

TECHNICAL REPORT
66-9-CM

**SYNTHESIS
OF
CHROMOTROPIC COLORANTS**

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by
**Ralph A. Coleman, Walter H. Foster,
John Kazan, and Marion Mason**

**American Cyanamid Company
Bound Brook, New Jersey**

Contract No. DA19-129-AMC-269(N)

February 1966

**UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760**



**Clothing and Organic
Materials Division
TS-138**

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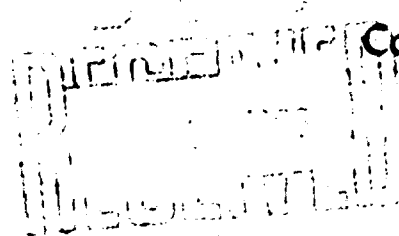
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TECHNICAL REPORT
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SYNTHESIS OF CHROMOTROPIC COLORANTS

by

Dr. Ralph A. Coleman
Project Leader

Dr. Walter H. Foster, Jr. Dr. John Kazan
Mrs. Marion Mason

American Cyanamid Company
Bound Brook, New Jersey

Contract No. DA19-129-AMC-269(N)

Project Reference:
1KO-24401-A113

Series: TS-138

February 1966

U.S. Army Materiel Command
U.S. ARMY NATICK LABORATORIES
Natick, Massachusetts

FOREWORD

Chromotropy is a well-known phenomena which, in the general field of colorants for textile surfaces, has been considered to be troublesome and, therefore, a matter to be avoided. Other activities involving chromotropy have utilized colorant systems which cannot be adapted to textile materials.

This report covers the first year of effort in a three-year program designed to synthesize colorant systems that may have applicability to fibrous substrates as part of a general plan to develop materials that could be useful in the development of a dynamic camouflage system for the individual soldier. The study is, at present, a fundamental synthetic organic effort with resolution of the properties of the developed colorants.

The work covered in this report was performed under Contract DA19-129-AMC-269(N) and covers the period April 1964 to April 1965. It was conducted under the leadership of Dr. Ralph A. Coleman. The principal participating American Cyanamid Co. personnel were Dr. Walter H. Foster, Jr., Dr. John Kazan and Mrs. Marion Mason.

This study was initiated under Project No. 1KO-24401-A113 by Mr. Frank J. Rizzo, who acted as Project Officer, assisted by Mr. Alvin O. Ramsley initially and later by Dr. Edward M. Healy, all of the Clothing and Organic Materials Division of the U. S. Army Natick Laboratories.

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ABSTRACT

In a study of photochromic colorants potentially useful for a "chameleon" type camouflage system, a number of metal dithizonates have been synthetically modified by introduction of groups in the ortho, meta and para positions of both phenyl rings of dithizone. The resulting complexes were tested for spectral, photochromic and lightfastness properties. While spectral changes and increases in both solubility and lightfastness were affected by some ortho substituents, the photochromic properties (photostationary conversion and thermal return rate) were only slightly affected by substitution.

The complexes of mercury exhibit the best all-round performance although some zinc complexes approach the performance of mercury. The complexes of palladium exhibit potentially useful spectral and photochromic behavior that is quite different from the mercury type complexes and more application research is recommended regarding the incorporation of these palladium complexes in textile fibers.

Fiber reactivity (on nylon) has been introduced into the mercury dithizonate system via a dichlorotriazinyl reactive group. This compound exhibited photochromic properties when reacted with nylon.

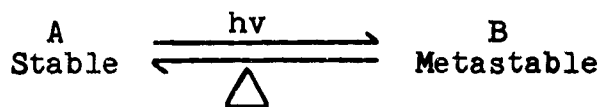
Recommendations for future synthetic work are presented.

SYNTHESIS OF CHROMOTROPIC COLORANTS

I. GENERAL INTRODUCTION

The work described in this report was carried out as part of the program to obtain background data on colorant systems that might be used to develop a "chameleon" type camouflage system for protection of personnel and equipment in various environments.

The results of a prior feasibility study¹ in this area indicated that photochromic colorants currently represent the most feasible approach for the development of a "chameleon" camouflage system. In its simplest form a photochromic system consists of a stable (A) and a metastable (B) form in a photo-equilibrium.



