPA)$_3$, 0.064% terbium (w/w).

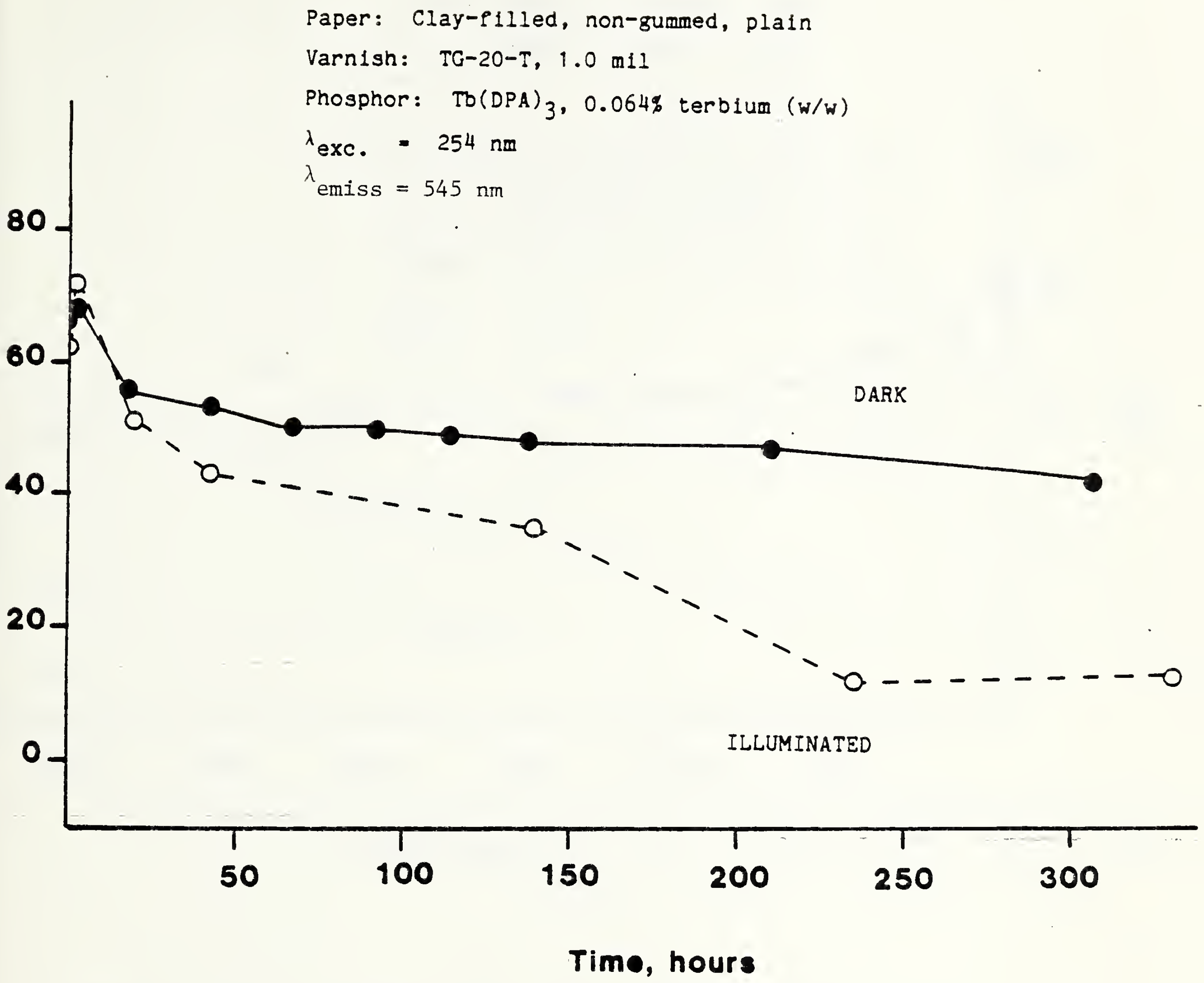


Figure 17 Phosphorescence decay during humid aging (94% RH, 91° F) of coated stamp paper (Varnish TG-20-T, 1.0 mil; phosphor Tb(DPA)$_3$, 0.064% terbium (w/w).

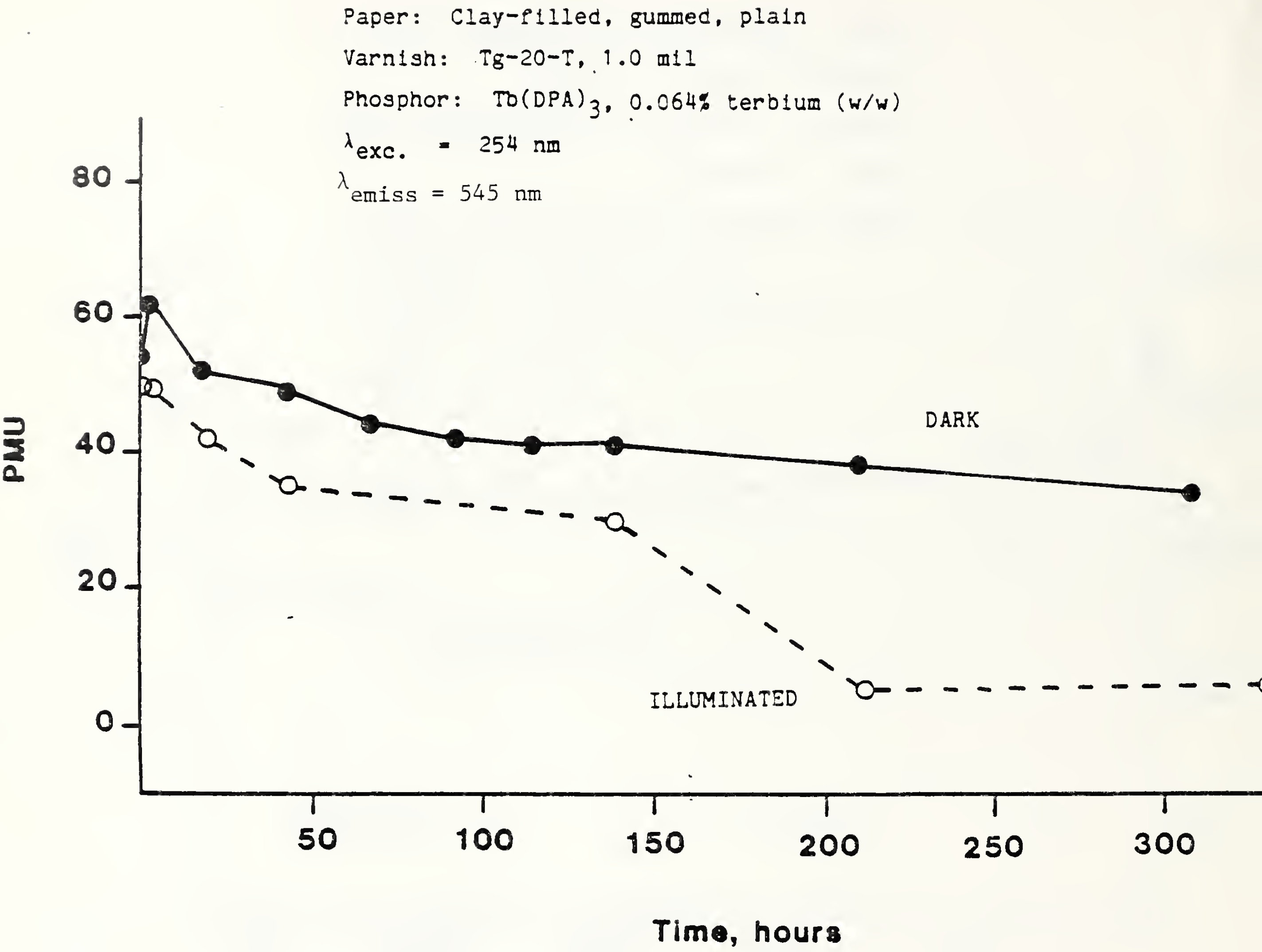
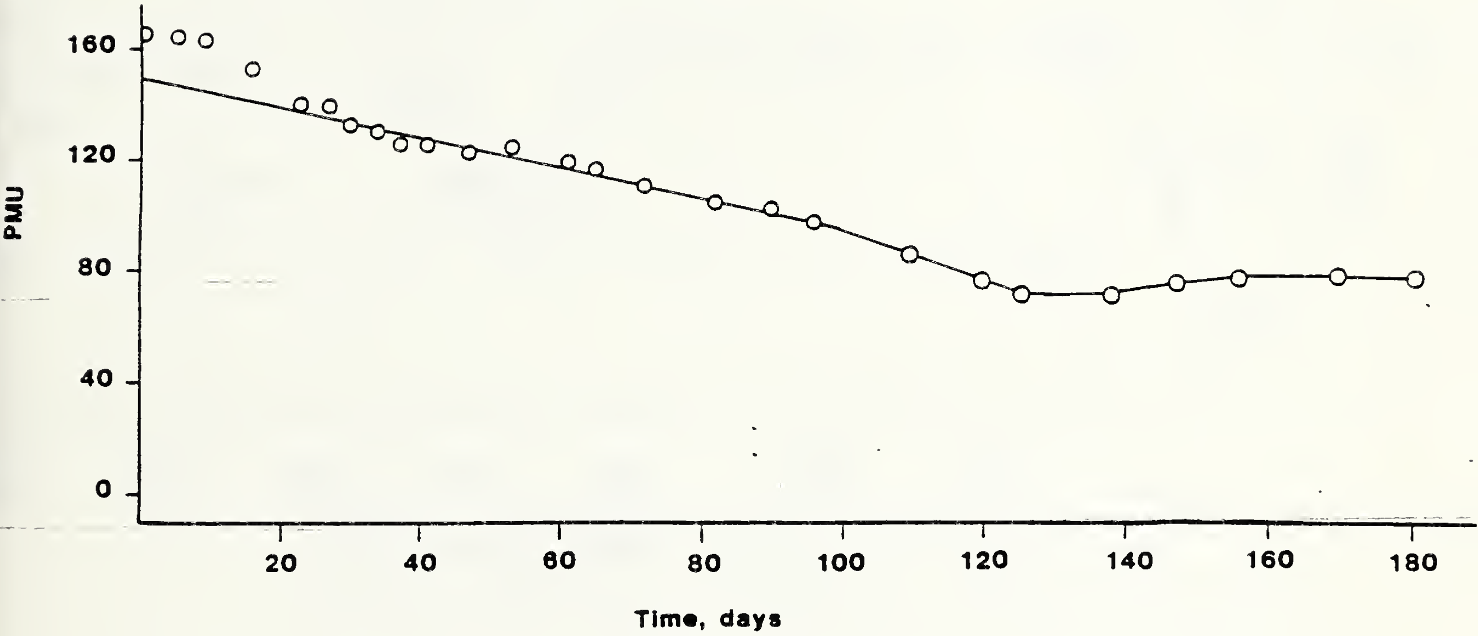


Figure 18 Phosphorescence decay during humid aging (94% RH, 91° F) of coated stamp paper (Varnish TG-20-T, 1.0 mil; phosphor Tb(DPA)$_3$, 0.064% terbium (w/w).



Sunlight aging in a south-facing office window

STAMP: Clay-filled, non-gummed, plain

Varnish: TG-2407-RV, thickness 1.0 mil

Phosphor: $TB(DPA)_3$; Tb concentration 0.066 % (w/w)

$\lambda_{exc.}$ = 254 nm

$\lambda_{emiss.}$ = 545 nm

Figure 19 Natural aging of coated stamp paper exposed to sunlight in a south-facing window for aprolonged period of time. Doped varnish ($Tb(DPA)_3$), 1.0 mil thickness, coated on paper No. 5, clay-filled, non-gummed, plain.

Sunlight aging in a South-facing window.

STAMP: non-filled, gummed, plain

Varnish: None

Phosphor: Tb(DPA)$_3$; Tb concentration 0.037 % (w/v)

$\lambda_{exc.}$ = 254 nm

$\lambda_{emiss.}$ = 545 nm

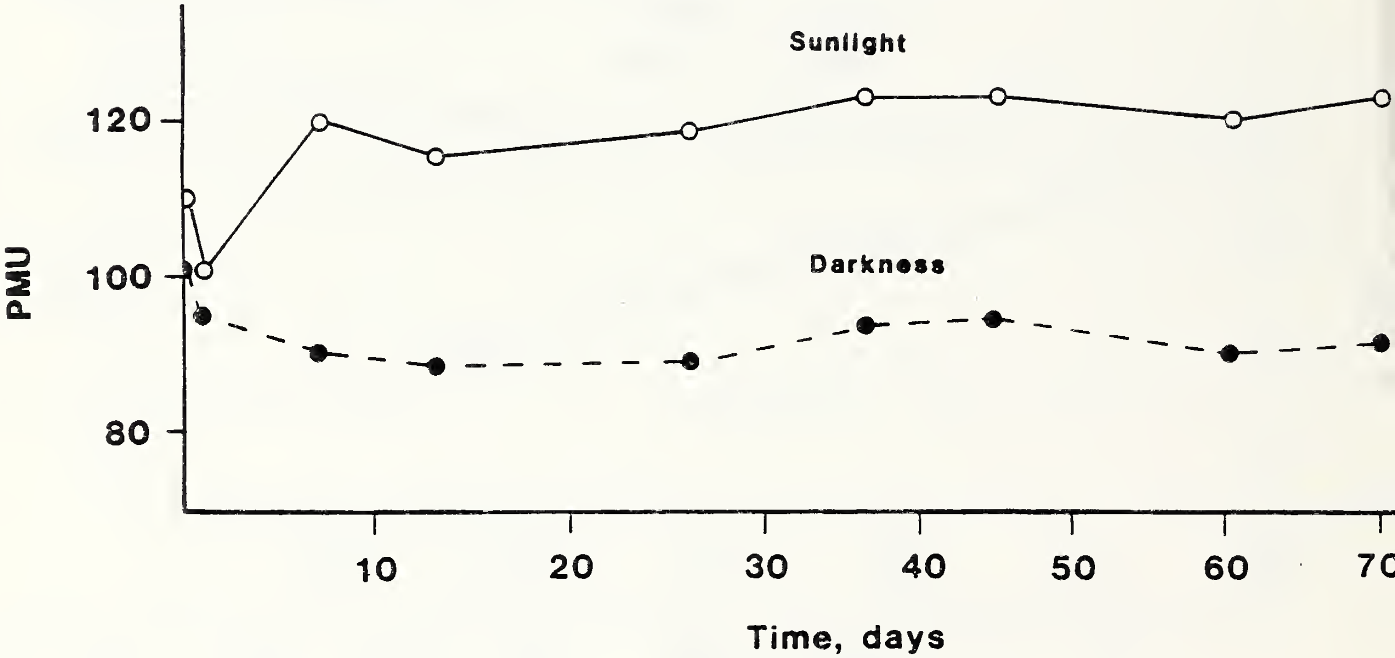
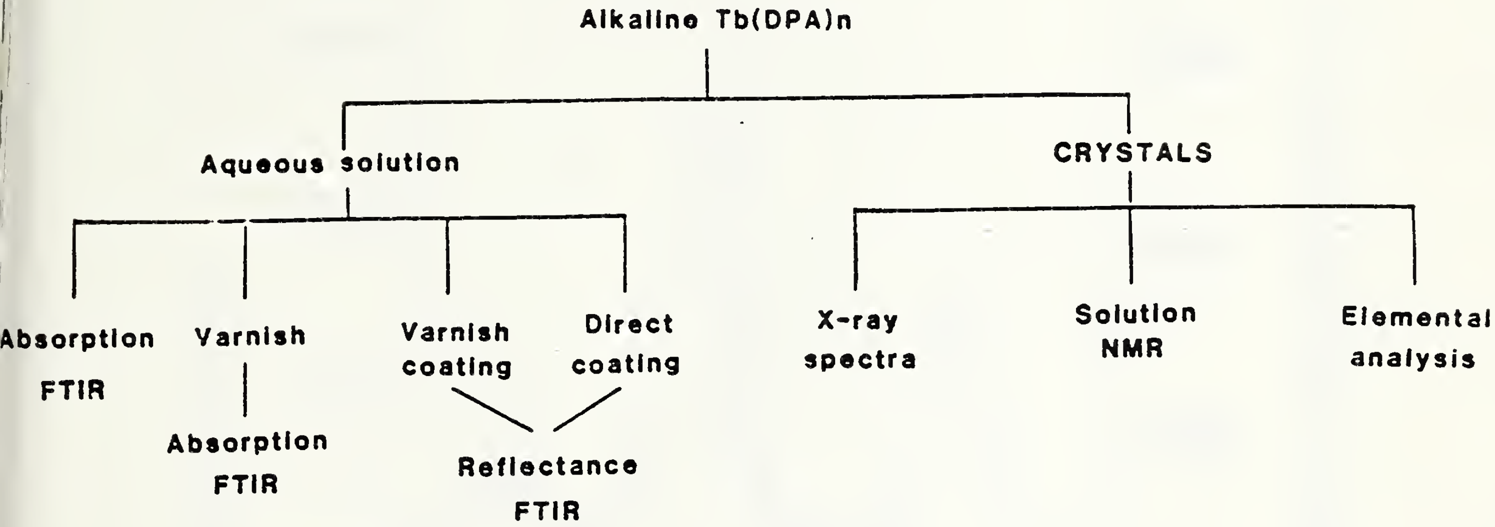
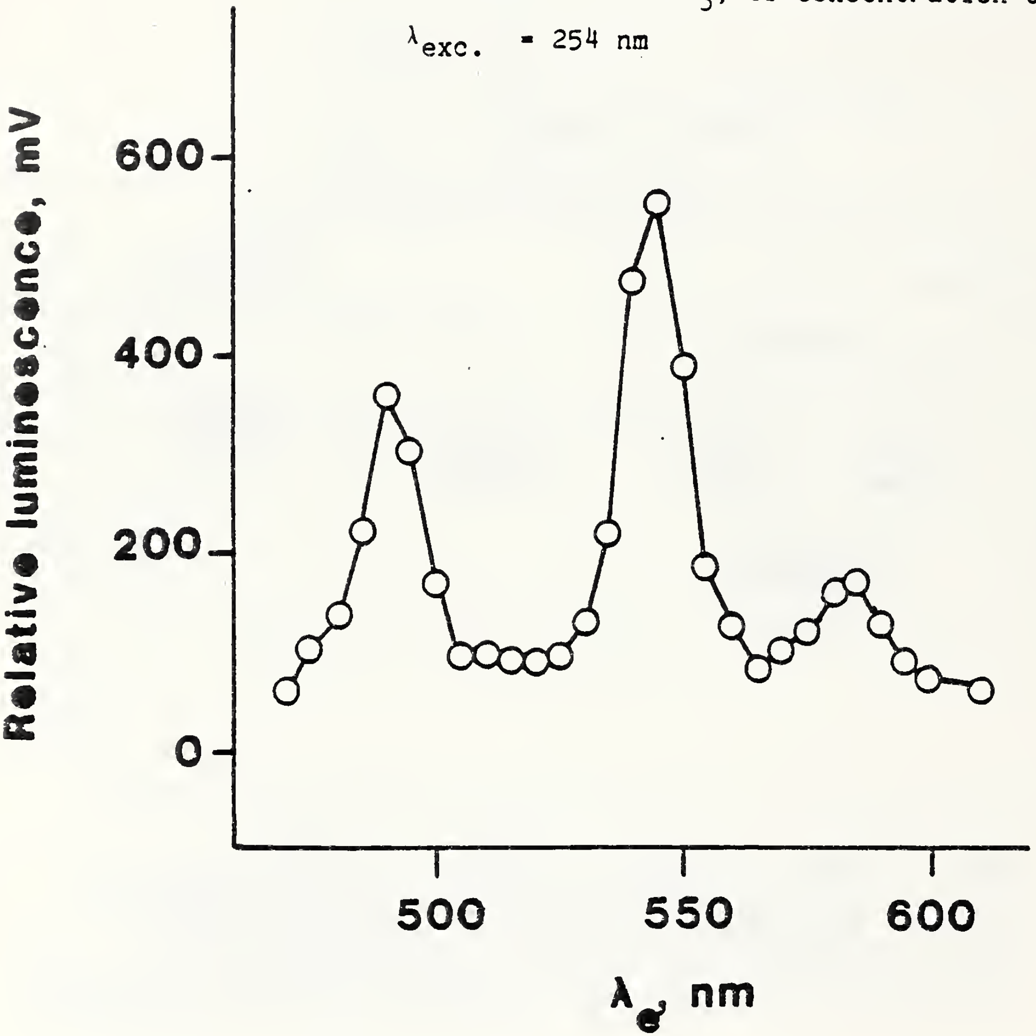


Figure 20. Natural aging of tagged stamp paper exposed to sunlight. Tb(DPA)$_3$ was applied directly to paper by the drawdown technique used for varnishes. A control specimen, similarly prepared, was kept in a closed desk drawer.



Characterization scheme

Figure 21. Characterization scheme for Tb(DPA). Samples prepared in alkaline solution are analyzed in water or in varnish by absorption FTIR, and on coatings by reflectance FTIR. Purified crystals are examined by X-ray spectroscopy, placed in solution for ^{1}H NMR, and subjected to elemental analysis.