The position of the photoequilibrium is determined at any time by the intensity of the light absorbed by A (converting into B) and by the temperature of the substrate and of B which returns to A as the result of thermal vibrations of the molecule. During this feasibility study, a brief evaluation of a number of presently available photochromic compounds indicated that the system based upon the metal complexes of dithizone (diphenylthiocarbazone) offers the following advantages for photochromic camouflage:

1. Large differences in spectrum of the stable (A) and metastable (B) forms (i.e., large color changes).
2. Fast photo and thermal rates in polymers.
3. Favorable photostationary conversions (from stable to metastable form) at sunlight intensity levels.
4. Absence of complicating side reactions (no photo back reaction).
5. Thermal (dark) return rate adjustable by the use of additives.
6. Good photostability when protected with a near ultraviolet absorber.

None of the other presently available photochromic systems appeared to offer this unique combination of favorable properties. For this reason, the primary synthetic and evaluation efforts during the first year of the present three-year contract were directed toward synthetic modification of the metal dithizonate systems with the specific objectives of:

- a. Varying the color of the stable and metastable forms.
- b. Reducing the fast thermal return rates of the nonmercury complexes.
- c. Improving the light fastness of the system.
- d. Exploring fiber reactivity.

A smaller effort was also directed toward synthetic modification of some other available photochromic systems.

II. SYNTHESIS

A. Introduction

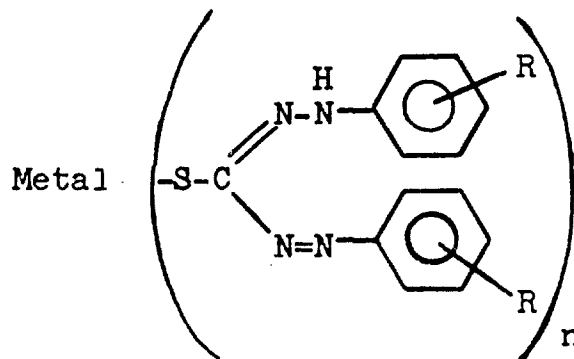
The synthetic effort during the first contract year has been governed by the considerations outlined in Section I. The major effort was concentrated on the preparation of a variety of substituted metal dithizonates in order to provide the compounds necessary for the proper evaluation of this system. A limited portion of the effort was directed towards other areas, such as fiber reactivity, modification of the dithizonate and other systems, and theoretical studies. It should be emphasized that the amount of time spent on these latter areas was limited by the effort necessary to prepare and purify to analytical grade the sixty-odd dithizonate derivatives made during the year.

B. Results and Discussion

The substituted metal dithizonates (diphenylthio-carbazones) were prepared by two general synthetic procedures. The monodithizonates and certain bisdithizonates were prepared by an extraction procedure using a two-phase system consisting of water and an organic solvent, while the bulk of the bisdithizonates were prepared in a homogeneous solvent system. The stable and rapid-forming bisdithizonates were prepared by the homogeneous procedure; the acid sensitive monodithizonates and certain bisdithizonates that formed slowly were prepared by the two-phase method. These procedures offered no difficulty except in the case of certain mercury compounds where there was a tendency to form mixtures containing chloromercurydithizonates (I) rather than bisdithizonates unless an excess of ligand was used.

TABLE I

Summary of Compound Numbers of Metal Dithizonates
Synthesized in This Report



| <u>R</u> | <u>Metal</u> | | | | | | <u>Bi</u> | <u>Ag</u> | <u>Pt</u> |
|---------------------------|--------------|-----------|-----------|-----------|-----------|---|-----------|-----------|-----------|
| | <u>Hg</u> | <u>Zn</u> | <u>Cd</u> | <u>Pb</u> | <u>Pd</u> | | | | |
| H | 14* 15* | | | 10* | | | 13* | | |
| <u>o</u> -Ethyl | 12 | 18 | 17 | 19 | 8 | | 6 | 9 | |
| <u>p</u> -Ethyl | 30 | 31 | 33 | 32 | 59 | | | | |
| <u>o</u> -Methoxy | | 3 | 4 | 7 | 16 | 5 | | 11 | |
| <u>m</u> -Methoxy | 45 | 52 | | 53 | 51 | | | | |
| <u>p</u> -Methoxy | 44 | 60 | | 61 | 50 | | | | |
| <u>o</u> -Trifluoromethyl | 24 | 25 | 29 | 27 | 28 | | | | |
| <u>o</u> -Chloro | 20 | 22 | 21 | 23 | 26 | | | | |
| <u>m</u> -Chloro | 40 | 39 | 43 | 42 | 41 | | | | |
| <u>p</u> -Chloro | 35 | 34 | 37 | 36 | 38 | | | | |
| <u>o</u> -Fluoro | 46 | 47 | | 48 | 49 | | | | |
| <u>m</u> -Fluoro | 54 | 56 | | 58 | 62 | | | | |
| <u>p</u> -Fluoro | 55 | 57 | | 64 | 63 | | | | |

*10 Triphenyllead 1,5-diphenylthiocarbazonate

*13 Phenylbismuth bis(1,5-diphenylthiocarbazonate)

*14 p-Aminophenylmercury 1,5-diphenylcarbazonate

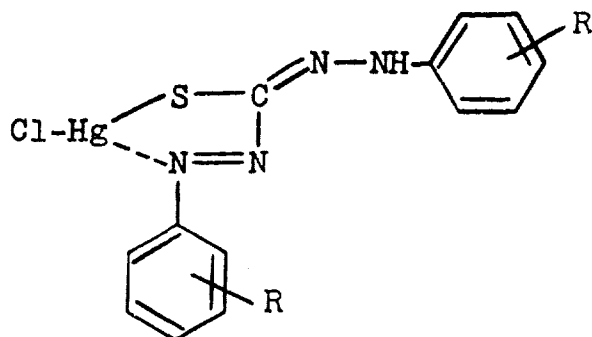
*15 p-[4,6-Dichloro-s-triazin-2-yl]amino7phenylmercury 1,5-diphenylthiocarbazonate

1 1,5-Di(o-methoxyphenyl)thiocarbazone

2 1,5-Di(o-ethylphenyl)thiocarbazone

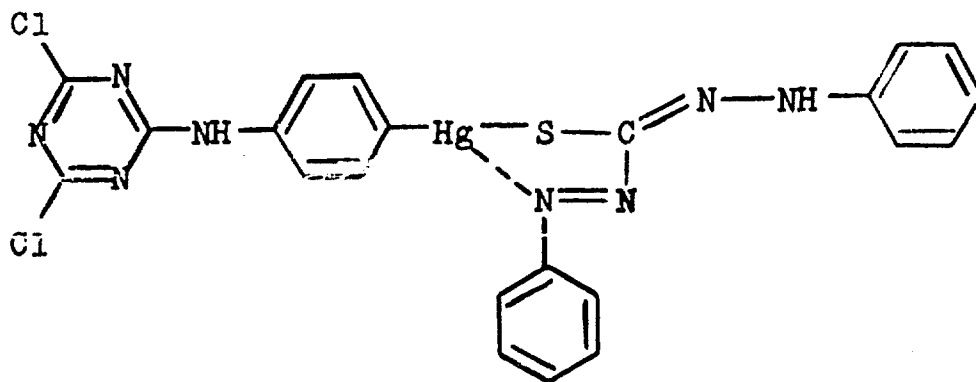
65 1,5-Diphenylcarbazone

Note: These compound numbers (1-65) are those given on the data sheets.



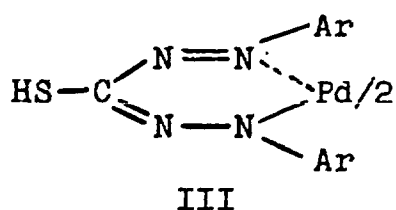
I

Difficulties in purification were encountered with derivatives of ligands containing halogen substituents and with lead and cadmium compounds. These resulted from insolubility and a tendency to decompose when purification was attempted using high boiling solvents. A few of the derivatives formed molecular compounds with solvents. A model fiber reactive compound (II) (Compound 15) was prepared by treating *p*-amino-phenylmercurydithizonate (Compound 14) with cyanuric chloride in the presence of sodium bicarbonate.