STAMP: Multicolored "Experimental" using non-colored are

Varnish: TG-2407-RV, 1.0 mil

Phosphor: $Tb(DPA)_3$; Tb concentration 0.064% (w/w)

$\lambda_{exc.}$ = 254 nm

Figure 22. Luminescence spectrum for a non-colored area of a multicolored "Experimental" USPS stamp, coated with Varnish TG-2407-RV doped with $Tb(DPA)_3$ with a terbium concentration of 0.064% (w/w).

STAMP: Multicolored "Experimental" using non-colored area

Varnish: TG-20-T, 1.0 mil

Phosphor: $Tb(DPA)_3$; Tb concentration 0.064% (w/w)

λ_{exc} = 254 nm

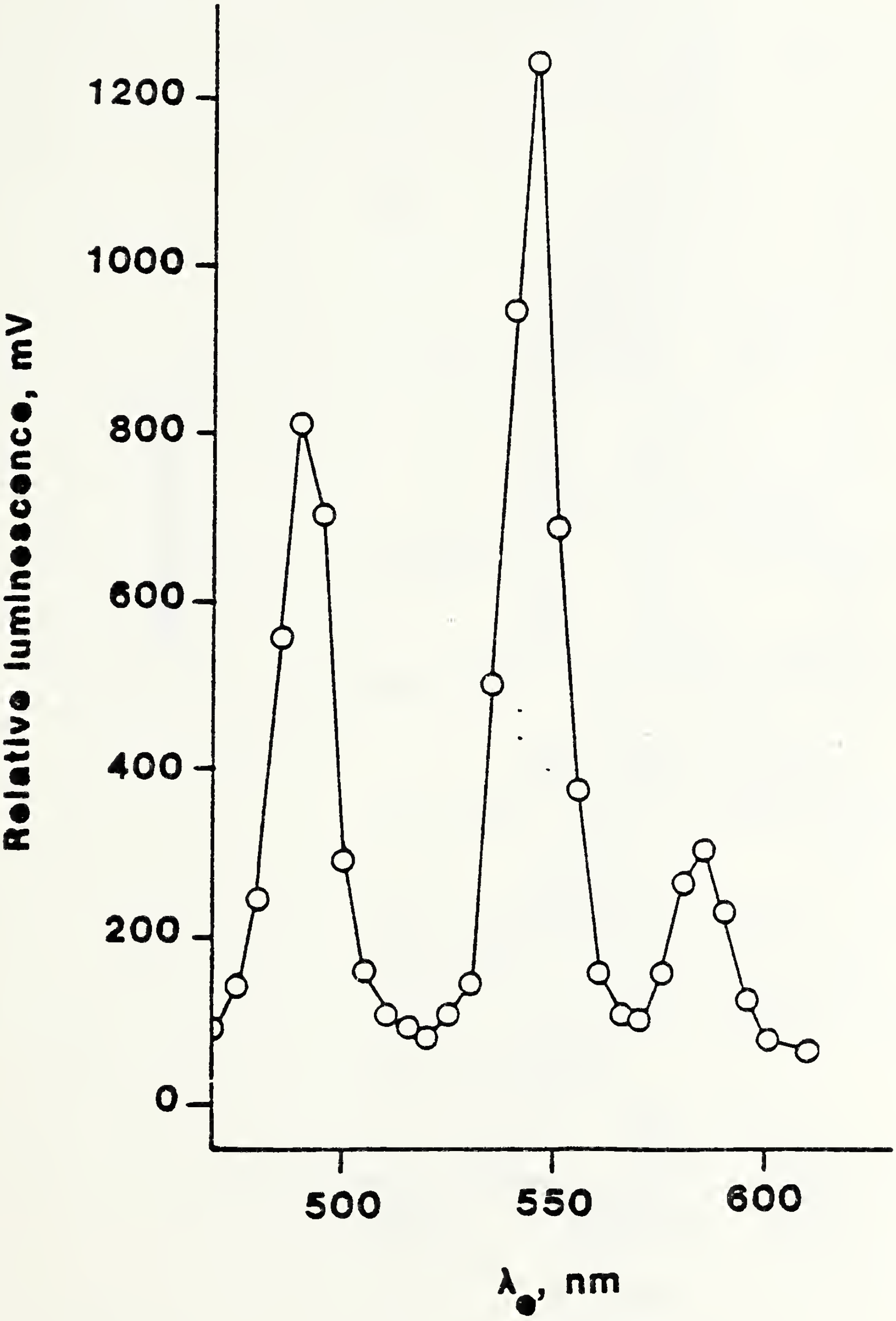
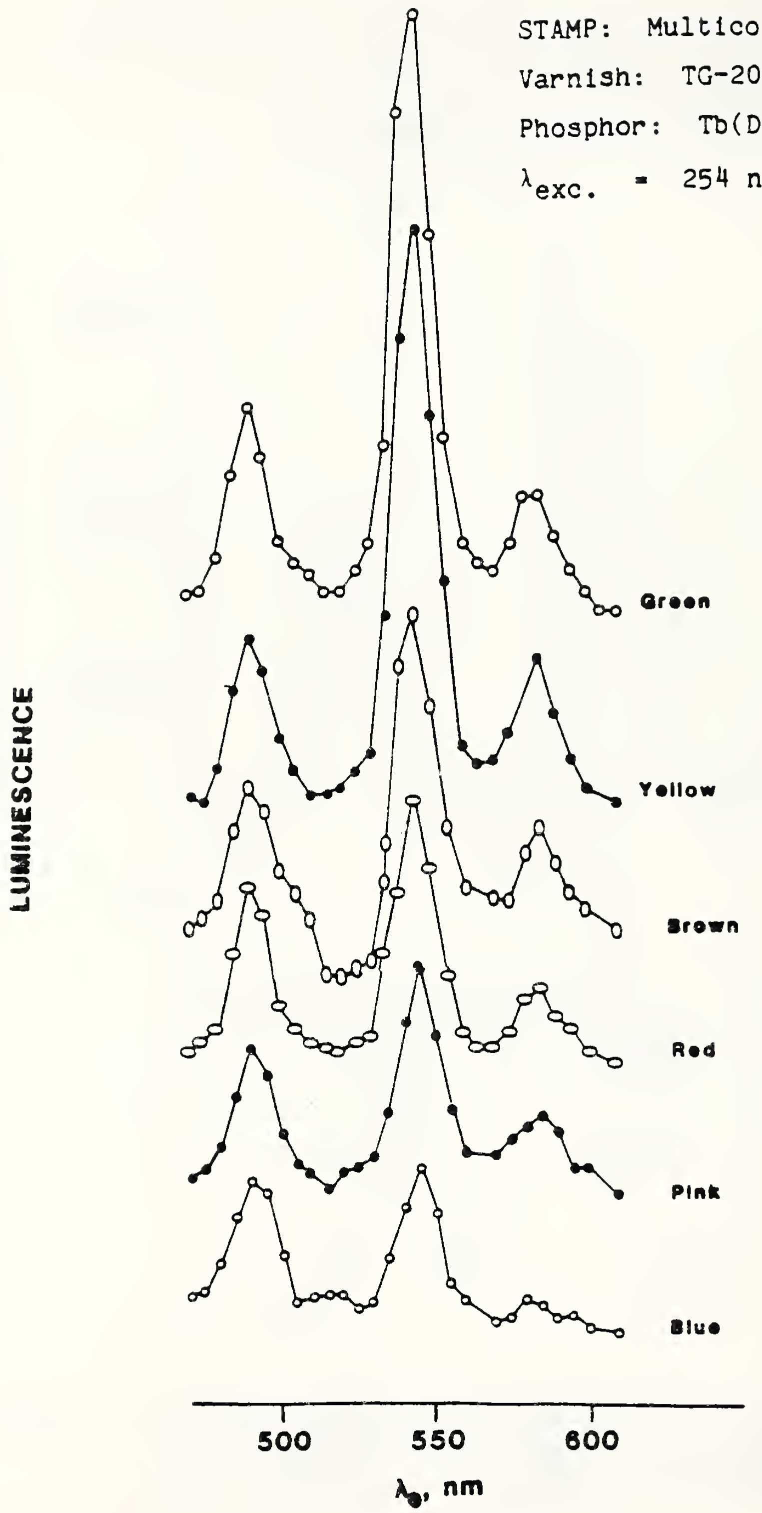


Figure 23. Luminescence spectrum for a non-colored area of a multicolored "Experimental" stamp, coated with Varnish TG-20-T doped with $Tb(DPA)_3$ with a terbium concentration of 0.064% (w/w).



STAMP: Multicolored, "Experimental"

Varnish: TG-20-T, thickness 1.0 mil

Phosphor: $Tb(DPA)_3$; Tb concentration 0.064% (w/w

$\lambda_{exc.}$ = 254 nm

Figure 24. Luminescence spectra for six individual colored areas of a multicolored experimental stamp, coated with Varnish TG-20-T doped with $Tb(DPA)_3$, with a terbium concentration of 0.064% (w/w).

STAMP: Multicolored, "Experimental"

Varnish: TG-2407-RV, thickness 1.0 mil

Phosphor: $Tb(DPA)_3$; Tb concentration 0.064% (w/w)

$\lambda_{exc.}$ = 254 nm

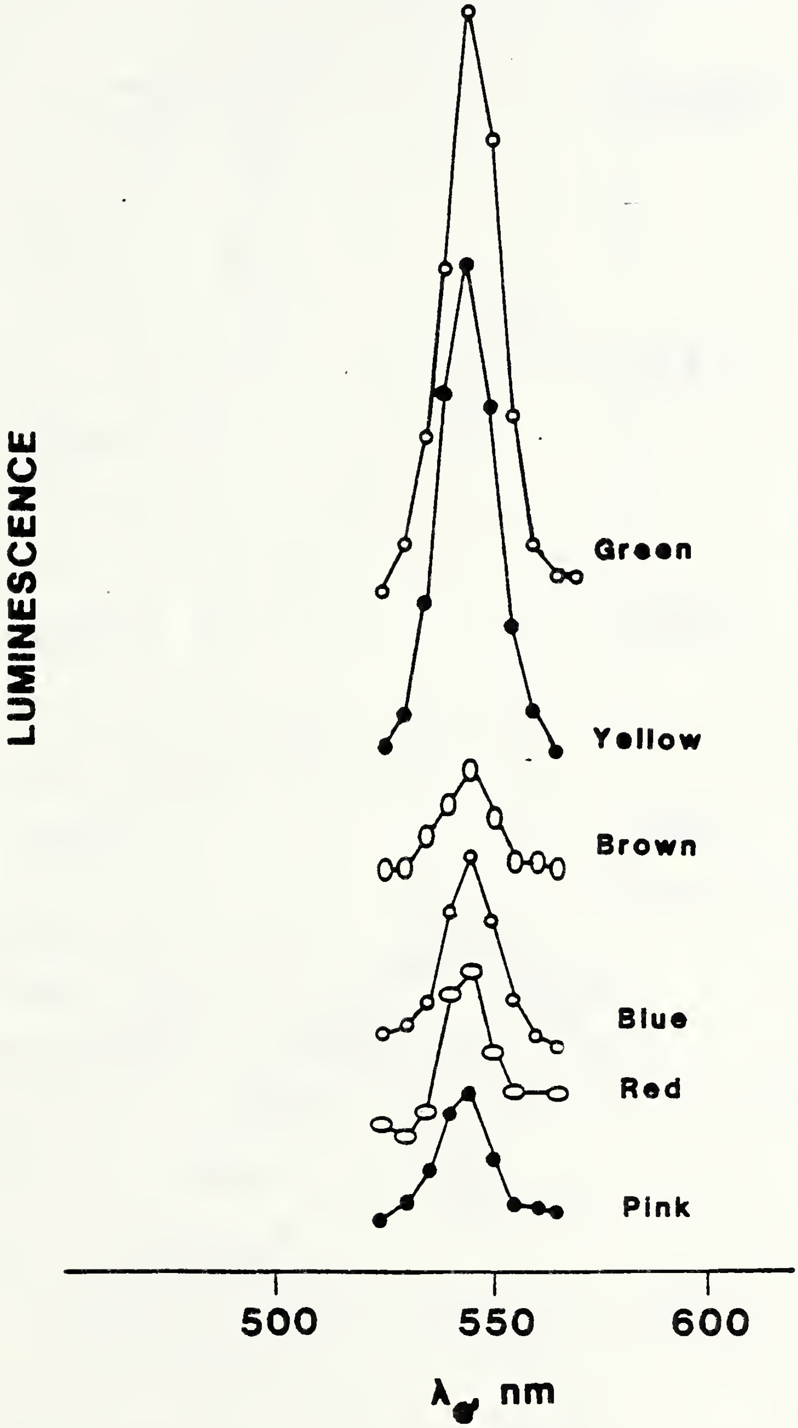
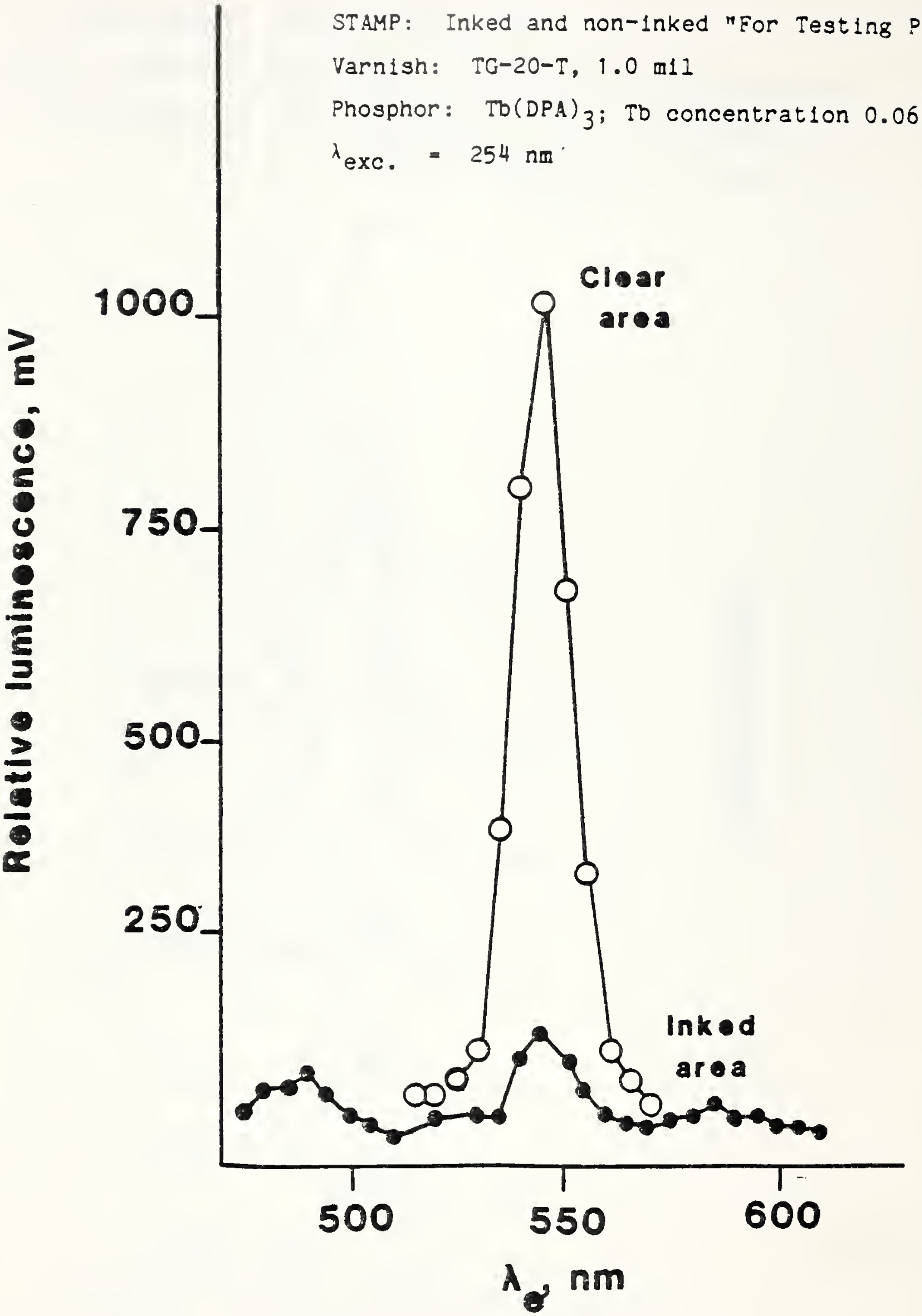


Figure 25. Luminescence spectra for six individual colored areas of a multicolored "Experimental" USPS stamp, coated with Varnish TG-2407-RV doped with $Tb(DPA)_3$, with a terbium concentration of 0.064% (w/w).

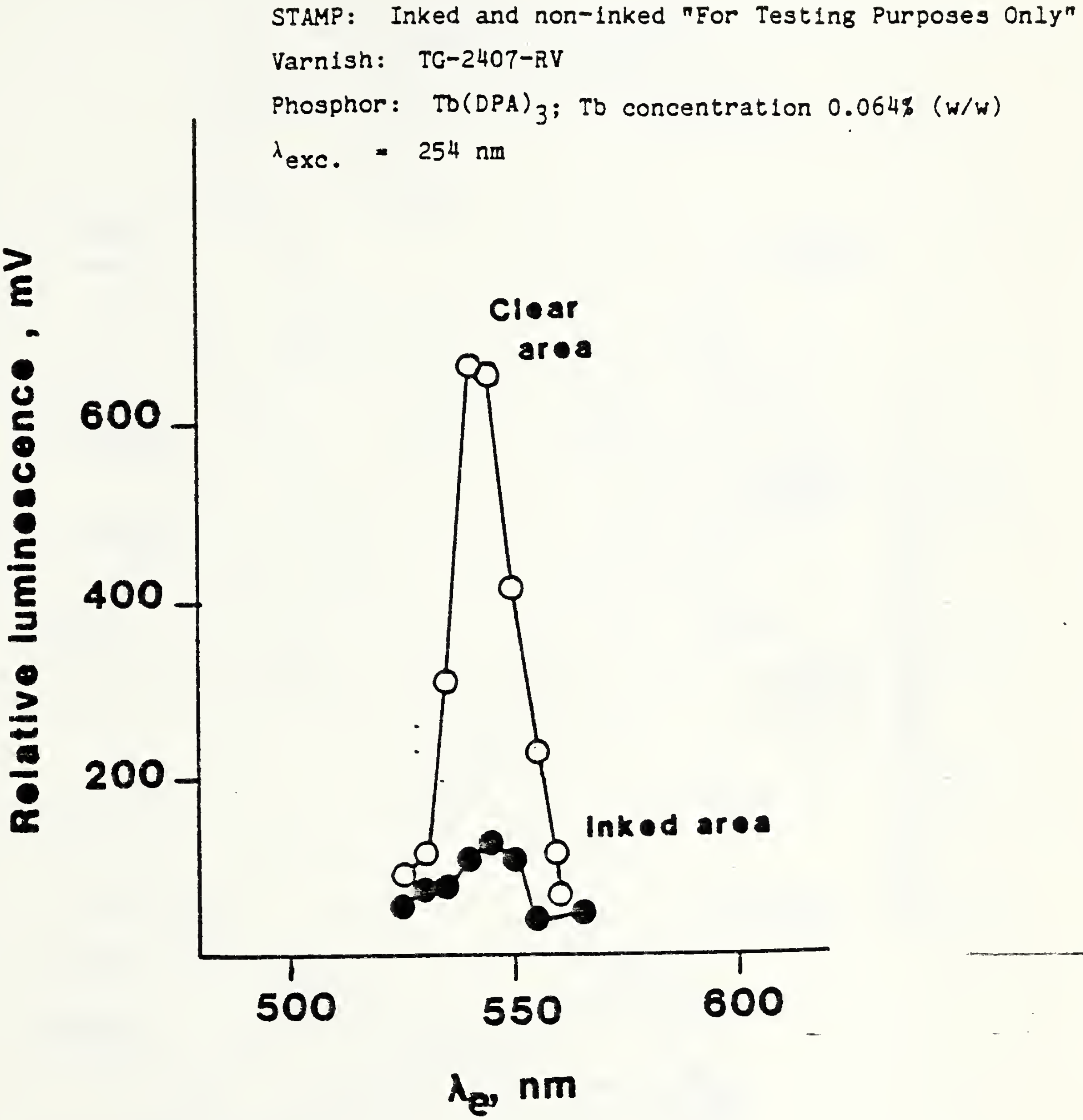

STAMP: Inked and non-inked "For Testing Purposes Onl

Varnish: TG-20-T, 1.0 mil

Phosphor: $Tb(DPA)_3$; Tb concentration 0.064% (w/w)

$\lambda_{exc.}$ = 254 nm

Figure 26. Luminescence spectra of inked and clear areas of the USPS sta "For testing purposes only," coated with varnish TG-20-T dope with $Tb(DPA)_3$, with a terbium concentration of 0.064% (w/w).



STAMP: Inked and non-inked "For Testing Purposes Only"

Varnish: TG-2407-RV

Phosphor: $Tb(DPA)_3$; Tb concentration 0.064% (w/w)

$\lambda_{exc.}$ = 254 nm

Figure 27. Luminescence spectra of inked and noninked areas of the USPS stamp "For testing purposes only," coated with varnish TG-2407-RV doped with $Tb(DPA)_3$, with a terbium concentration of 0.064% (w/w).