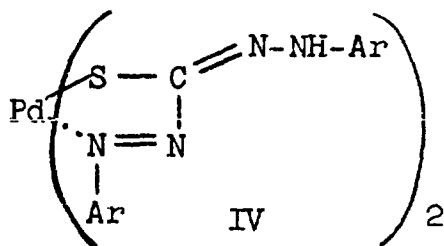


II

Since the palladium dithizonates have spectral and photochromic properties different from those of the mercury class of compounds, it was thought that these changes might be due to a different type of chelation, i.e., III instead of IV. If III is a possible form, 3-methylthio-1,5-diphenyl-



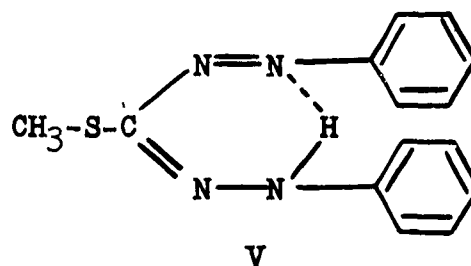
III



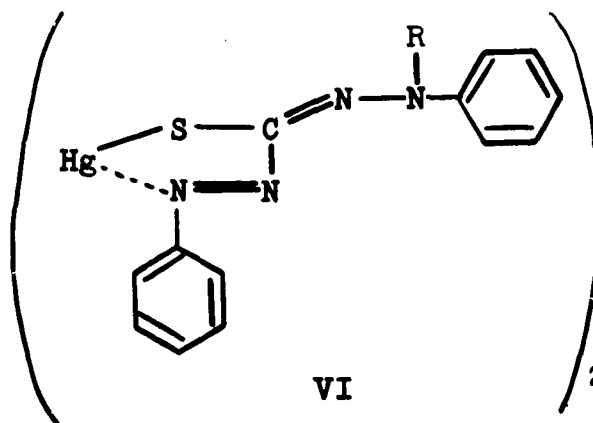
IV

formazan (V) should form a palladium derivative similar to III under the conditions for the preparation of the palladium

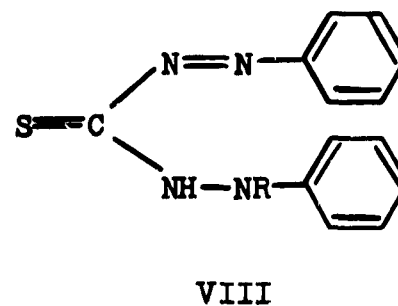
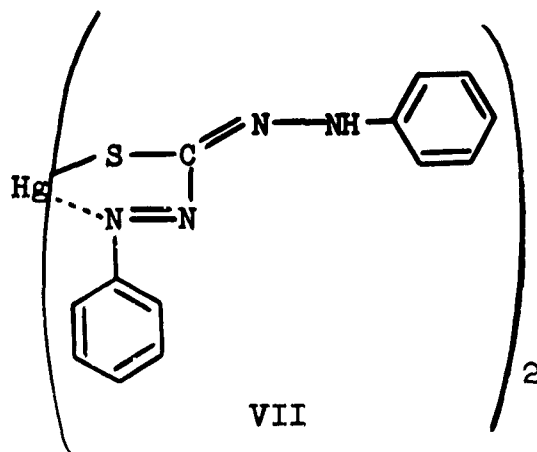
dithizonates. The only material isolated from such an attempt was an orange powder which charred, but did not melt and had a very poor analysis with high palladium content. Similar results are reported by Irving and Bell².