STAMP: Multicolored, "Experimental"

Varnish: TG-20-T, thickness 0.1 mil

Phosphor: $Tb(DPA)_3$, varied concentration

$\lambda_{exc.}$ = 254 nm

$\lambda_{emiss.}$ = 545 nm

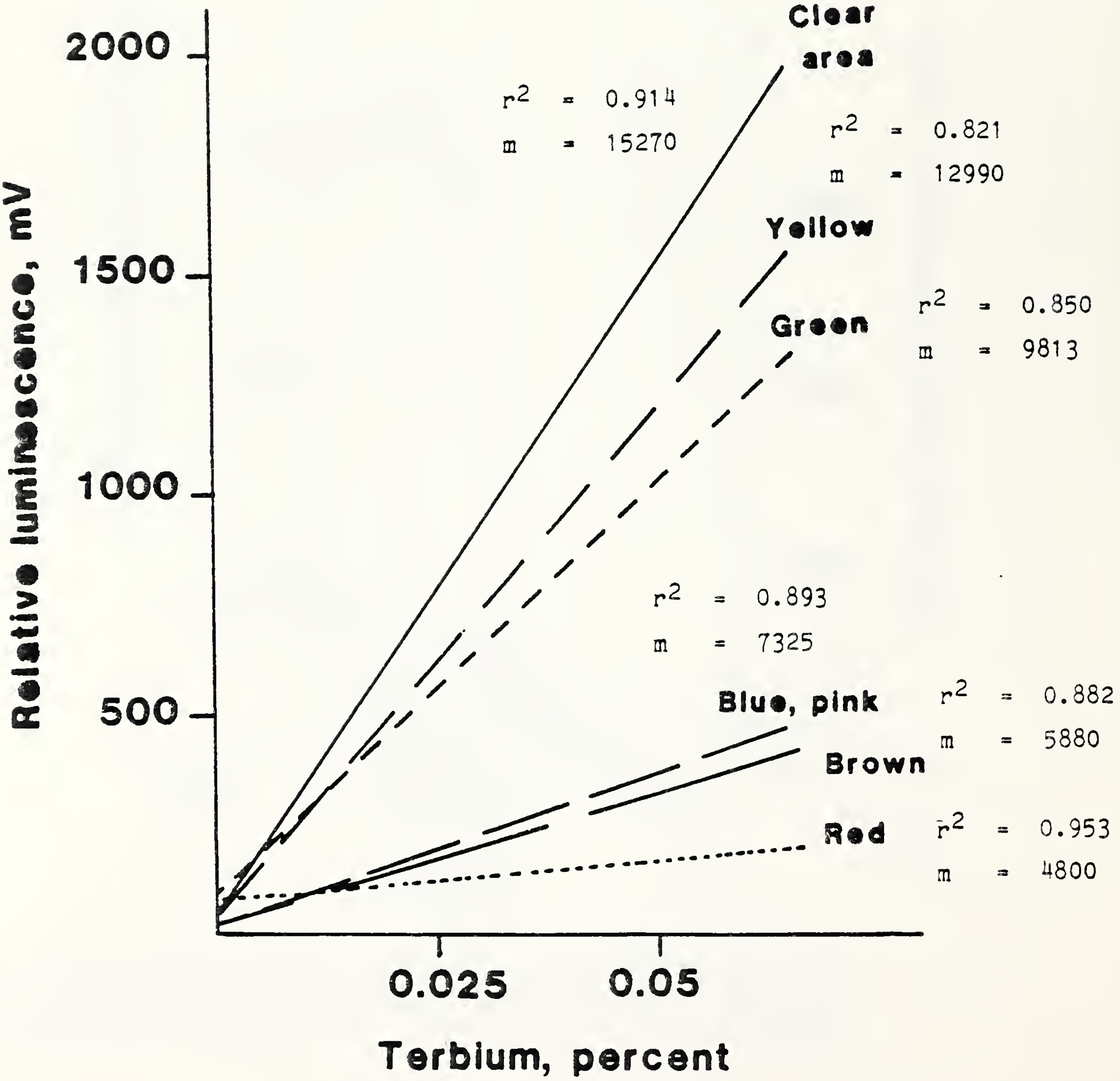


Figure 28 Luminescence (EMI units) of individual colored areas of a multicolored experimental stamp coated with $Tb(DPA)_3$-doped varnish TG-20-T in various terbium concentrations, with a coating depth of 1.0 mil.

STAMP: Multicolored, "Experimental"

Varnish: TG-2407-RV, thickness 1.0 mil

Phosphor: $Tb(DPA)_3$, varied concentration

$\lambda_{exc.}$ = 254 nm

$\lambda_{emiss.}$ = 545 nm

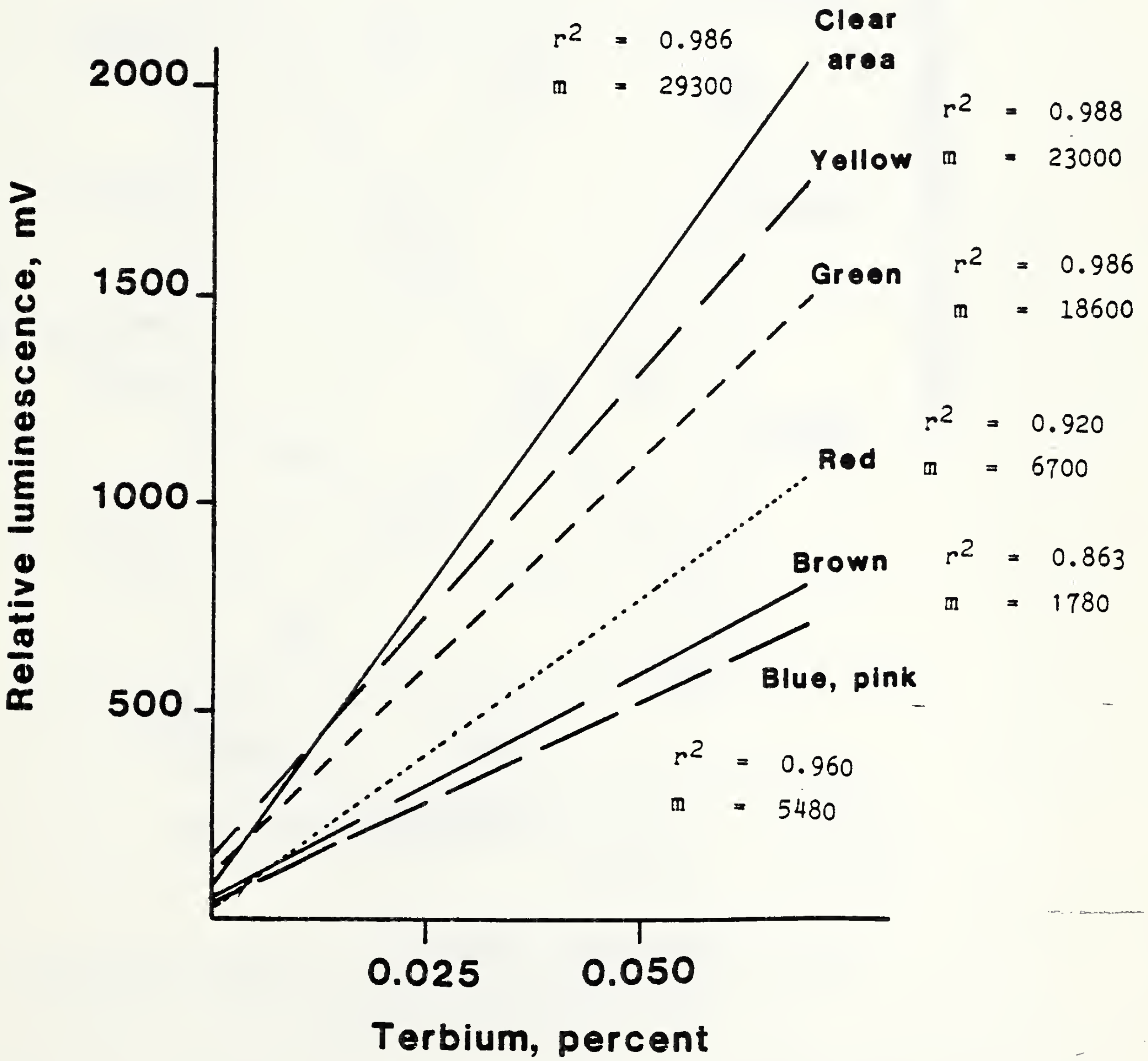


Figure 29 Luminescence (EMI units) of individual colored areas of a multicolored experimental stamp coated with Tb(DPA)-doped varnish TG-2407-RV in various terbium concentrations, with coating depth of 1.0 mil.

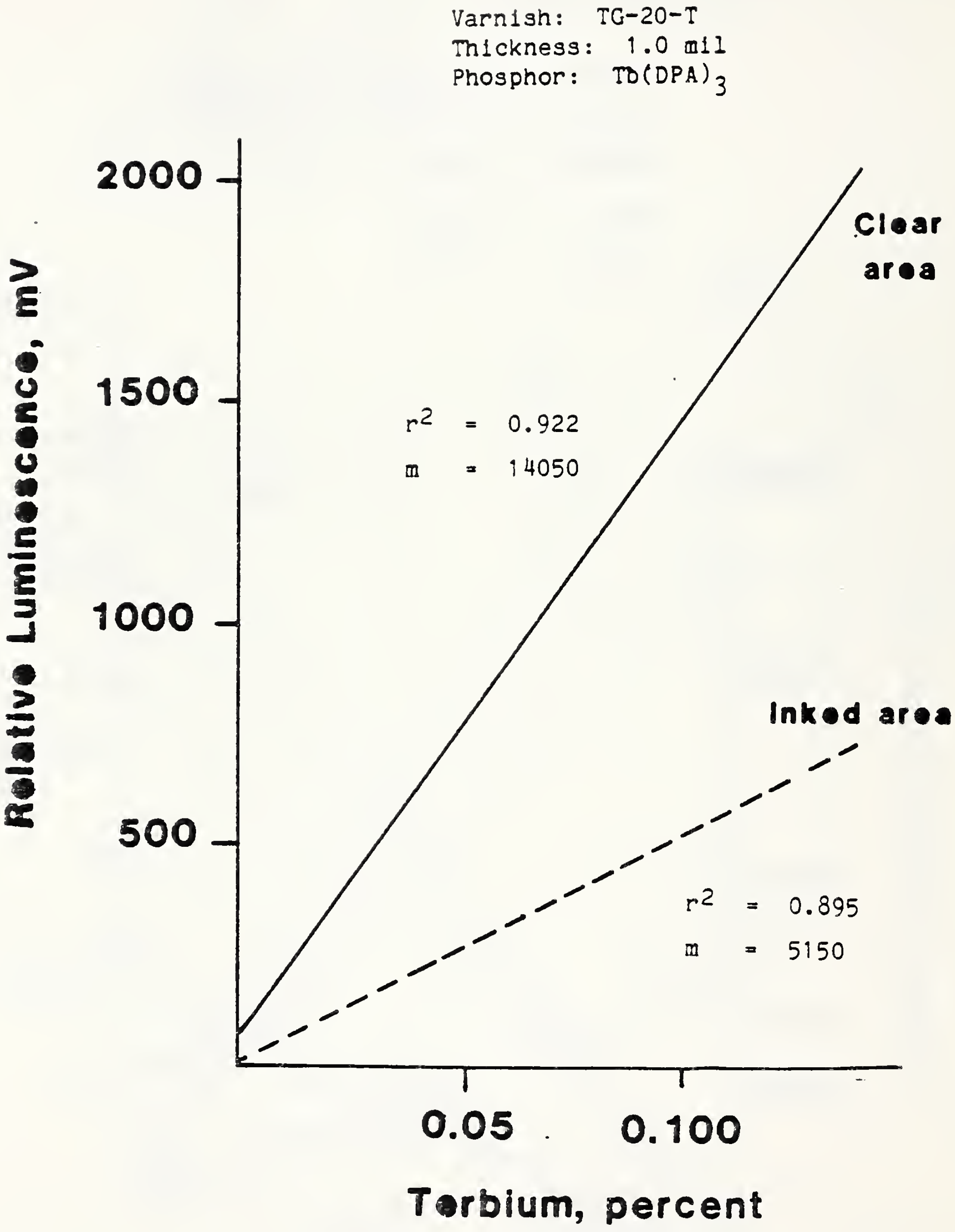


Figure 30 Luminescence (EMI units) of inked experimental stamp coated with $Tb(DPA)_3$-doped varnish TG-20-T in various concentration at a thickness of 1.0 mil.

Phosphorescence as a function of Tb-chelate concentration

Varnish: TG-2407-RV, thickness 1.0 mil

Phosphor: $Tb(DPA)_3$

Stamp papers: ○ = non-filled, gummed paper No. 2

● = Pigmented, multicolored USPS "Experimental" stamp sheet

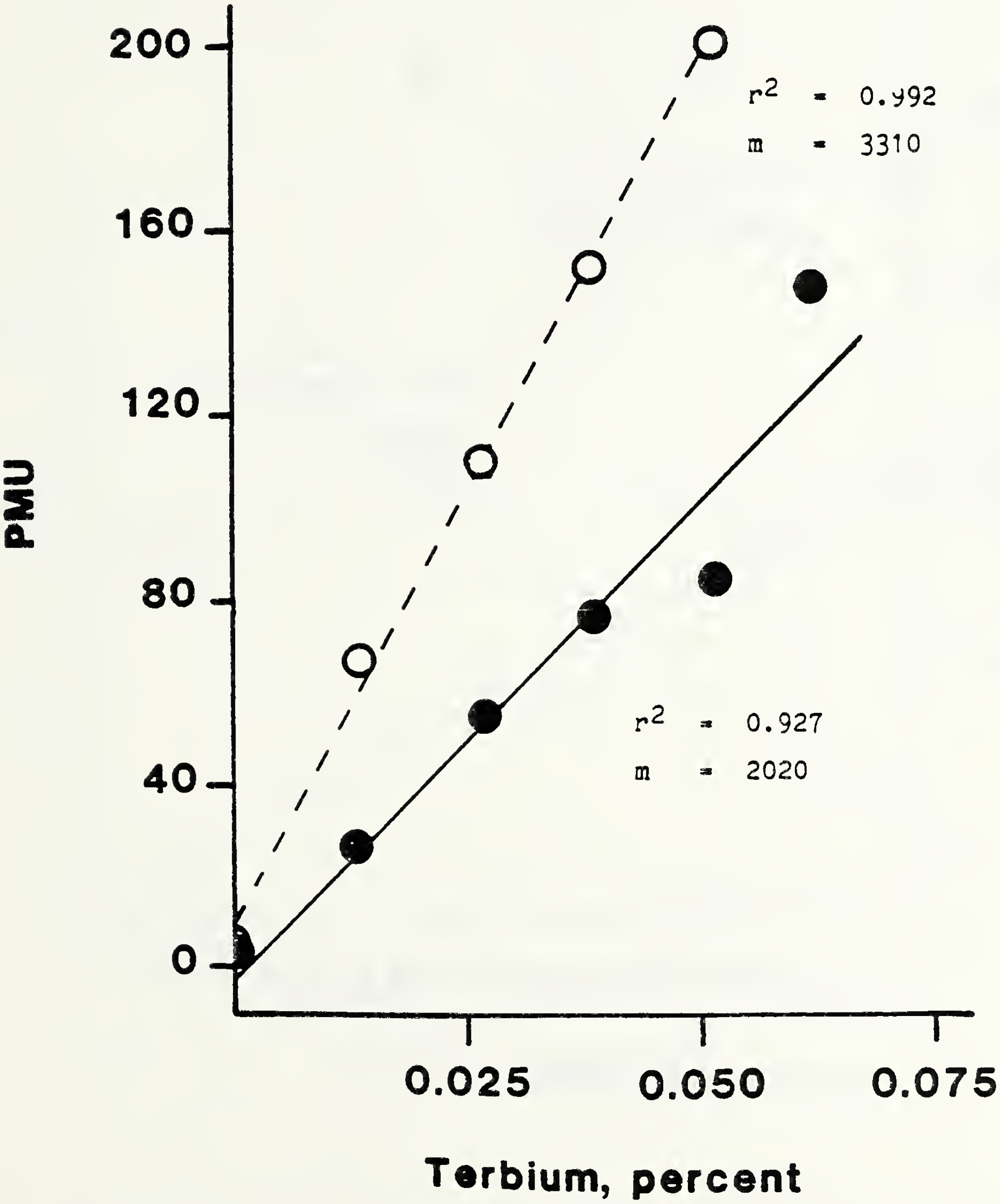


Figure 31. Phosphorescence of non-pigmented paper and of multicolored USPS "Experimental" stamp paper, coated with $Tb(DPA)_3$-doped varnish TG-2407-RV in various terbium concentrations, with a coating depth of 1.0 mil.

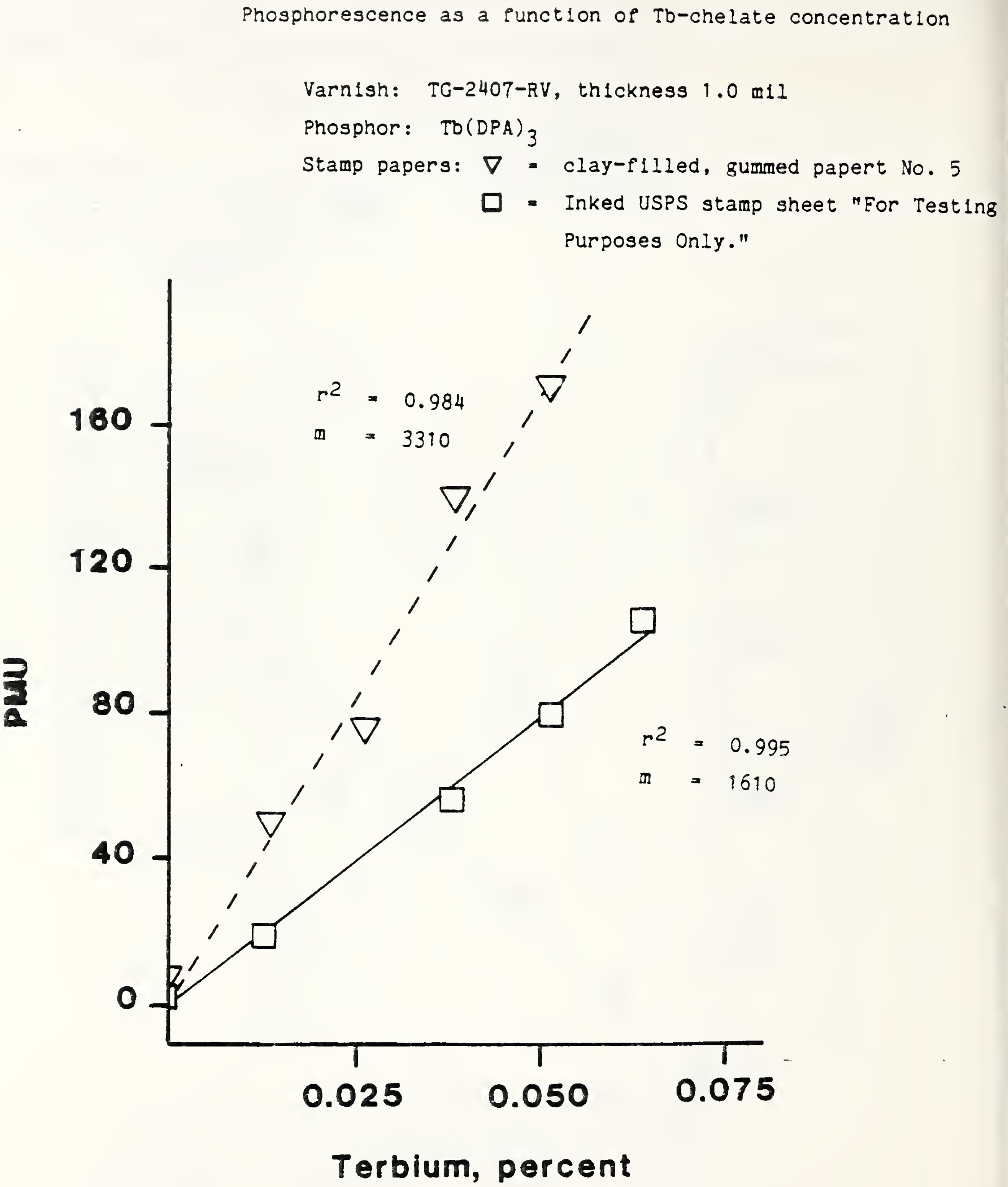

Phosphorescence as a function of Tb-chelate concentration

Figure 32. Phosphorescence of plain, clay-filled, gummed paper and of USPS inked paper "For Testing Purposes Only," coated with $Tb(DPA)_3$-doped varnish TG-2407-RV in various terbium concentrations with a coating depth of 1.0 mil.