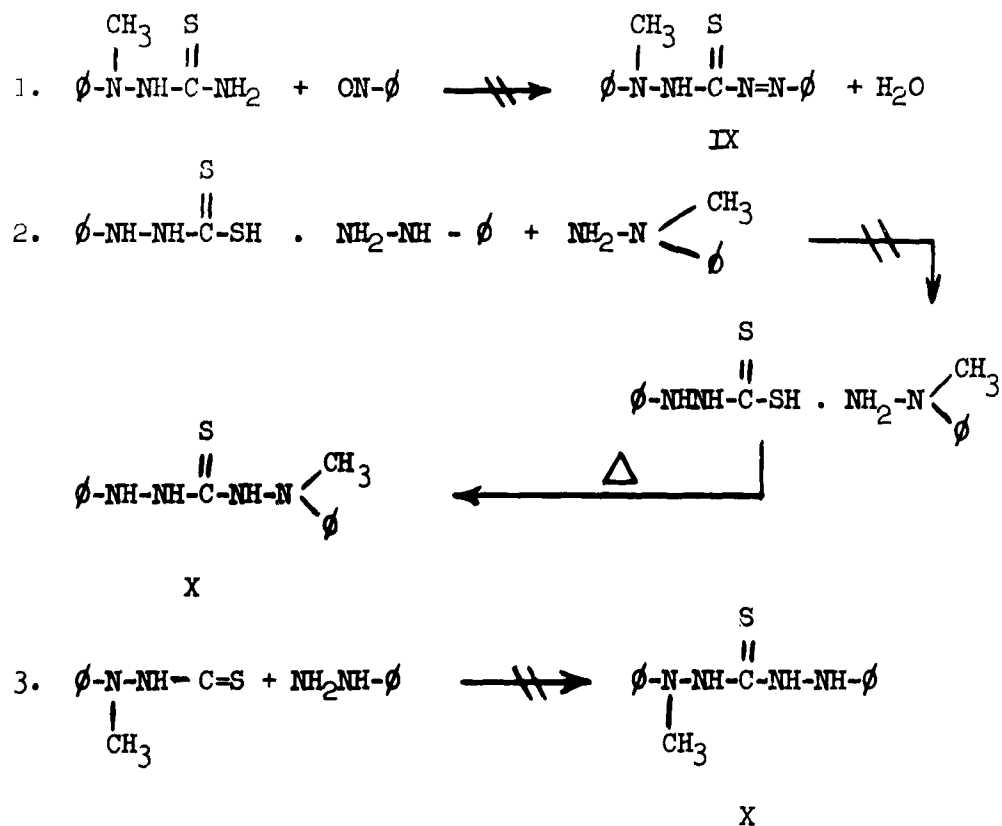
Another compound which would be of theoretical interest with regard to the photochromic mechanism of the metal dithizonates would be a dithizonate without a proton on nitrogen (VI). Unfortunately, such a compound has eluded preparation, although



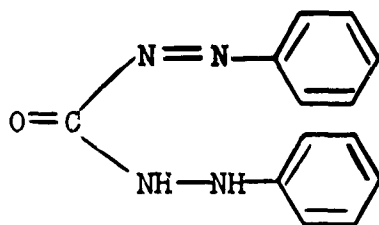
several methods have been tried both here and in a company-sponsored program which was not connected with the contract. These procedures can be grouped into two general classes: Attempts to acetylate or methylate mercury bis(dithizonate) (VII) or attempts to prepare the ligand (VIII).



Attempts to acetylate the derivative resulted either in no reaction or in the formation of amorphous, insoluble solids which charred and did not melt. Methylation led to the formation of 3-methylthio-1,5-diphenylformazan (V). Unsuccessful procedures for the preparation of the ligand have included (a) the reaction of *N,N*-methylphenylthiosemicarbazide with nitrosobenzene (Eq. 1); (b) an exchange reaction between the phenylhydrazine salt of β -phenyldithiocarbamic acid and phenylmethylhydrazine (Eq. 2) to form the unsymmetrical compound, followed by conversion of this material to the unsymmetrical thiocarbazine (X) with oxidation of the latter to the thiocarbazonone (IX); and (c) reaction between *N*-isothiocyano-*N*-methylaniline and phenylhydrazine (Eq. 3) to give the thiocarbazine (X). The mercury derivative of the ligand produced in this reaction was shown to be mercury bis(dithizonate). However, since this compound is a minor product of the reaction, further work on the procedure is warranted.

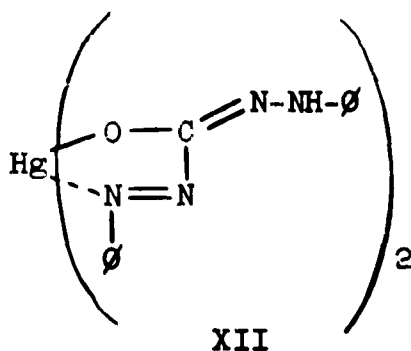


A limited amount of work has been carried out on diphenylcarbazonone (XI) and its derivatives.

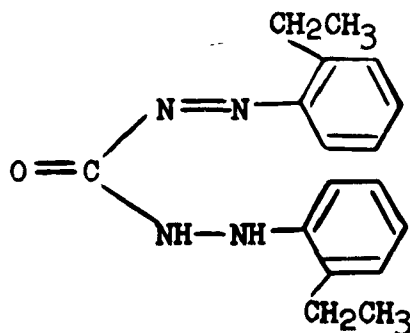


XI

Diphenylcarbazone was prepared and an attempt was made to synthesize its mercury derivative (XII). The resulting **purple** solid had a very poor analysis for compound XII. A study of the analysis indicates that the product is a mixture of mercury chelates in which both protons on the ligand have been replaced. This result is in accord with the work of Balt and Van Dalen³. The preparation of the di-ortho-ethyl derivative of diphenylcarbazone (XIII) is almost complete, with the purification of the compound remaining to complete the synthesis.

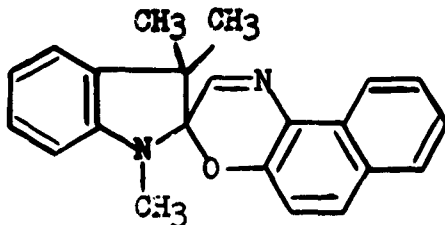


XII



XIII

The preparation of compound XIV, a modified spiropyran, is still under investigation, since the reaction of 1,3,3-trimethylindoline and 1-nitroso-2-naphthol gave a complex mixture, the components of which have not been characterized.



XIV

C. Experimental

Except for the ligands reported in this paper, all others were prepared in a company-sponsored program which was not connected with the contract (the ligands were prepared by the procedure of Hubbard and Scott⁴ with modifications). Physical data on the compounds prepared will be found on data sheets at the end of the report.

Homogeneous Solvent System for the Preparation of Dithizonate Derivatives (Procedure 1)

The dithizone (diphenylthiocarbazon) (1 or 2 g.) was dissolved in 100 ml. of refluxing tetrahydrofuran, and a solution of the metal salt in 20 ml. of water was added. The solution was refluxed 5-15 minutes and solid sodium bicarbonate was added in cases where the color indicated that the reaction was not proceeding to conclusion. The resulting mixture was drowned in 200-800 ml. of water and the solid isolated by filtration. In cases where an oil was formed, it was extracted into methylene chloride, the solution was dried and the solvent was removed by evaporation. The product was purified by chromatography and/or crystallization.

Two-Phase System for the Preparation of Dithizonates (Procedure 2)

The metal salt was suspended or dissolved in a mixture of 100 ml. of methylene chloride or benzene and 100 ml. of a hydrochloric acid, phosphate buffer (pH 7) or sodium bicarbonate solution; the dithizone was added in portions (or all at once in the case of slowly reacting systems). The organic layer was separated from the aqueous solution and washed with ammonium hydroxide and water. Drying followed by evaporation of the solvent gave a residue which was purified by crystallization or chromatography. In cases where a solid was formed during the reaction, giving a three-phase system, the solvent was evaporated from the mixture and the product was isolated by filtration and purified by crystallization.

Preparation of Fiber Reactive Compound 14 (II) (Procedure 3)

The p-aminophenylmercurydithizonate (Compound 14) was dissolved in a 9-1 mixture of acetone and water and two equivalents of sodium bicarbonate and one equivalent of cyanuric chloride were added. The resulting solution was stirred at ice bath temperature for 15 minutes and drowned in ice water. Filtration and crystallization from acetone gave the pure product as orange-red plates.

Preparation and Purification of Diphenylcarbazon (XI) (Compound 65) (Procedure 4)

Diphenylcarbazon was prepared from commercial diphenylcarbazonide by air oxidation in the presence of potassium hydroxide. The product was purified by the procedure of Da Silva, Calado and De Moura⁵.

Preparation of 1,5-Di-o-ethylphenylcarbazon (XIII)

1,5-Di-o-ethylphenyl-3-nitroformazan, prepared by the procedure of Tarbell et al.⁶, m.p. 105.5-106.5^t, was converted to 5-hydroxy-2,3-bis(o-ethylphenyl)tetrazolium betaine (explosion

point 159°) by a modification of a procedure reported by Dubenko and Pelkis⁷. The betaine was reduced with ammonium hydrosulfide to the corresponding carbazide, m.p. 152-153°, and the latter was oxidized to the carbazone with air using potassium hydroxide in methanol. Purification of this compound is not complete.

Attempted Preparation of Mercury Bis(1,5-diphenylcarbazonate)
(XII)

Mercuric acetate was allowed to react with diphenylcarbazone according to Procedure 2 to give a bronze-purple solid, m.p. 159-160° (chloroform-methanol).

Analysis: Calc'd for $C_{26}H_{22}N_8O_2Hg$: C 45.9; H, 3.17; N, 16.5;
Hg, 29.5.

Found: C, 27.2; H, 1.91; N, 9.6;
Hg, 57.2.