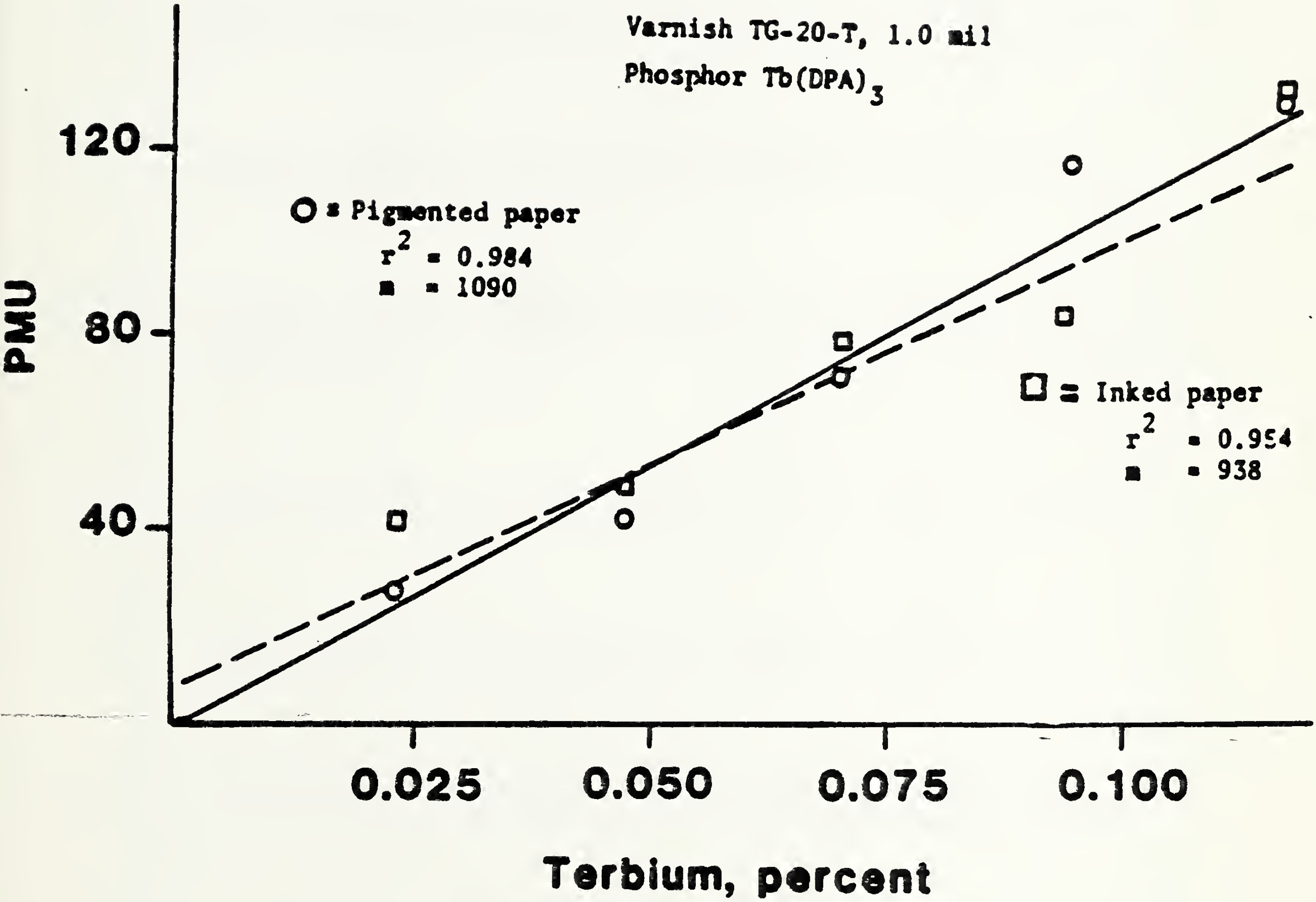


Figure 33. Phosphorescence (PMU) of inked or pigmented paper coated with $Tb(DPA)_3$-doped varnish TG-20-T in various concentrations at a thickness of 1.0 mil.

CAPTIONS FOR COLOR PHOTOGRAPHS, FIGURES 34-43 (IN ALL PHOTOGRAPHS BLACK BAR REPRESENTS 100 μm)

Fig. 34 Photomicrograph of colloidal precipitate of $Tb(DPA)\cdot 2H_2O$ from THF.

Fig. 35 Photomicrograph of crystals of $Tb(DPA)_3\cdot 2H_2O$ obtained by evaporating a drop of the alkaline solution.

Fig. 36 Photomicrograph of $Tb(DPA)_3\cdot 2H_2O$ crystals precipitated by acid from an alkaline solution.

Fig. 37 Photomicrograph of crystals of $Tb(DPA)_3\cdot XH_2O$, precipitated directly from alkaline solution.

Fig. 38 Photomicrograph of crystals of $Tb(DPA)_3\cdot XH_2O$ suspended in supernatant alkaline solution over precipitate. Shows hexagonal seed crystals.

Fig. 39 Photomicrograph of the surface of a current stamp ("Science and Technology") showing surface crystals.

Fig. 40 Photomicrograph of $Tb(AcAc)_3$ (1.44%) distributed, but not completely dissolved, in varnish TG-20-T.

Fig. 41 Photomicrograph of $Tb(DPA)_3$ (0.12%) in varnish TG-20-T, showing microcrystals distributed over the surface of a stamp depth 1.0 mil.

Fig. 42 Photomicrograph of $Tb(DPA)_3$ dissolved in varnish TG-2407-RV. No crystals are evident.

Fig. 43 Photomicrograph of $Tb(DPA)_3$ applied in water directly to the surface of a stamp paper. No crystals are evident.