Reaction of 3-Methylthio-1,5-diphenyl Formazan (V) with
Palladium Chloride

The reaction was carried out using the same procedure (C) utilized for the preparation of the palladium dithizonates. The product isolated was an insoluble orange solid which charred above 280° but did not melt.

Analysis: Calc'd For $C_{28}H_{26}N_8S_2Pd$: C, 52.1; H, 4.06; N, 17.4;
S, 9.9; Pd, 16.5.

Found: C, 37.6; H, 3.46; N, 12.5;
S, 8.1; Pd, 25.4.

Attempted Preparations of Mercury Bis(1-methyl-1,5-diphenyl-
thiocarbazonate) (VI, R=CH₃)

(A) Treatment of mercury bis(dithizonate) with methyl iodide in the presence of sodium hydroxide gave a black solid which when purified by chromatography gave as the only isolable product 3-methylthio-1,5-diphenylformazan, m.p. 128-129° (mixed melting point with an authentic sample gave no depression). Thin layer chromatography indicated the product gave the same R_f value as the authentic material.

(B) N-Isothiocyano-N-methylaniline was prepared from phenylmethylhydrazine and thiophosgene by a modification of the method of Beckett and Dyson⁸. The oil was treated with phenylhydrazine in ethanol to give, after a complicated workup, a small quantity of a thiocarbazone. Mercuric chloride treatment of the thiocarbazone from several reactions gave a red solid which when crystallized from n-butyl alcohol melted with charring at 192-194°. Comparison of the infrared spectrum of the solid with that of authentic mercury bis(dithizonate) indicated that it was predominantly composed of the latter material.

Attempted Preparations of Mercury Bis(1-acetyl-1,5diphenyl-thiocarbazonate) (VI, R=COCH₃)

(A) Mercury bis(dithizonate) in acetic anhydride was refluxed in the presence of a small quantity of aluminum chloride. Thin layer chromatography and the melting point and mixed melting point indicated that the product was starting material.

(B) Mercury bis(dithizonate) in pyridine was treated with acetyl chloride. A yellow precipitate formed which was insoluble in organic solvents and did not melt below 300° (charred above that temperature).

III. EVALUATION

A. Introduction

In order to determine if the specific objectives of the synthetic program (listed in Section I) were being accomplished, it was necessary to develop a standardized evaluation procedure which would yield unambiguous results permitting conclusions to be drawn and providing guidance for the synthetic effort.

B. Experimental

1. Solution Studies

Photochromic systems are frequently characterized by spectral and kinetic behavior which is critically dependent upon environmental conditions⁹. The thermal return of the present metal dithizonate system was known to be very dependent upon the proton transfer ability of the medium¹⁰. Because of this, and particularly since the dithizonates of all metals except mercury were known to have very fast thermal returns, rate and conversion measurements were carried out in solvent which was dried to remove water.

Methylene chloride was chosen as a general evaluation solvent because of the following advantages which it has over the other solvents considered:

1. Easy to obtain in pure form.
2. Good solvent for organic compounds.
3. Low freezing point (-96.7°C.) which facilitates low temperature studies.
4. Good transmittance to allow spectral studies from 240-900 m μ .

Three grades of CH_2Cl_2 were used:

Matheson Coleman and Bell No. 5509
Matheson Coleman and Bell Spectral Grade (No. SG-5509)
Mallinckrodt Analytical Reagent Grade

The CH_2Cl_2 was dried by passage through a column of Linde 3A molecular sieves. This "dry" CH_2Cl_2 was stored (over fresh 3A sieves) in an automatic burette. Karl Fischer titration of this "dry" CH_2Cl_2 indicated that the water content was reduced to approximately 10 p.p.m. H_2O as claimed in the Linde literature¹¹.

Considerable experimental difficulty was encountered in obtaining reproducible thermal return measurements in this CH_2Cl_2 . Different batches of dried CH_2Cl_2 showed large variations and each batch showed variations with age. Return rate measurements on mercury bisdithizonate were used to standardize each dried batch of CH_2Cl_2 . These measurements varied from a room temperature half life of 50-60 minutes for "dry" material to two to three minutes for material which had apparently picked up water (or acids or bases). Contamination of some of the batches of CH_2Cl_2 by substances other than water seems likely, since once the CH_2Cl_2 gave "dry" performance, it was quite stable toward contamination by atmospheric water. Considerable care was necessary regarding glassware and spectrophotometric cells during handling of this CH_2Cl_2 .