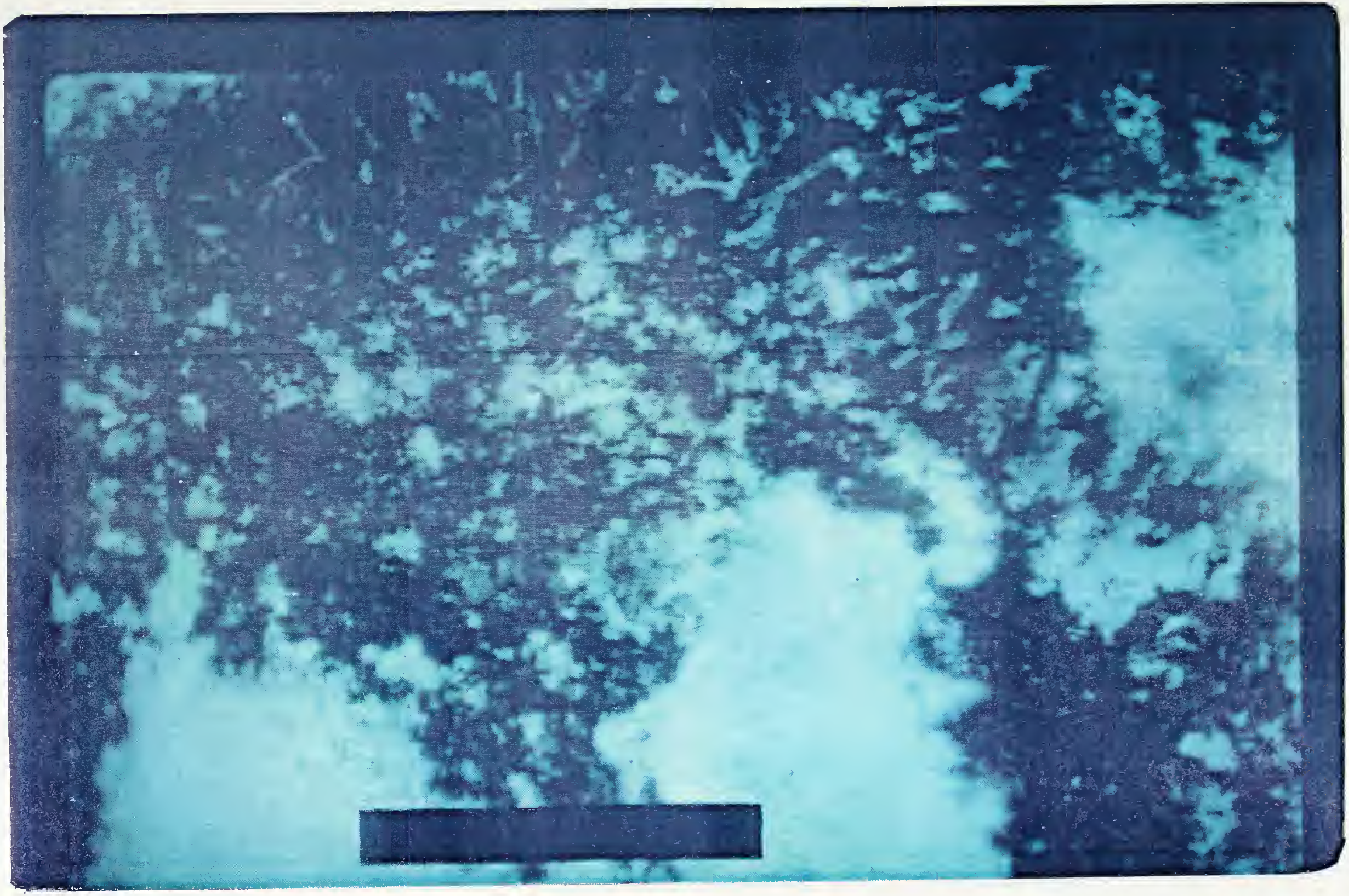


Fig 34

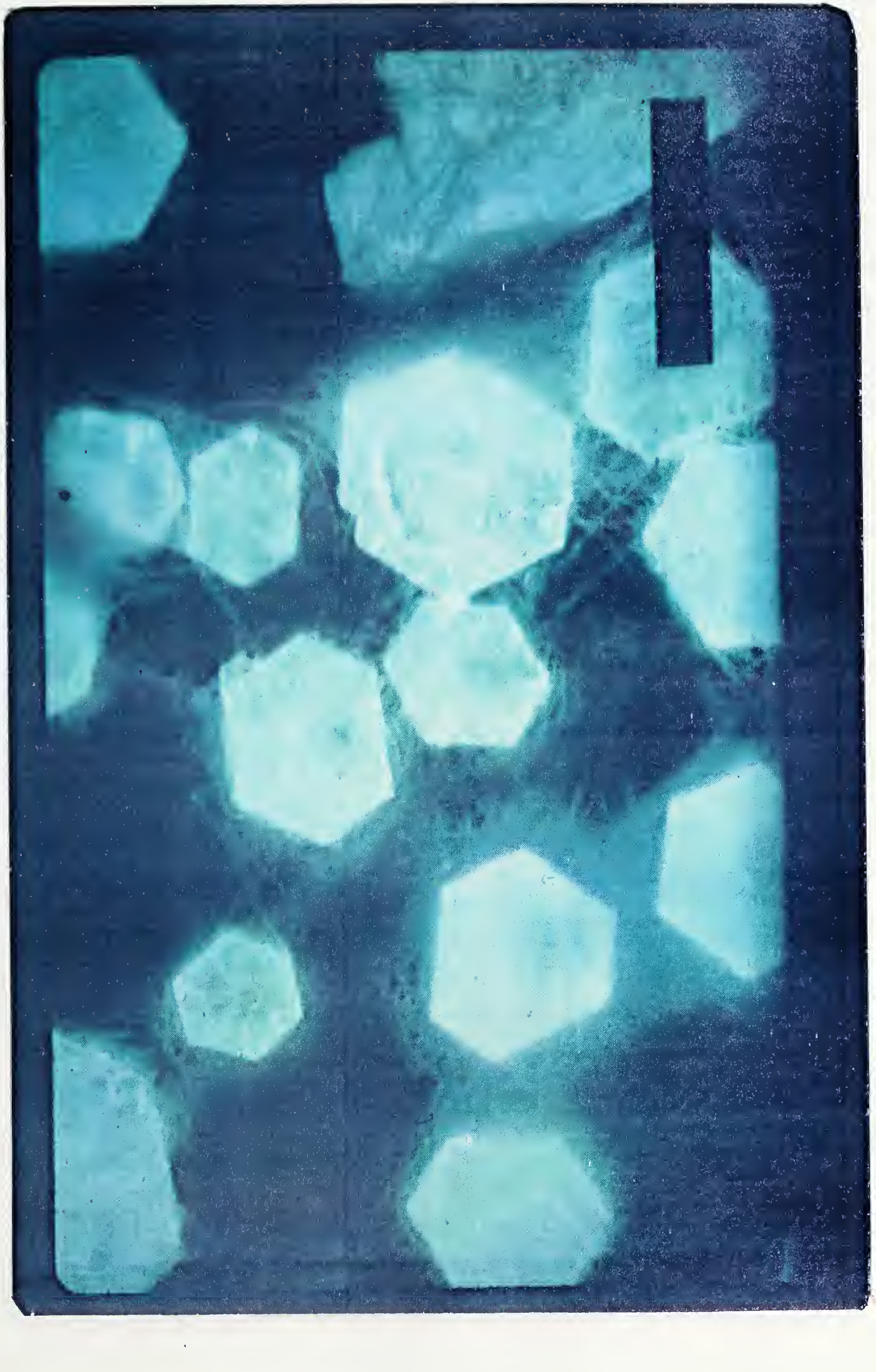


Fig 35

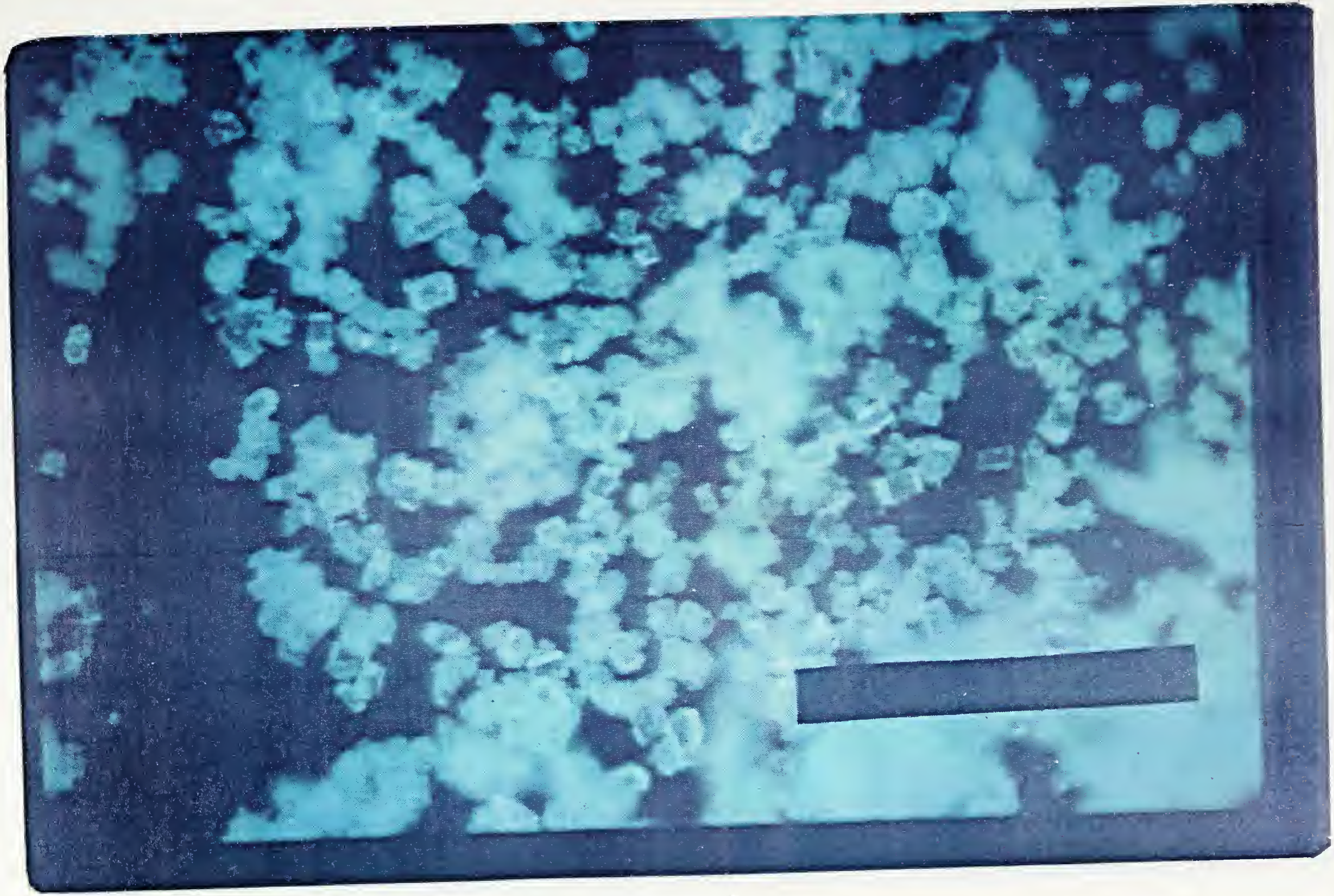


Fig 36

Fig 37

Fig 38

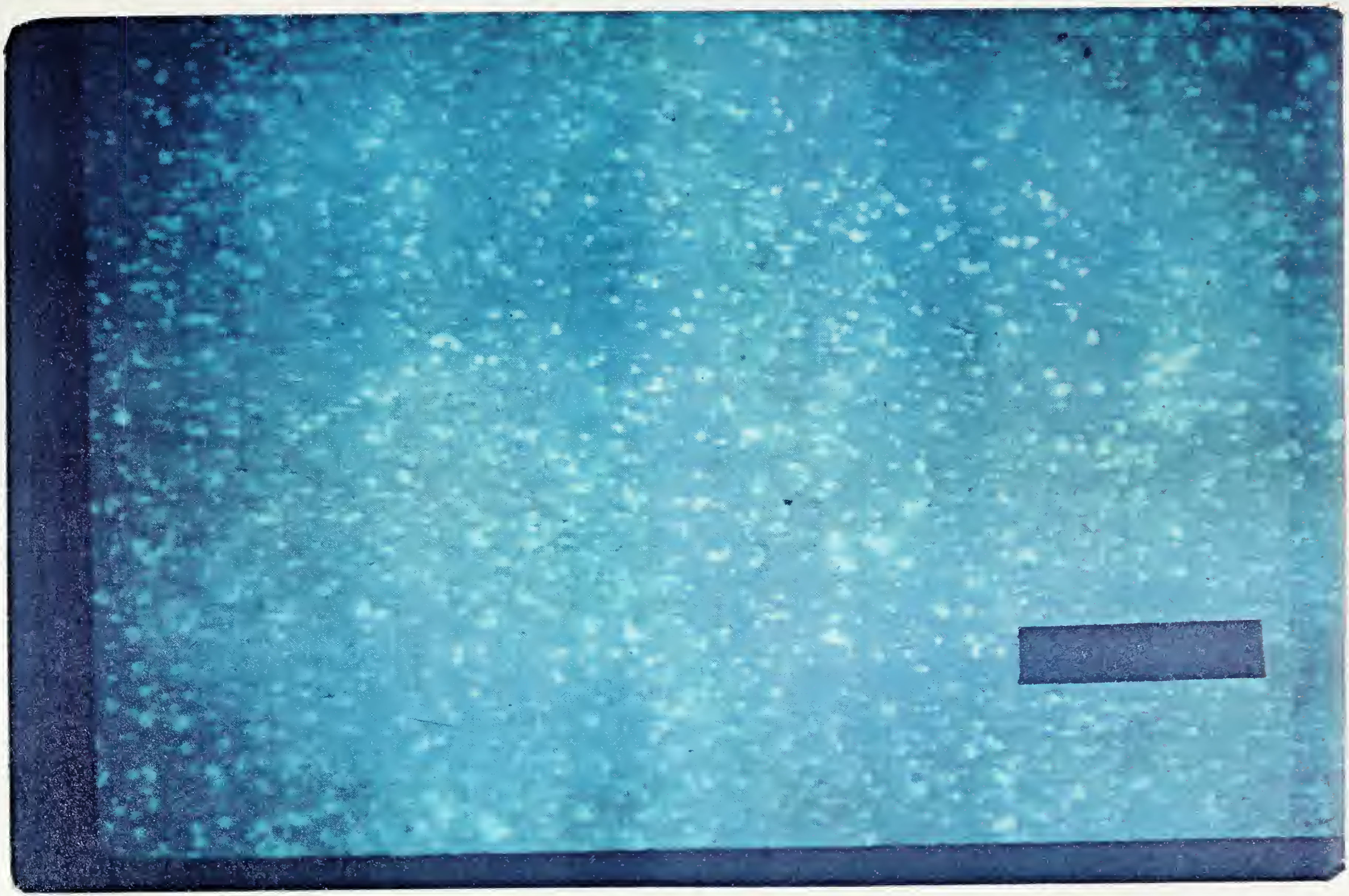


Fig 39

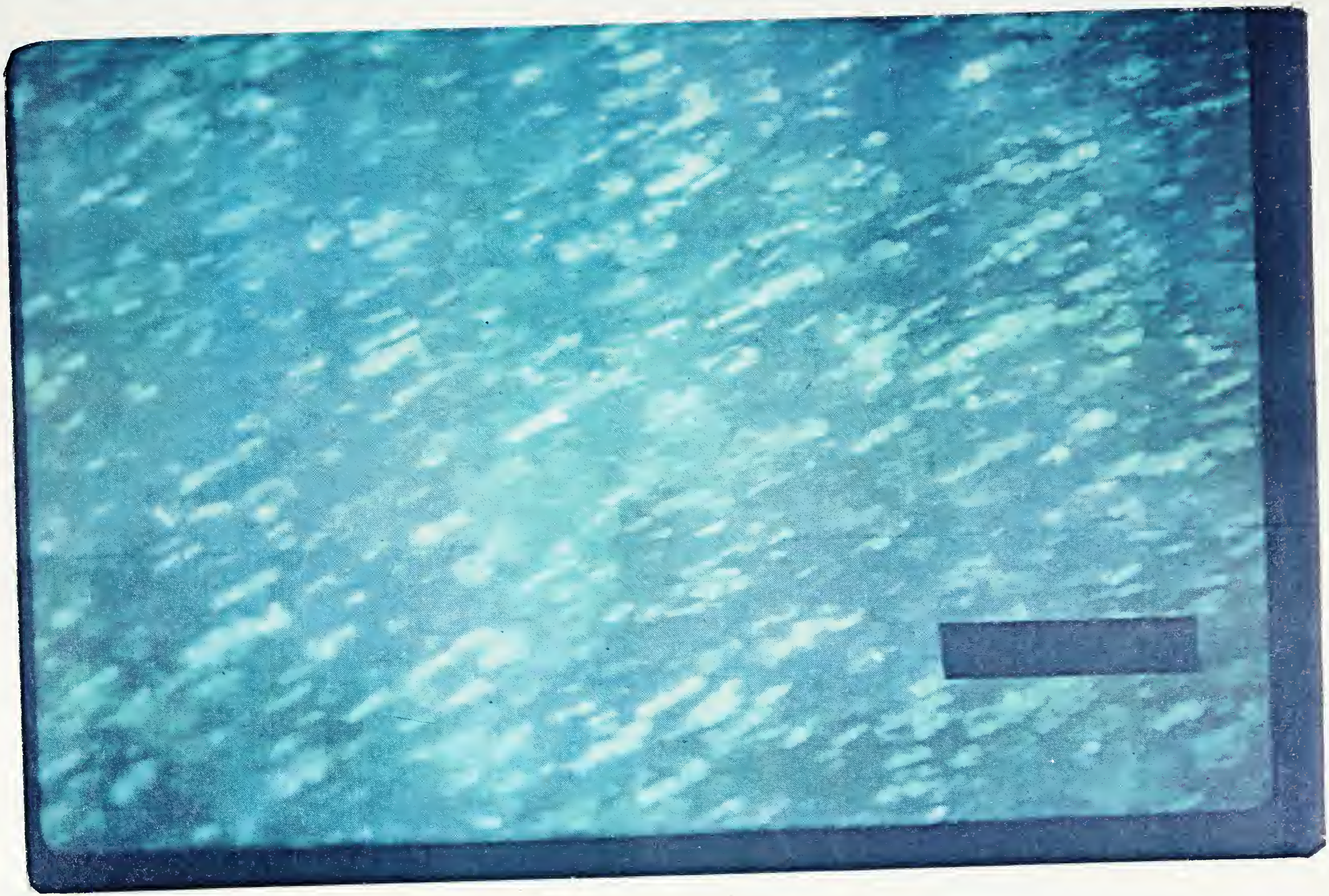


Fig 40

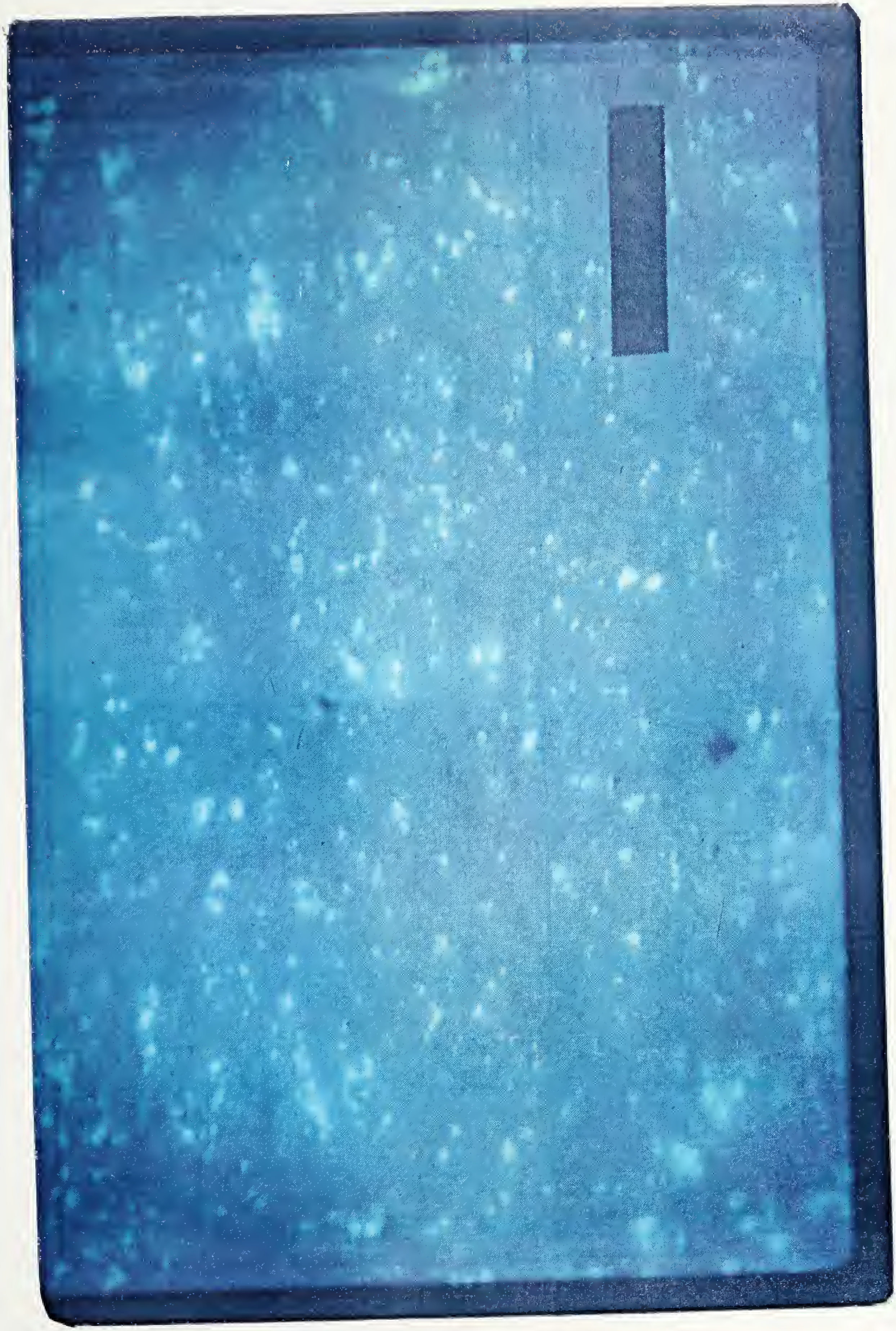


Fig 41

Fig 42

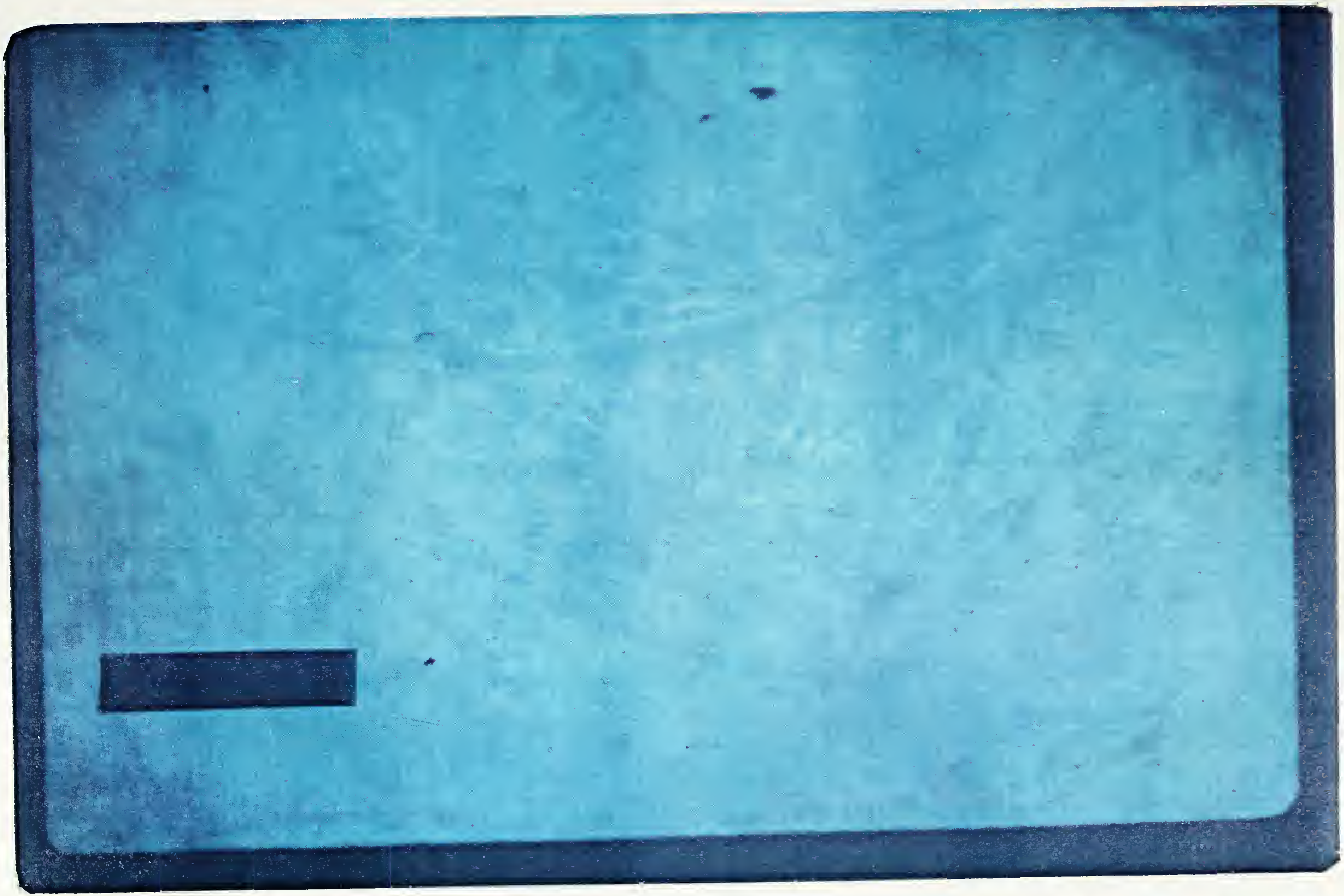


Fig 43

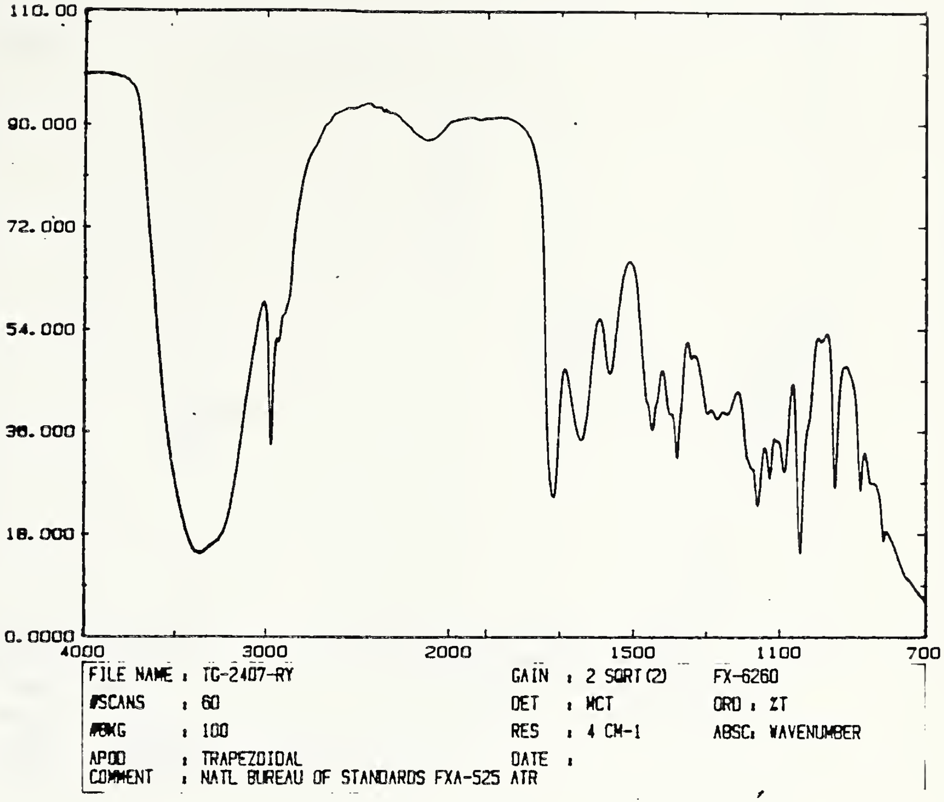


Figure 44 Fourier Transform IR absorption spectrum of varnish TG-2407-RV

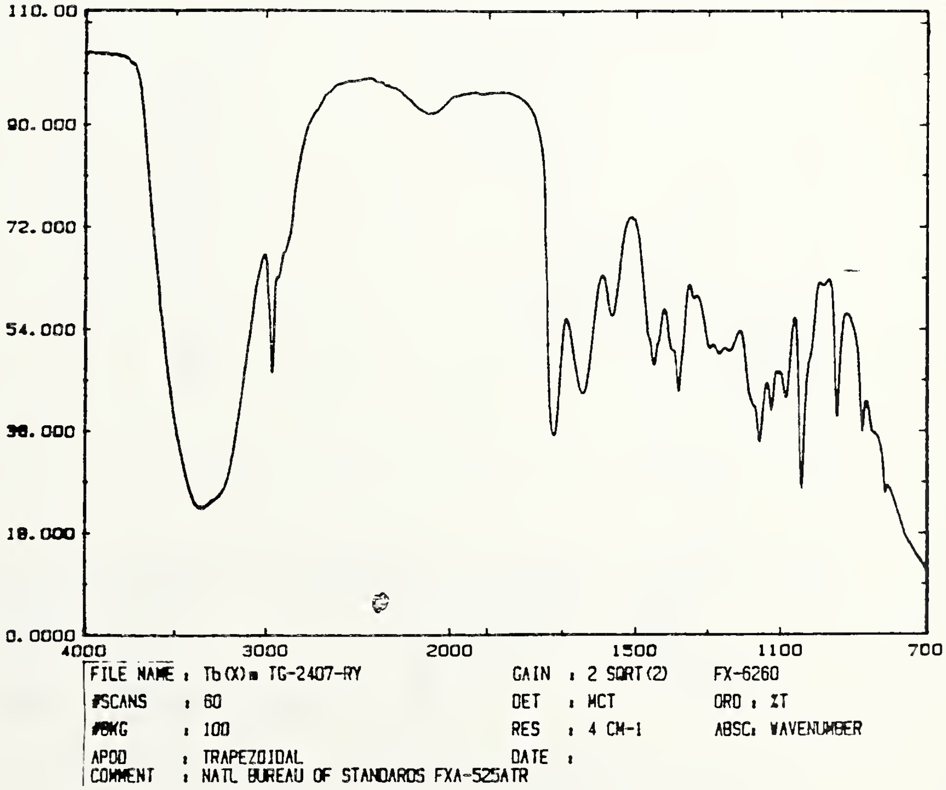


Figure 45 FTIR absorption spectrum of varnish TG-2407-RV containing 0.12 percent $Tb(DPA)_3$

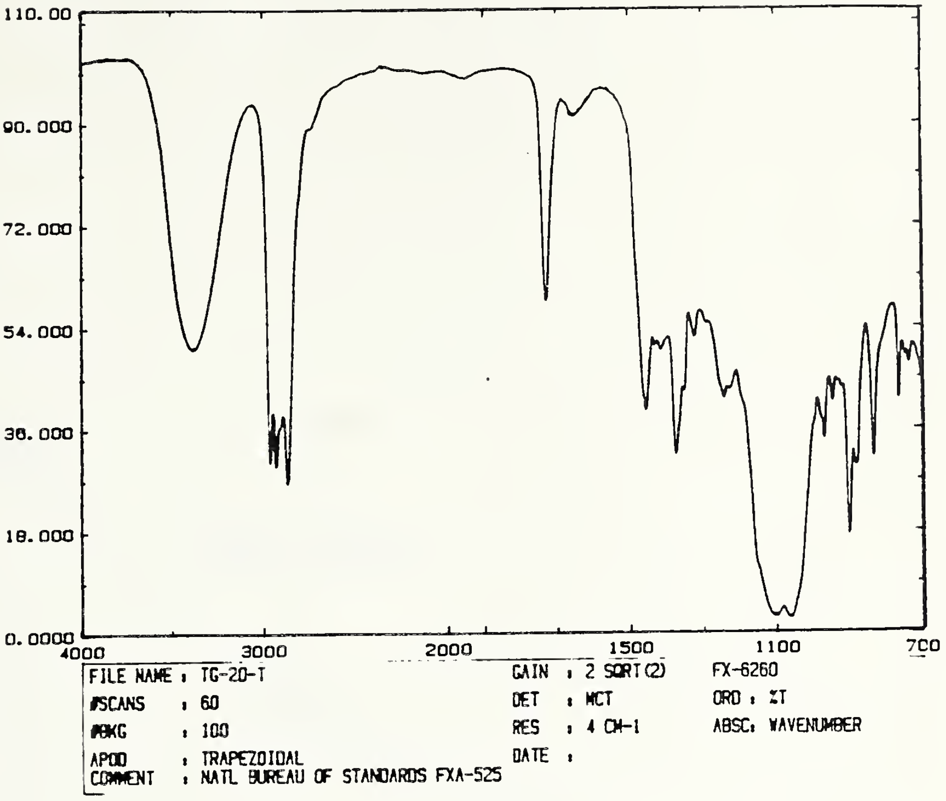


Figure 46 FTIR absorption spectrum of varnish TG-20-T

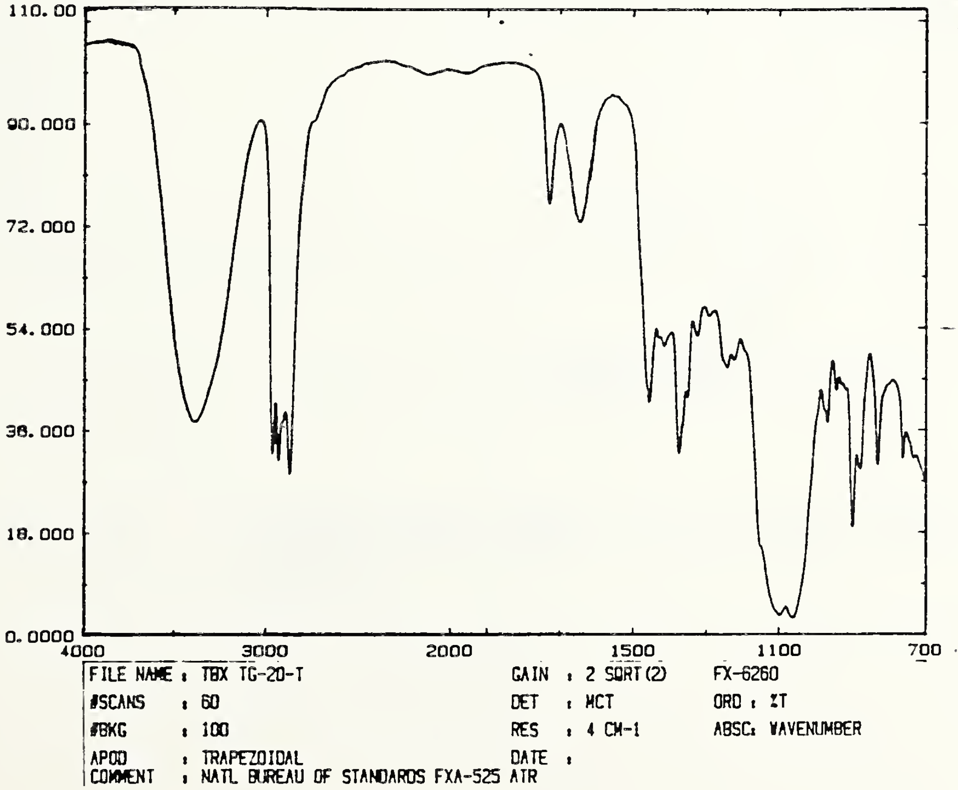


Figure 47 FTIR absorption spectrum of varnish TG-20-T containing 0.12 percent $Tb(DPA)_3$

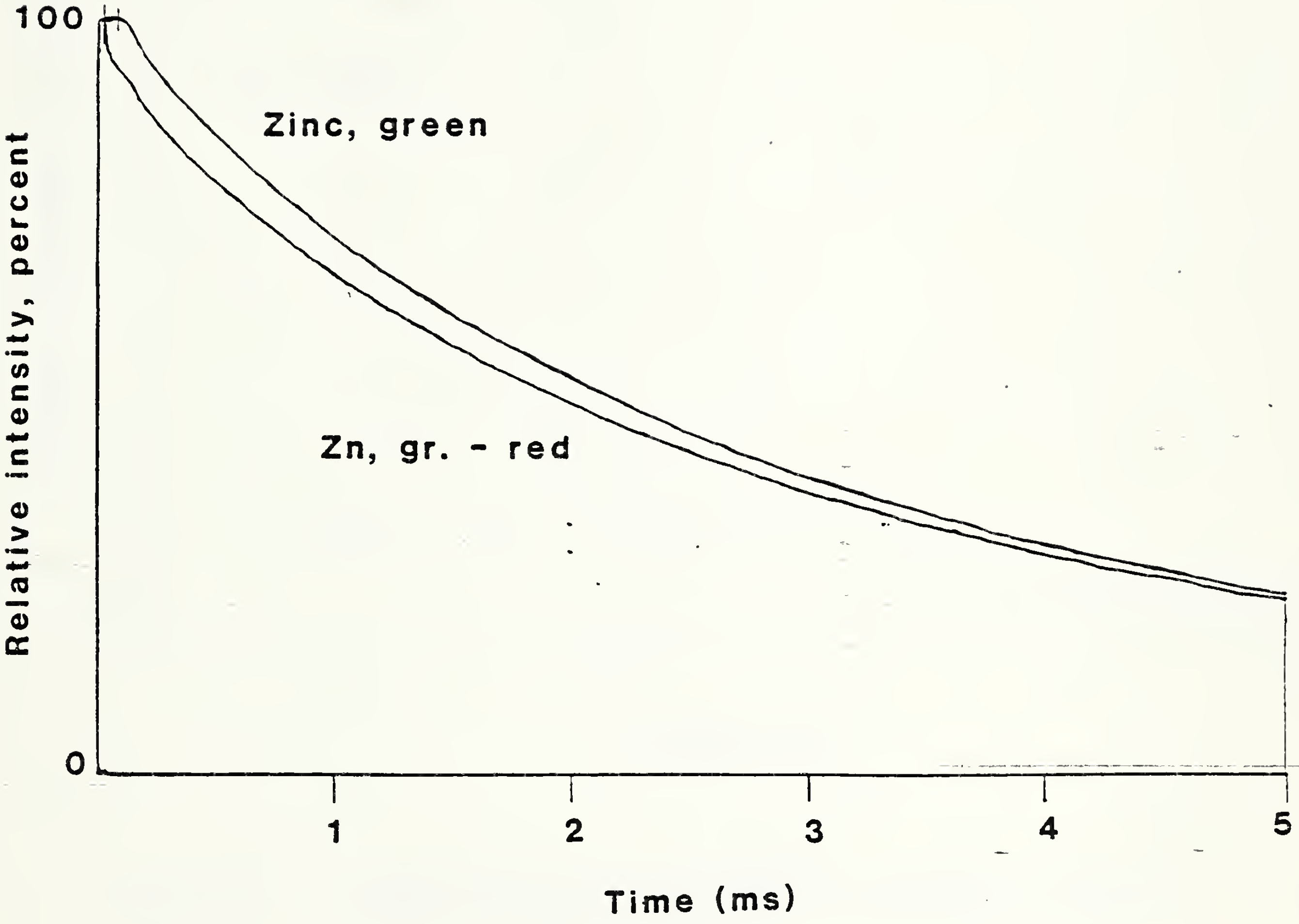


Figure 48. Phosphorescence decay of zinc orthosilicate doped with manganese.

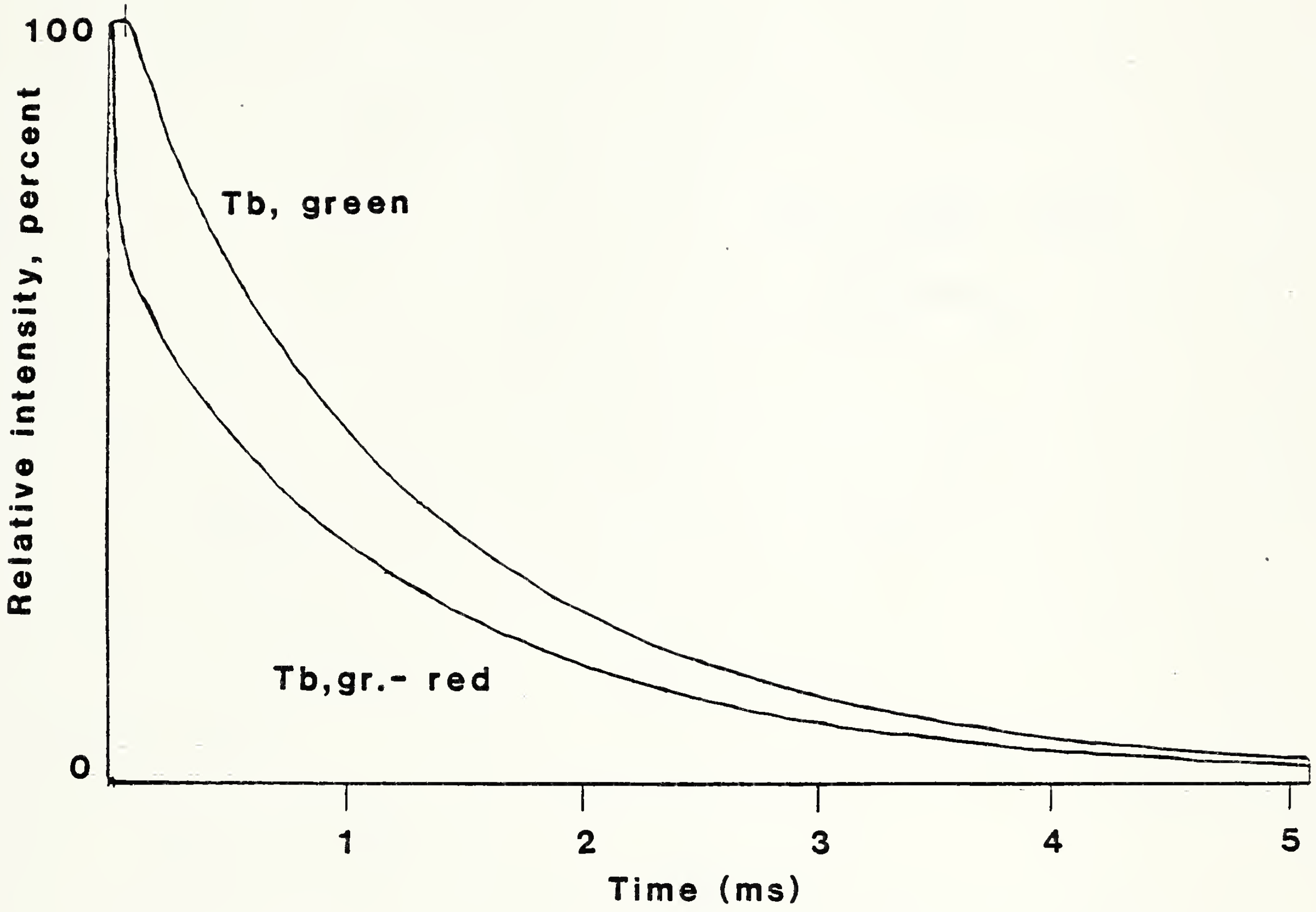


Figure 49. Phosphorescence decay of $Tb(DPA)_n$ applied as the aqueous solution, to unfilled paper by the drawdown process.

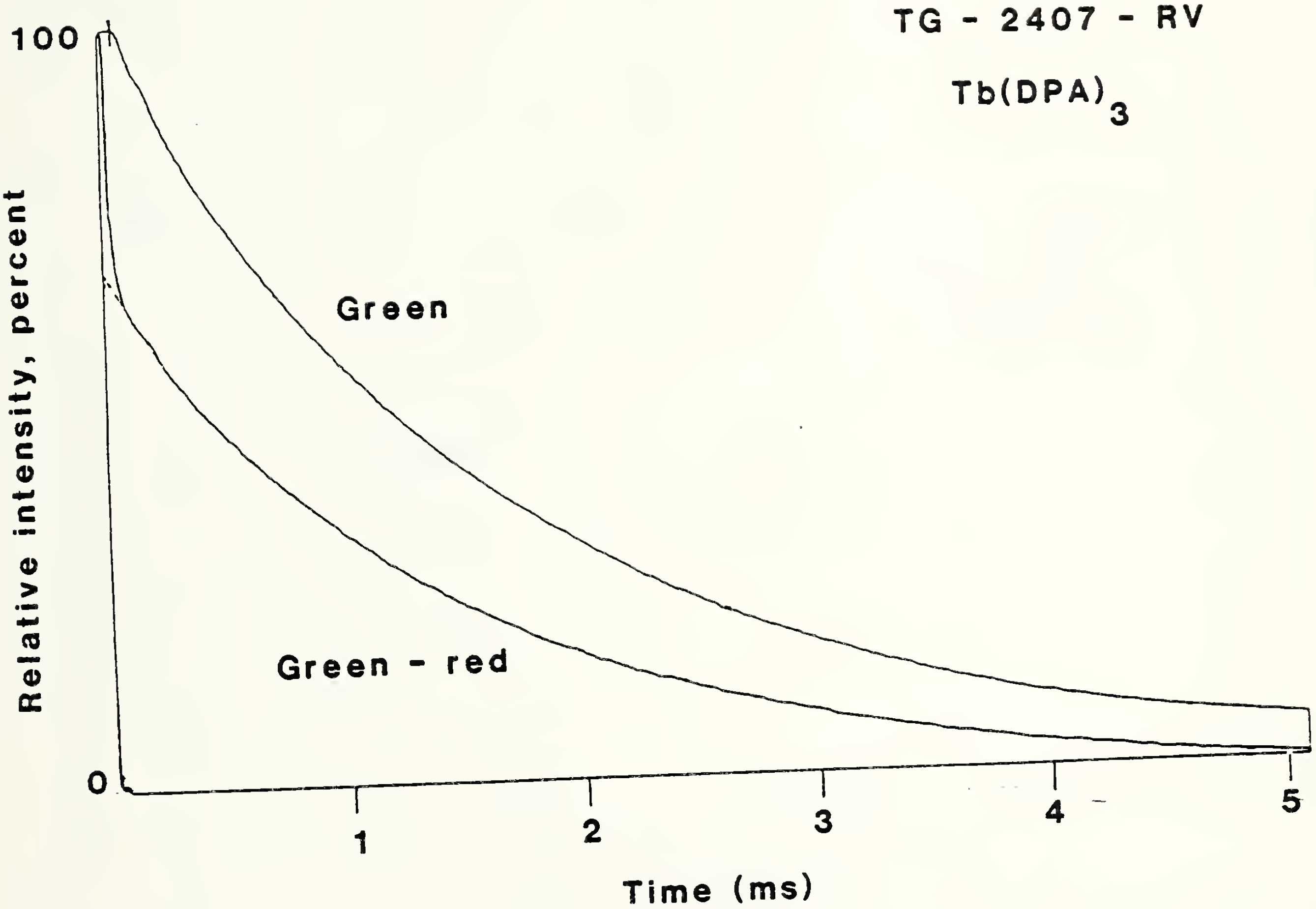


Figure 50. Phosphorescence decay of $Tb(DPA)_3 \cdot 2H_2O$ in varnish TG-2407-RV applied to paper. Tb concentration 0.037 percent (w/w).

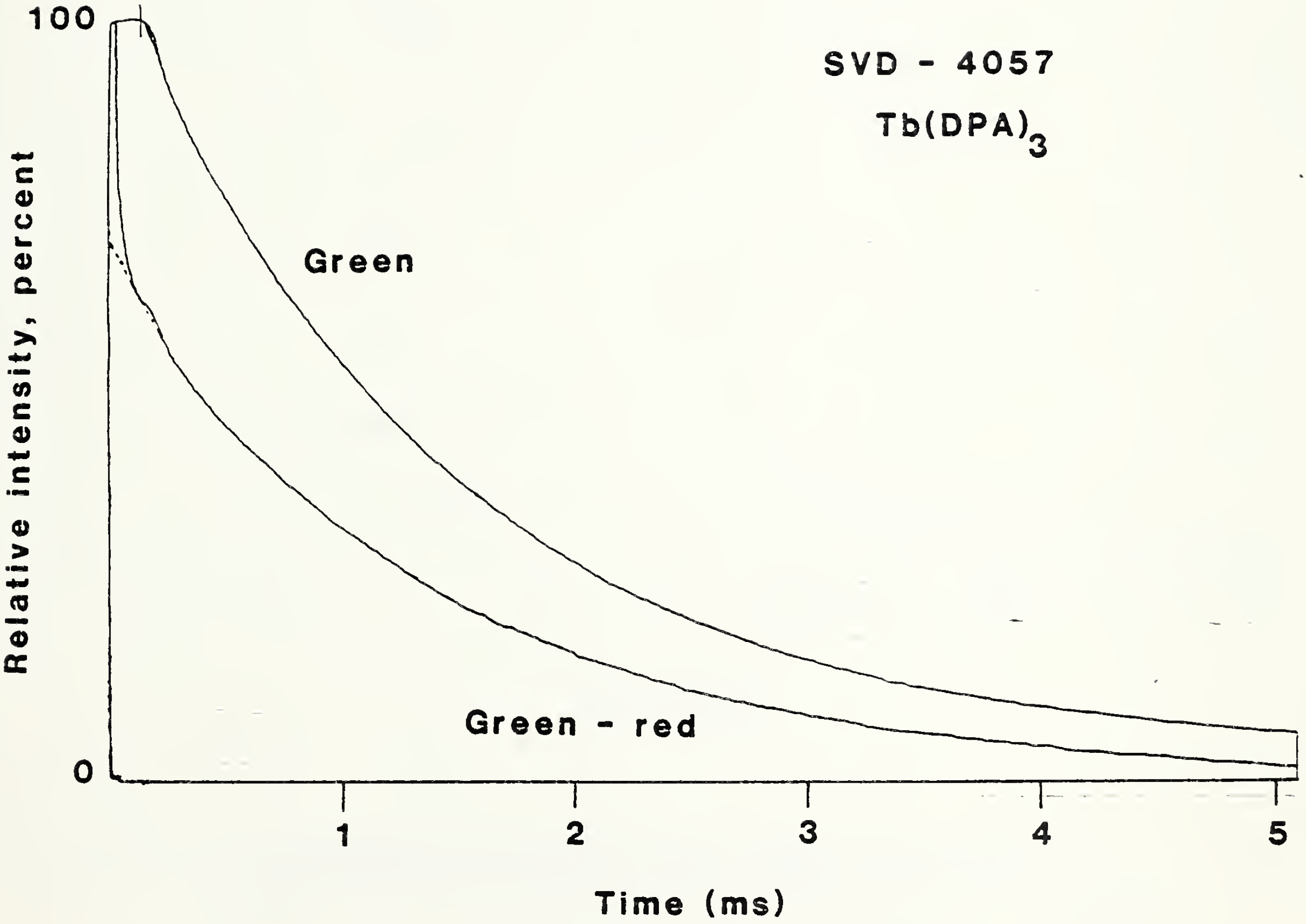


Figure 51. Phosphorescence decay of $Tb(DPA)_3 \cdot 2H_2O$ (0.115 percent Tb) in varnish SVD-4057.

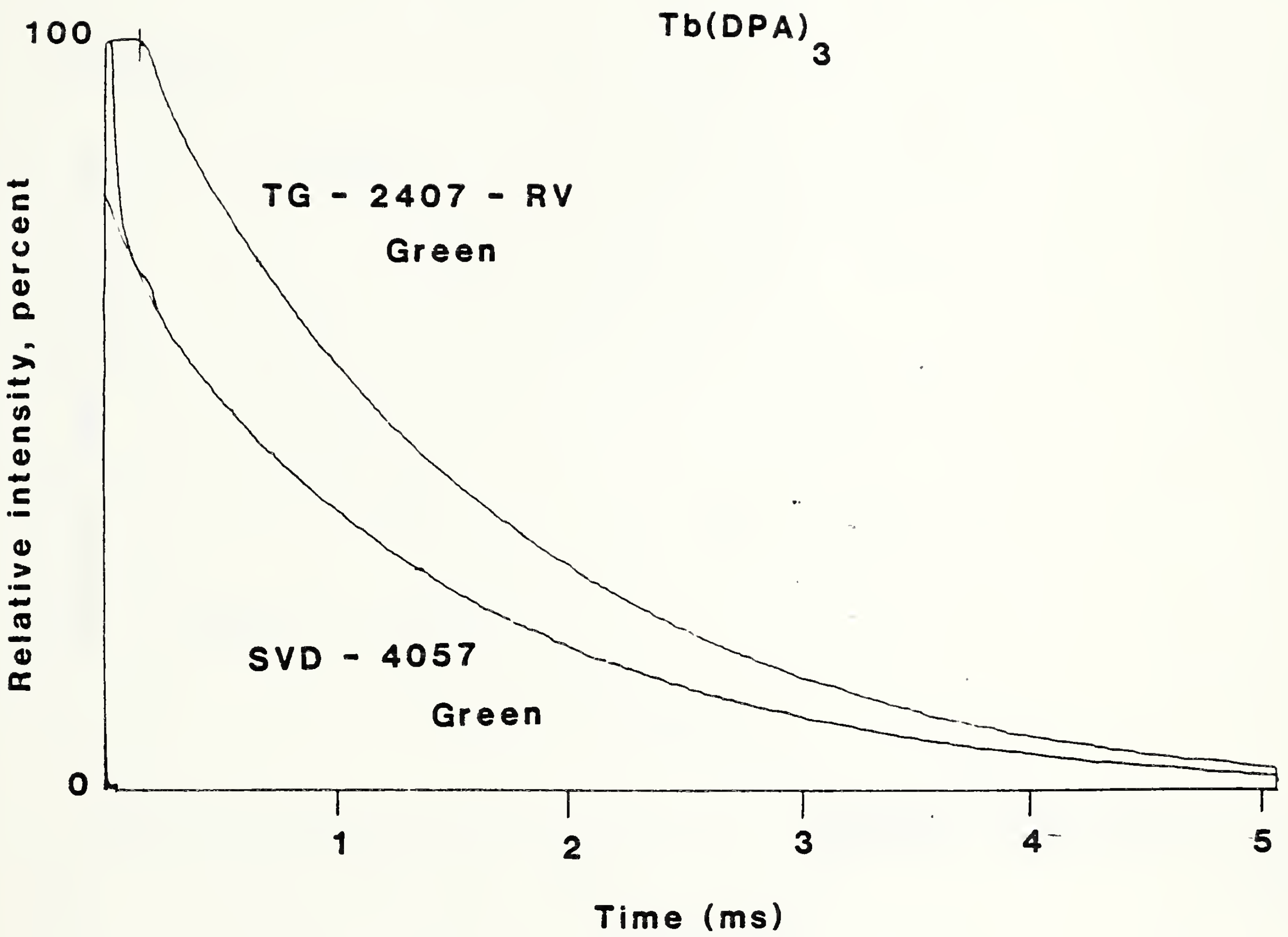


Figure 52. Phosphorescence decay of $Tb(DPA)_3 \cdot 2H_2O$ in varnish TG-2407-RV (0.037 percent, w/w) or SVD-4057 (.115 percent w/w).

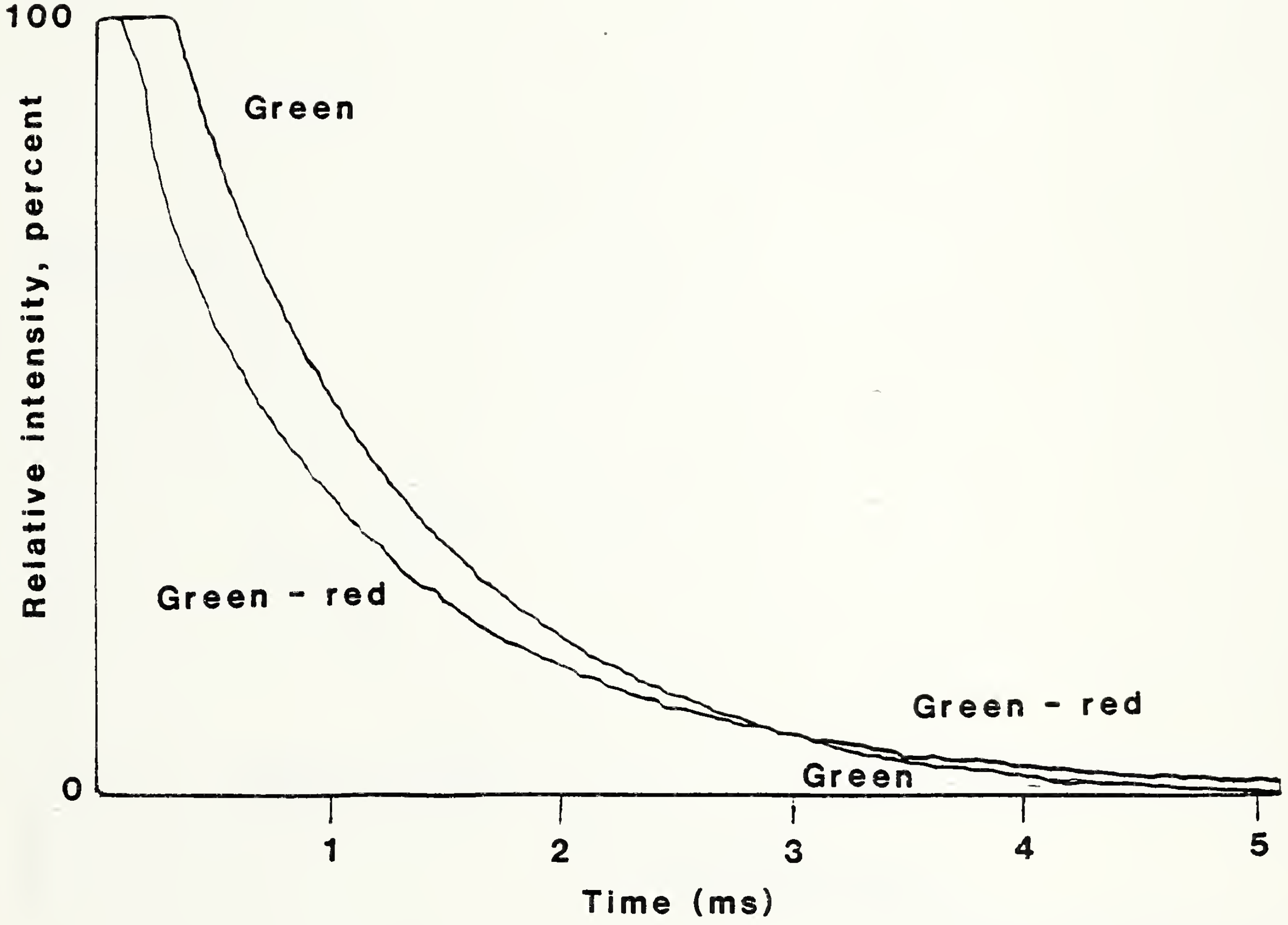


Figure 53. Phosphorescence decay of $Tb(AcAc)_3$ (0.44 percent Tb) in varnish TG-2407-RV after six months' exposure to sunlight.

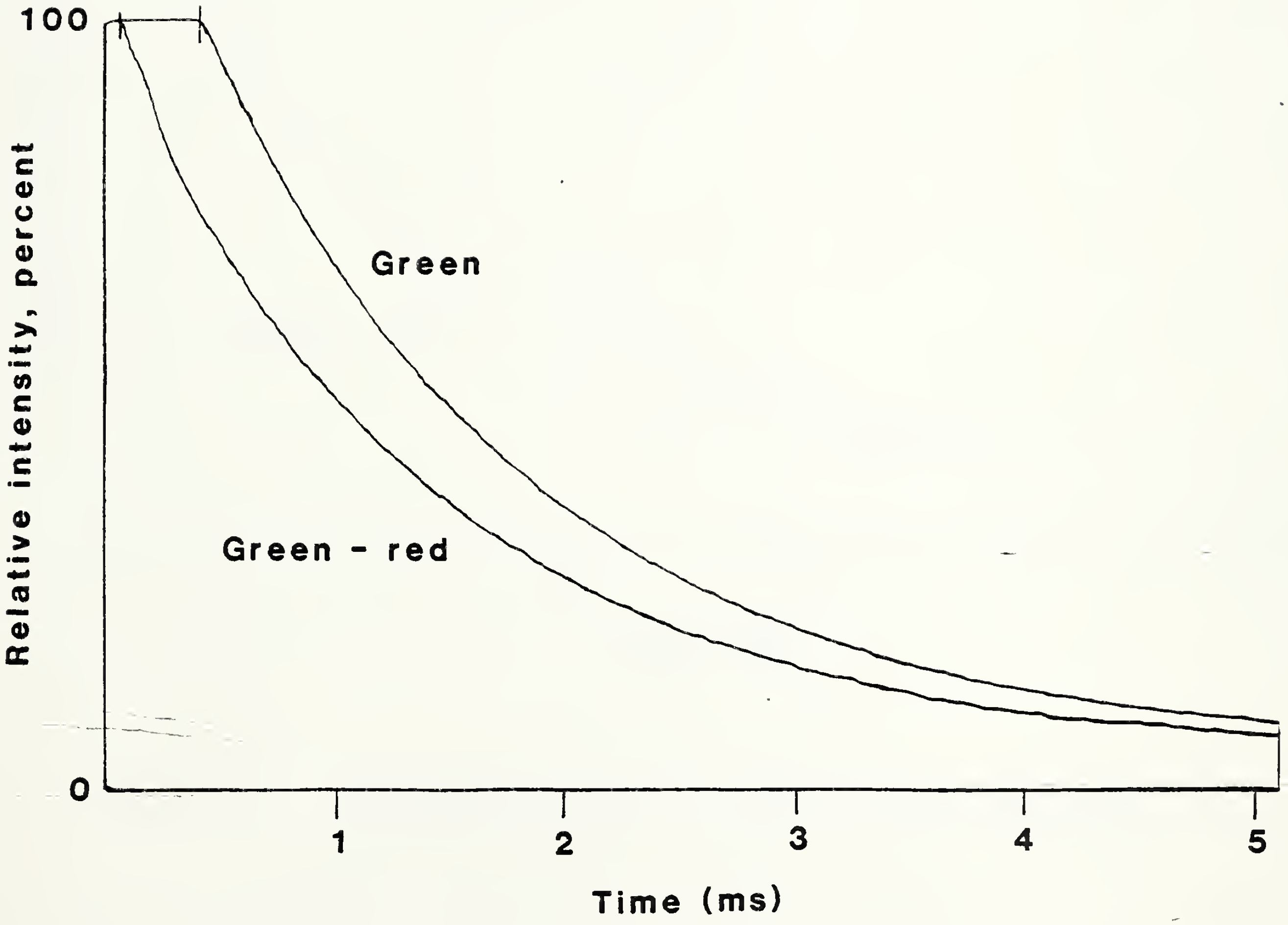


Figure 54. Phosphorescence decay of Tb(AcAc)$_3$ (0.44 percent w/w) in varnish TG-20-T after six months' exposure to sunlight.

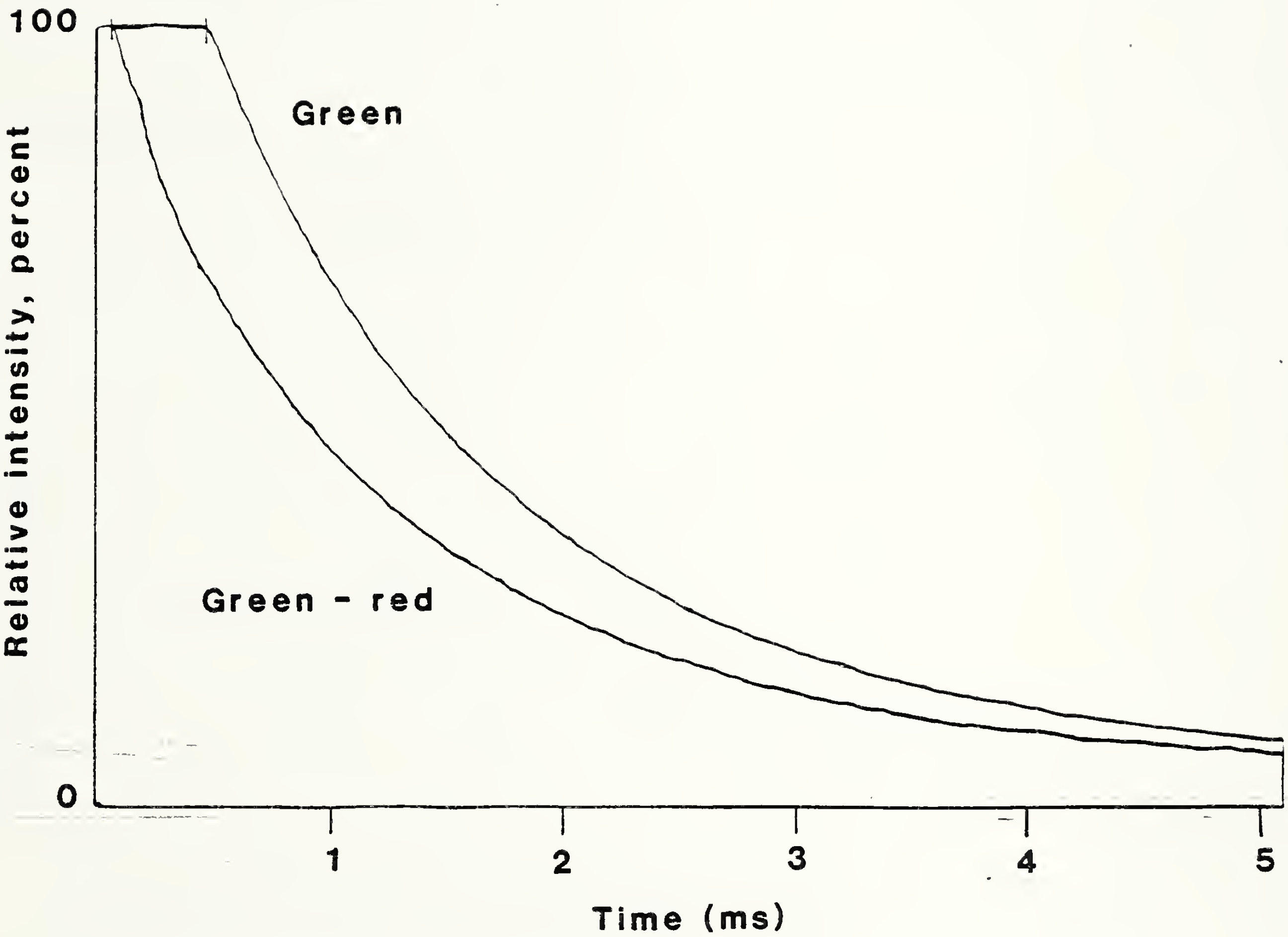


Figure 55. Phosphorescence decay of Tb(DPA)$_3$ (0.066 percent Tb, w/w) in TG-2407-RV after six months' exposure to sunlight.

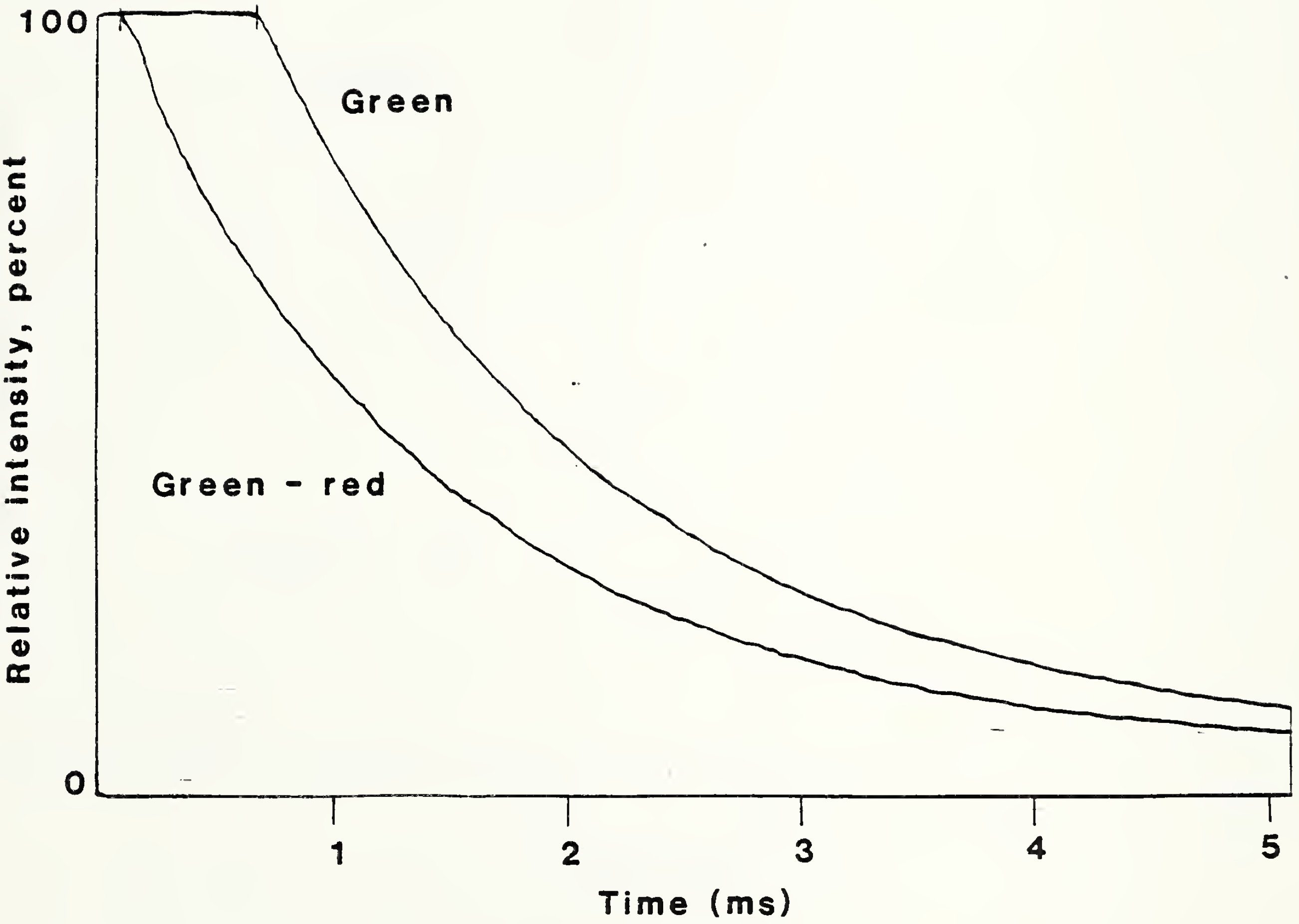


Figure 56. Phosphorescence decay of Tb(DPA)$_3$ directly coated on paper, after three months' exposure to sunlight.

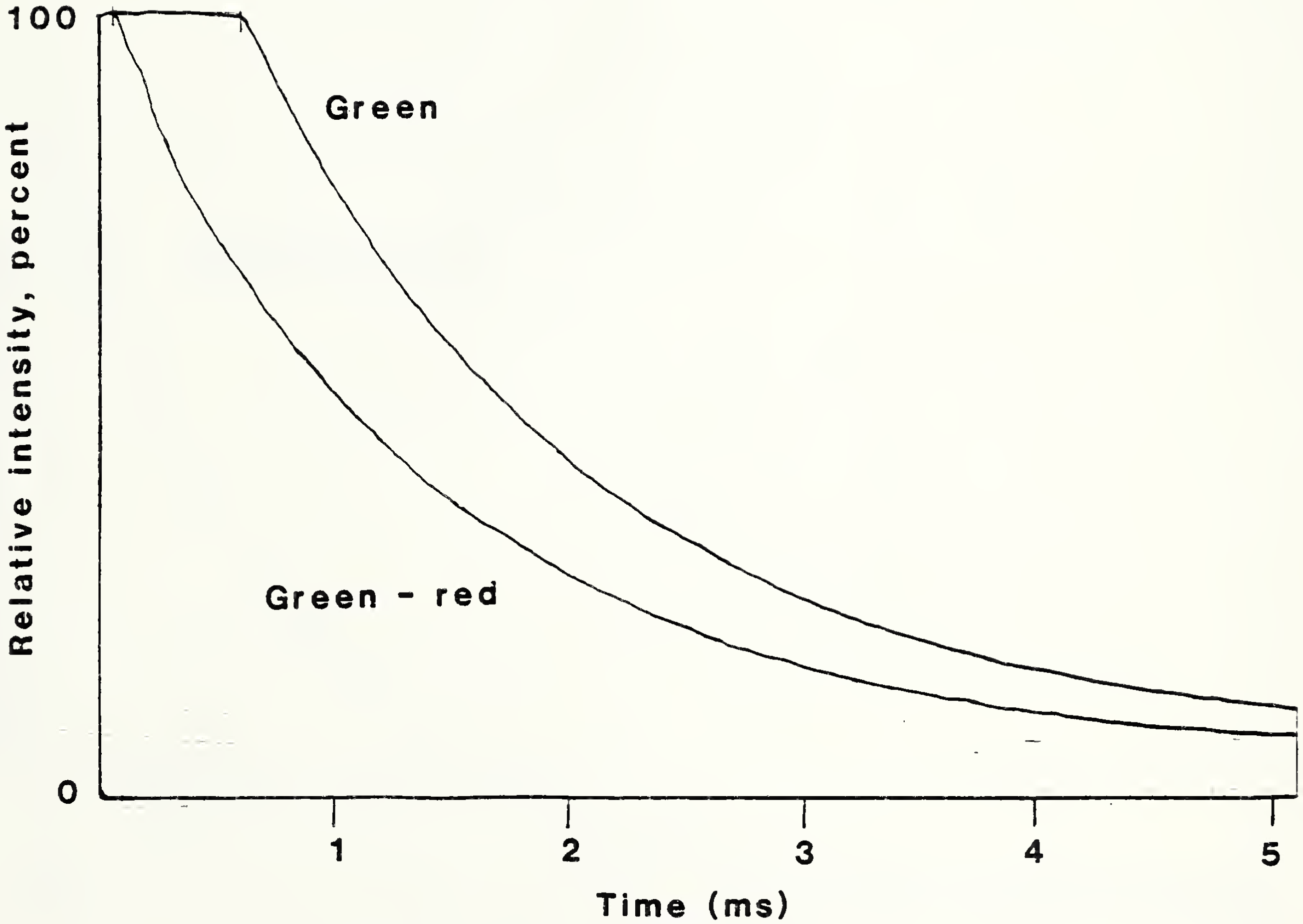


Figure 57. Phosphorescence decay of $Tb(DPA)_3$ directly coated on paper, after three months' storage in the dark.

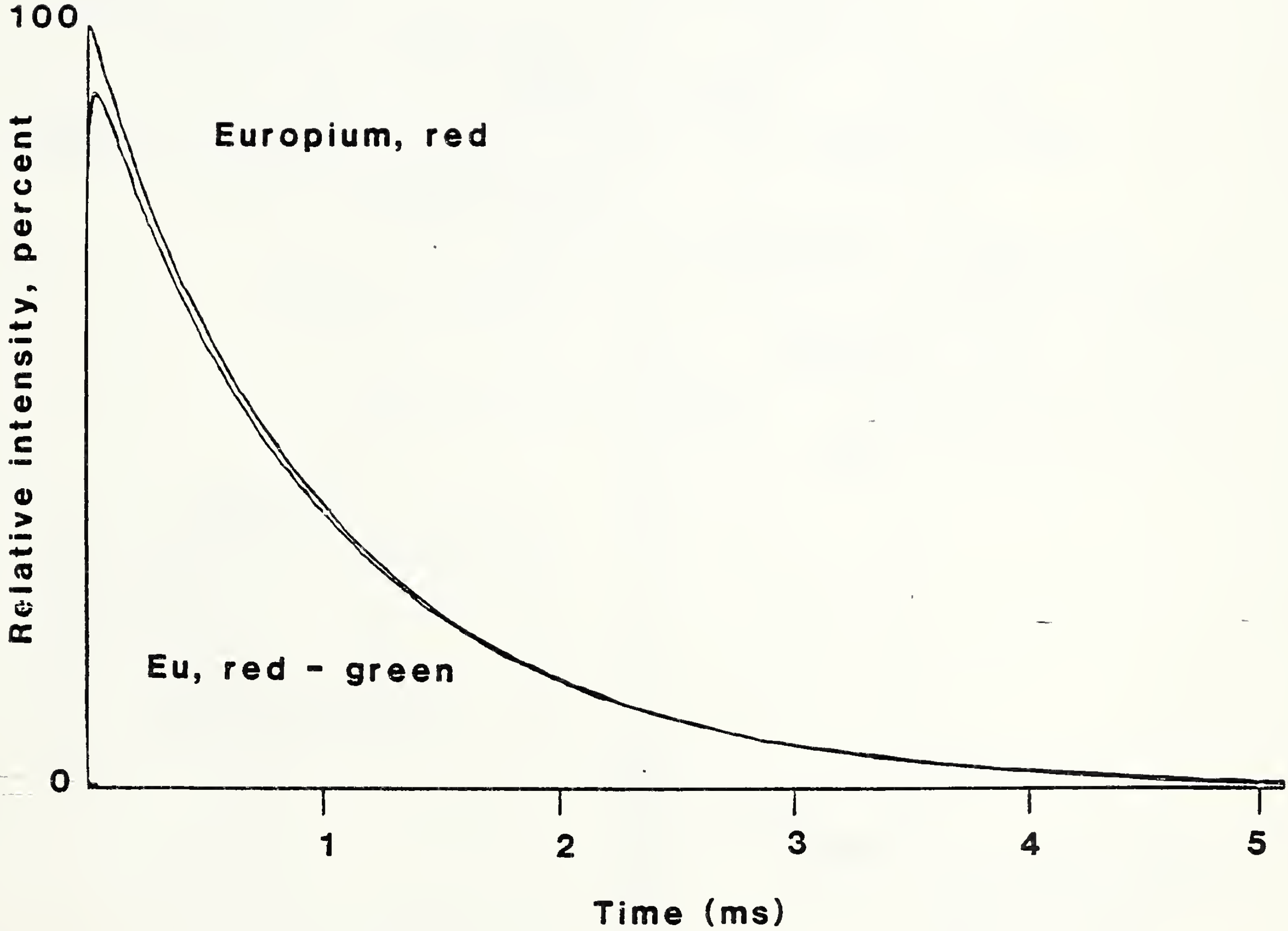
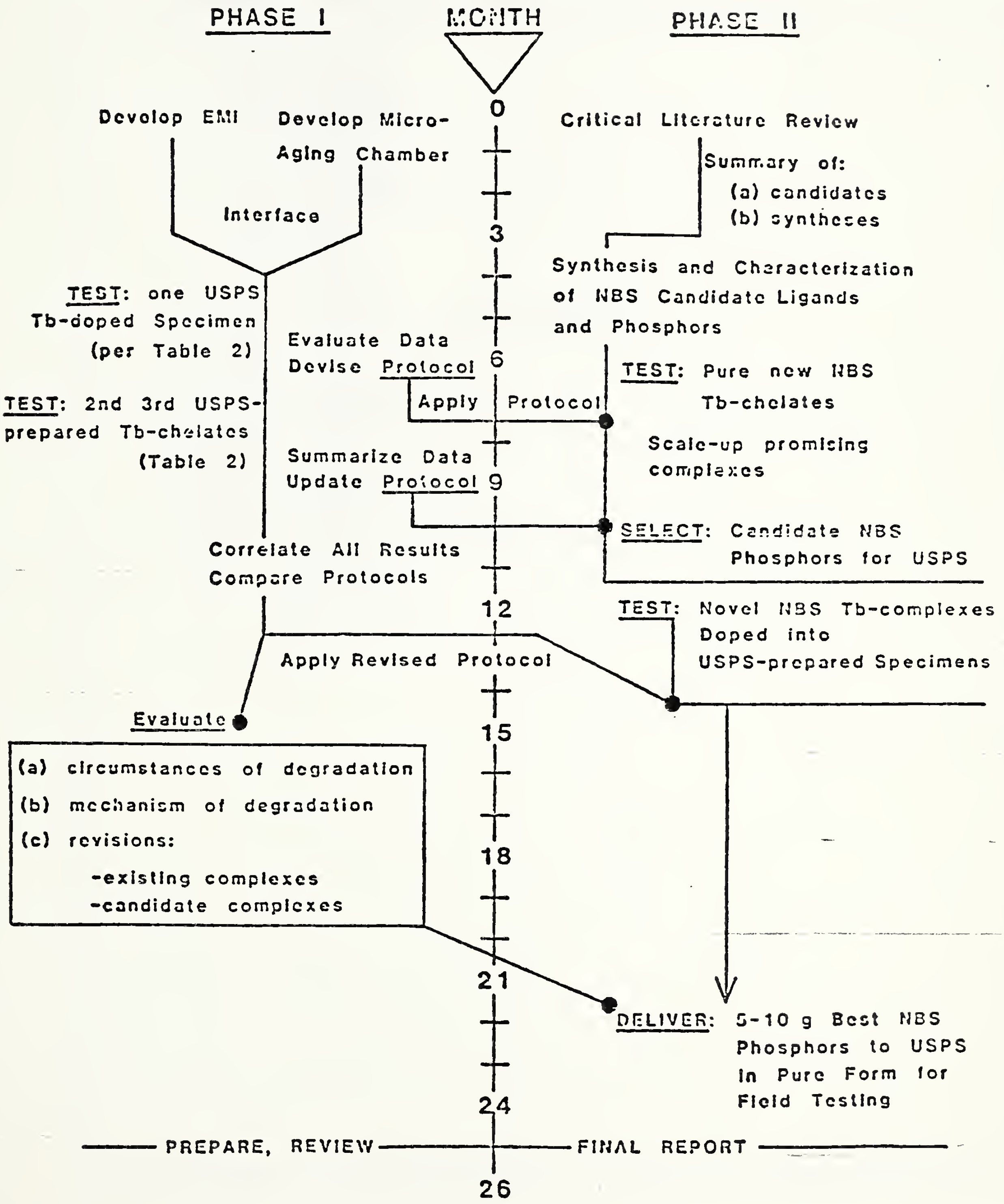


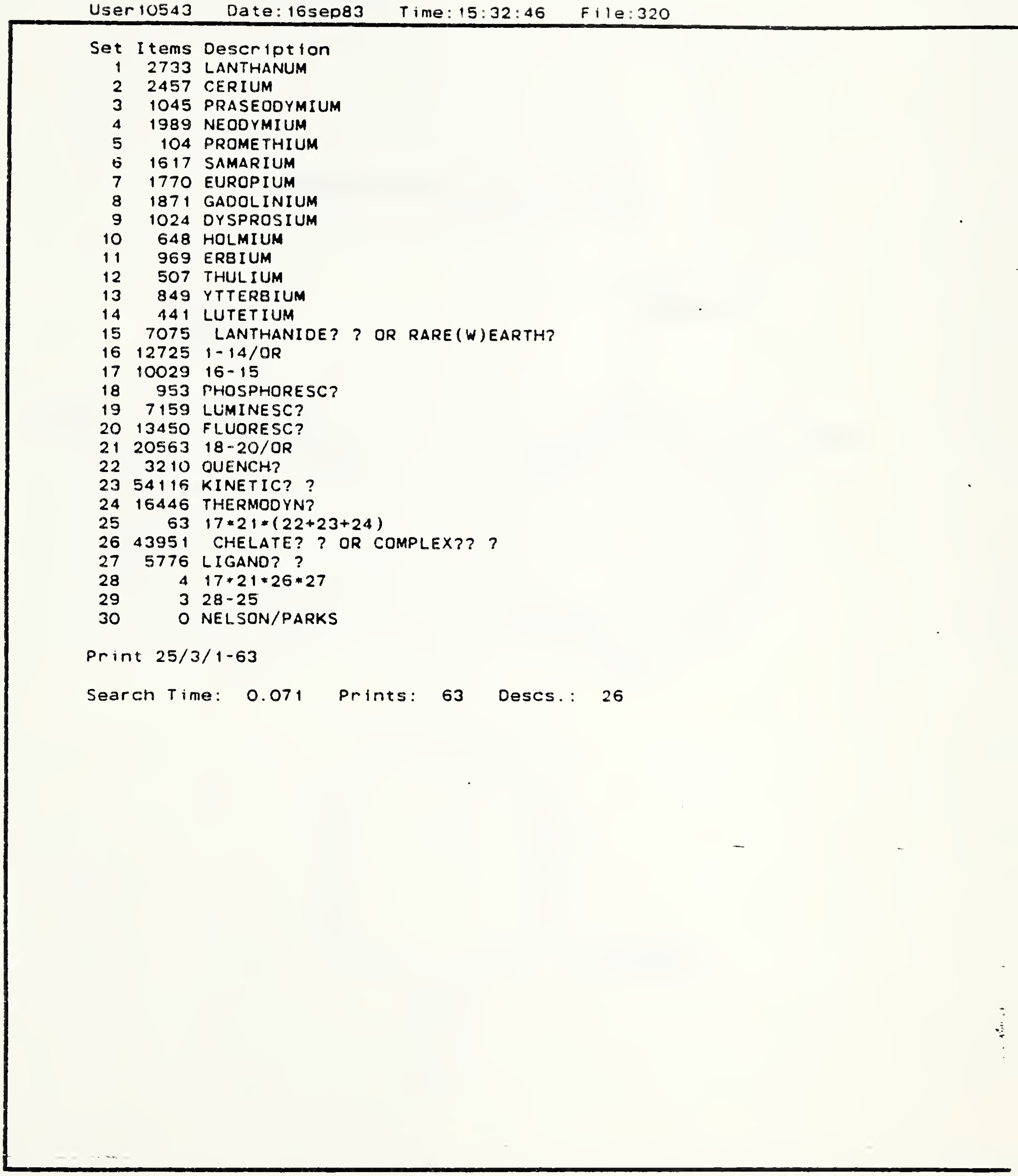
Figure 58. Phosphorescence decay of europium oxide coated on a ceramic card.

Figure 59

FY 83-4 SUMMARY WORK SCHEDULE



APPENDIX 1



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Set Items Description
  1  2733 LANTHANUM
  2  2457 CERIUM
  3  1045 PRASEODYMIUM
  4  1989 NEODYMIUM
  5   104 PROMETHIUM
  6  1617 SAMARIUM
  7  1770 EUROPIUM
  8  1871 GADOLINIUM
  9  1024 DYSPROSIUM
 10   648 HOLMIUM
 11   969 ERBIUM
 12   507 THULIUM
 13   849 YTTERBIUM
 14   441 LUTETIUM
 15  7075  LANTHANIDE? ? OR RARE(W)EARTH?
 16 12725 1-14/OR
 17 10029 16-15
 18   953 PHOSPHORESC?
 19  7159 LUMINESC?
 20 13450 FLUORESC?
 21 20563 18-20/OR
 22  3210 QUENCH?
 23 54116 KINETIC? ?
 24 16446 THERMODYN?
 25    63 17*21*(22+23+24)
 26 43951  CHELATE? ? OR COMPLEX?? ?
 27  5776 LIGAND? ?
 28     4 17*21*26*27
 29     3 28-25
 30     0 NELSON/PARKS

Print 25/3/1-63

Search Time:  0.071   Prints:  63   Descs.:  26
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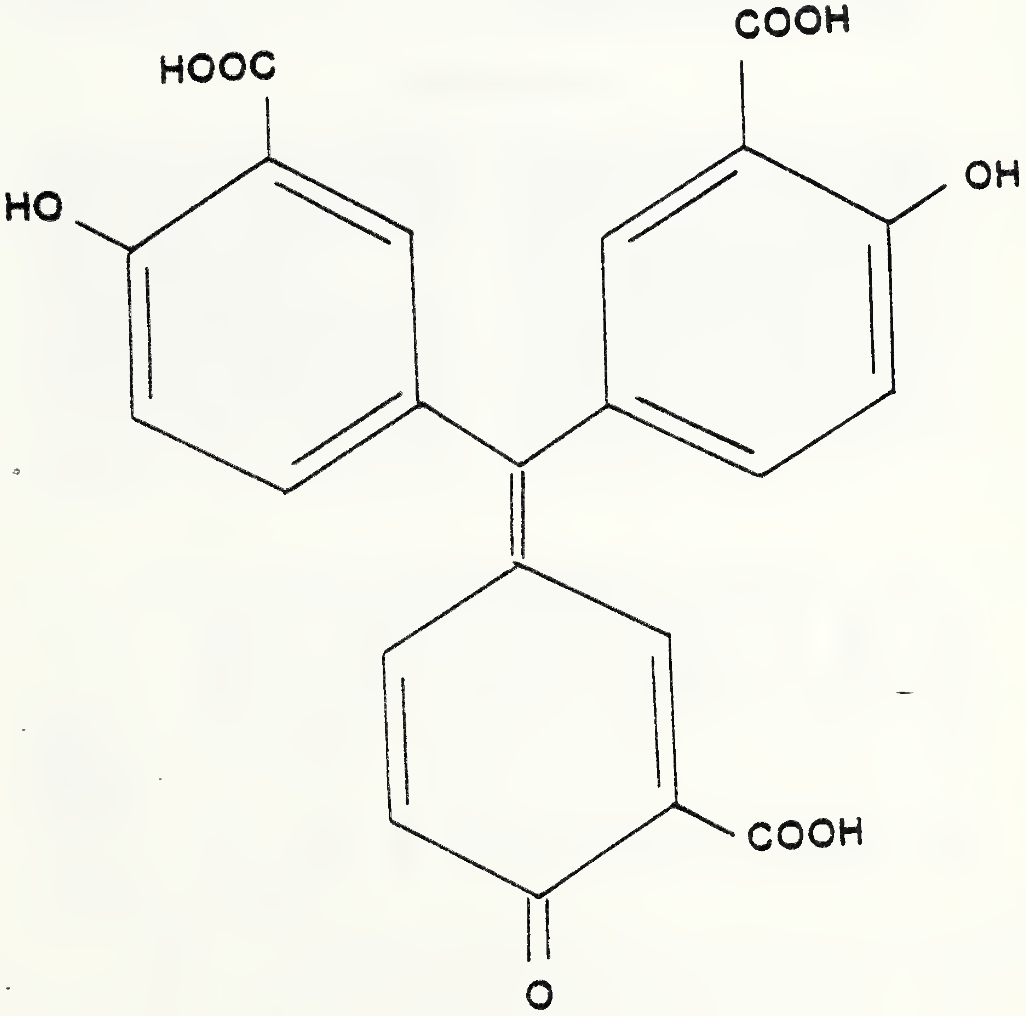
APPENDIX 2

Aurintricarboxylic Acid



APPENDIX 3a

Product (oxide)	Percent[1] purity	Quantity (pounds)	Price per pound
Cerium	99.9	1-199	$8.75
Europium	99.99	1-24	900.00
Gadolinium	99.99	1-49	65.00
Lanthanum	99.99	1-299	7.50
Neodymium	99.99	1-49	60.00
Praseodymium	95.0	1-299	17.50
Samarium	95.0	1-109	30.00
Terbium	99.99	1-49	575.00
Yttrium	99.99	1-49	50.00

[1] Purity expressed as percent of total REO.

Nominal prices for various rare-earth products were quoted by Research Chemicals, net 30 days, f.o.b. Phoenix, Ariz., effective October 1, 1982:

Element	Oxide[1] price per kilogram	Metal[2] price per kilogram
Cerium	$20	$125
Dysprosium	110	200
Erbium	200	650
Europium	1,300	7,500
Gadolinium	140	485
Holmium	650	1,600
Lanthanum	19	125
Lutetium	3,200	14,200
Neodymium	80	260
Praseodymium	130	310
Samarium	130	230
Terbium	1,200	2,800
Thulium	2,400	8,000
Ytterbium	225	875
Yttrium	94	430

[1] Minimum 99.9% purity, 1- to 20-kilogram quantities.
[2] Ingot form, 1 to 5 kilograms, from 99.9% grade oxides.

FOREIGN TRADE

Exports of ferrocerium and other pyrophoric alloys containing rare earths totaled 24,383 kilograms in 1982, a 145% increase from the 1981 level. Major destinations were the Republic of Korea (50%), Japan (30%), and Hong Kong (7%).

Exports of rare-earth metal ores, excluding monazite, decreased 50% from the 1981 total of 9,586,505 kilograms to a total of 4,836,389 kilograms in 1982. Exports in 1982 were valued at $11,347,652. Major destinations were Japan (53%), the Federal Republic of Germany (24%), and the United Kingdom (8%).

Exports of thorium ore, including monazite, decreased 29% in 1982 from the 1981 level. France received all of the reported total of 91,508 kilograms valued at $103,356.

Australia has been the principal import source of monazite for the United States since 1977. Imports of cerium oxide increased substantially in 1982 compared with that of 1981. France remained the largest source of imported rare-earth oxides. Imports of rare-earth alloys, including mischmetal, were significantly lower in 1982 as a result of the depressed state of the domestic steel industry. Brazil continued to be the leading supplier of imported rare-earth alloys.

Table 2.—U.S. imports for consumption of monazite, by country

Country	1978		1979		1980		1981		1982	
	Quantity (metric tons)	Value (thousands)	Quantity (metric tons)	Value (thousands)	Quantity (metric tons)	Value (thousands)	Quantity (metric tons)	Value (thousands)	Quantity (metric tons)	Value (thousands)
Australia	5,018	$1,154	5,686	$1,501	4,933	$1,749	7,469	$3,158	6,600	$2,830
Liberia	53	<1	--	--	--	--	--	--	--	--
Malaysia	1,157	255	561	161	215	101	--	--	603	240
South Africa, Republic of	--	--	3	2	--	--	--	--	--	--
Thailand	767	193	37	13	--	--	--	--	--	--
Total	6,995	1,603	6,287	1,677	5,148	1,850	7,469	3,158	7,203	3,070
REO content[e]	3,847	XX	3,458	XX	2,831	XX	4,108	XX	3,962	XX

[e] Estimated. XX Not applicable.

Taken from Minerals Yearbook, Vol I. Metals and Minerals, 1982. United States Department of the Interior. U.S. Government Printing Office, Washington, 1983. pp 705 - 714. James B. Hedrick, author.

APPENDIX 3b

TO: Ed Parks 31 July 84

FROM: Marietta Nelson, Librarian
Information Resources and Development Division
National Bureau of Standards

SUBJ: World production of Terbium

I talked to James Hedrick of the U.S. Bureau of Mines, who wrote the chapter on RARE EARTHS in "Minerals Yearbook."

He claims that the figures for total production are almost impossible to obtain, because the companies don't want to make the information public. In addition, they often don't separate Terbium from other rare earths.

The best he can do is to give you the estimated figures for production at the largest producer of separated Terbium (it's the second largest for rare earth production). It's called S. A. Rhone-Poulenc, and is located in France. When the company is working at full production, it produces about 8 metric tons of Terbium Oxide (Tb_4O_7) per year. Its U.S. subsidiary is Rhone-Poulenc of Monmouth Junction, N.J. (the mining operation is in Freeport, Texas). The U.S. branch hopes to produce 6.4 metric tons of Terbium Oxide when it gets into full operation.

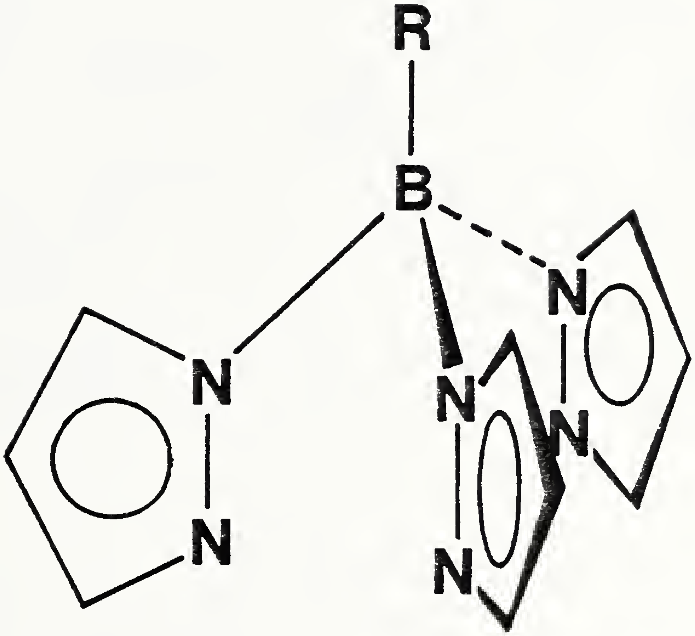
Mr Hedrick says that the producers hope to increase their capacity by 80%, if the demand can be sustained and increased.

He has not able to give me export/import figures--I could possibly try elsewhere, but I have a feeling that I would keep getting referred back to Mr Hedrick!

Let me know if you want me to try elsewhere, or if you have any specific questions that I could ask Mr Hedrick.

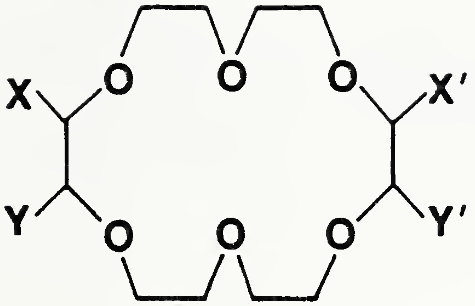
APPENDIX 4

R = H, alkyl, aryl

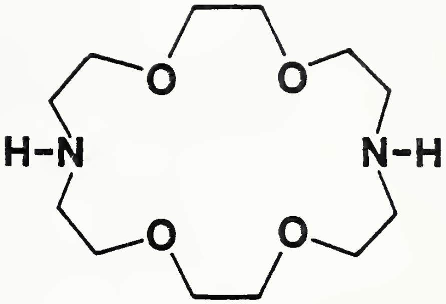


tris(Pyrazol-1-yl)borate Anion

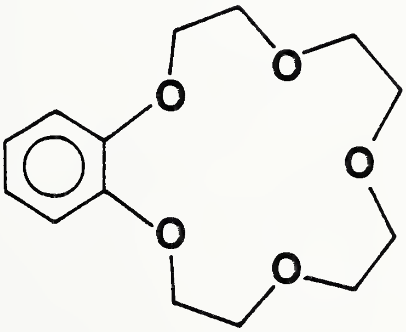
APPENDIX 5



A 18-Crown-6



B 1,4-Diaza-18-Crown-6



C Benzo-15-Crown-5

NBS-114A (REV. 2-80)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** *(See instructions)*	1. PUBLICATION OR REPORT NO. NBSIR 85-3132	2. Performing Organ. Report No.	3. Publication Date March, 1985

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Environmental Factors and Mechanisms Controlling Degradation of Tb(III) Chelates: Development of Effective new Phosphors for Postage Stamp Use.

5. AUTHOR(S)

E. J. Parks, G. J. Olson, and F. E. Brinckman

6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

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9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

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Rockville, MD 20852-8101

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

The USPS facer-canceller system annually cancels 30 billion stamps tagged with a bright green phosphor(λ_{exc}=254 nm;λ_{em}=500-550 nm) mixed or dissolved in organic varnish. Current inorganic phosphors are immiscible and subject to abrasive removal, causing expensive system failures. Miscible organic chelates of terbium (III) phosphoresce brightly in the green region of the spectrum. However, a USPS-sponsored study indicated that candidate organoterbium phosphors such as tris(acetoacetato)terbium(III) ($Tb(AcAc)_3$ were subject to luminescence decay in humid air. USPS requested that NBS determine the decay mechanism and design one or more stable organoterbium chelates of high quantum efficiency as candidate stamps phosphors. Our results show complex patterns of decay for $Tb(AcAc)_3$. In humid air,early luminescence decay is followed by prolonged increases to nearly the original phosphorescence, or else by little additinal change. However, this favorable stability is offset by unfavorably low quantum efficiency. General use by USPS would be prohibitively expensive. Tris(dipicolinato)terbium(III) $Tb(DPA)_3$, synthesized at NBS in alkaline aqueous solution, manifests the highest quantum efficiency of several phosphors selected from the literature, approximately 20 times that of $Tb(AcAc)_3$. Although it decays under intense UV illumination, $Tb(DPA)_3$ is stable in strong sunlight or in humid air (94 percent RH at 91 ^{o}F). This synthesis will be scaled up during FY85 to provide sufficient phosphor for field testing by USPS. Correlations of the molecular structure and luminescence behavior of $Tb(DPA)_3$ suggest concepts for improved design, to be tested in FY85.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

epifluorescence microscopy; humid air; luminescence; metallo-organic phosphors; molecular design; phosphorescence; postage stamps; sunlight; synthesis; terbium chelates ultraviolet light.

13. AVAILABILITY

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