For the standard evaluation procedure, 1-2 mg. of each dried, purified metal dithizonate sample was weighed out on a micro balance and dissolved in 25 ml. of the CH_2Cl_2 . Appropriate dilutions were made in 10-ml. volumetric flasks and spectra of unirradiated and irradiated solutions were run on the Cary 14 recording spectrophotometer in 1-cm. silica cells. Unirradiated spectra (stable forms) were recorded from 240 $m\mu$ (ultraviolet cutoff of CH_2Cl_2) to 740 $m\mu$ (instrument limitation). For irradiated spectra, the near infrared recording method of the Cary 14 was used. With this method, the full intensity of a strong tungsten lamp (a 108-watt CPR projection lamp, General Electric Company) is directed on the sample*. The intensity of this lamp at 490 $m\mu$ is approximately 15 times that of full sunlight; therefore, the conversions obtained with this lamp are higher than those obtainable in sunlight. True percent conversions can be calculated only if the spectra of the pure

*An infrared absorbing KG-3 filter (Fish Schurman Corporation, New Rochelle, N. Y.) was placed between the lamp and sample to eliminate heating effects.

A and B forms are known. At room temperature only methylmercury dithizonate (Figure 1) and the palladium dithizonates (e.g., Figure 5) can be converted to pure B. The percent conversions for all of the mercury type complexes were calculated (e.g., from Figure 4 for compound 3) assuming that the molar absorptivity of the B form (at $\lambda_{max.}$) was one-half that of the A form (at $\lambda_{max.}$), since this relationship was found for methylmercury dithizonate. Since the A form showed no absorption at the $\lambda_{max.}$ of the B form, and since the initial absorbance at $\lambda_{max.}$ of the A form corresponded to the total amount of complex, the percent conversions (for the mercury type) were calculated from:

$$\% \text{ Conversion} = \frac{\text{Abs (p.e.)}_B}{\text{Abs (int.)}_A} \times 200$$

where: Abs (p.e.)_B = absorbance at photo equilibrium at $\lambda_{max.}$ of the B form

Abs (int.)_A = initial absorbance (dark) at the $\lambda_{max.}$ of the A form

Thermal return half lives were measured by turning the samples over with the intense Cary source, then monitoring absorbance at a particular wavelength as a function of time, using only the weak monochromatic light beam ordinarily used in the Cary for measuring spectra in the visible region.

Plots of thermal return data rarely indicated true first order kinetics. The first order plots (log percent B remaining versus time) were usually convex toward the time axis, so that calculated $t_{1/2}$ values (for the very slow mercury compounds) are smaller than the experimental $t_{1/2}$'s. No detailed studies of concentration effects were carried out, but the $t_{1/2}$ value would undoubtedly depend on concentration.

2. Film Studies

Approximately 5 mg. of sample were dissolved in a solution of 5 g. of Tenite [®] cellulose acetate (Eastman) in 25 cc. of acetone. Films were cast on metal plates using a 25-mil drawdown bar. The final film thickness was approximately 2 to 3 mils.

Some samples were insoluble in this mixture even after standing overnight with the addition of 2.5 cc. of tetrahydrofuran. When this occurred, the compounds were not evaluated further. Such insolubility is noted on the data sheets.

The procedures for measurement of spectra and return rates were the same as used with solutions. All spectra were corrected for absorption and scattering by the film using the absorbance at 700 m μ where the complexes did not absorb.

Light fastness was evaluated by exposing a portion of the cast film in a holder behind a UV screen on a south window and measuring the percent remaining at various time intervals. The test was not designed to be highly accurate, but to show a measure of light fastness versus mercury bis-(dithizonate) which was included as a standard in all exposure data. Plots of log percent remaining versus sun-hours exposed were quite straight, indicating a first order reaction.

Light fastness is reported on the data sheets as sun-hours to 50% fade. Mercury bis(dithizonate) had an average value of 42 hours or five eight-hour sun-days.

C. Results and Discussion

For comparison purposes, reference data for some unsubstituted metal dithizonates* are listed in Table II.

Table II

Photochromic Properties of Unsubstituted Metal Dithizonates in "Dry" Methylene Chloride at Room Temperature

| <u>Compound</u> | <u>Visible Spectrum (Stable Form)</u> | | <u>Estimated % Conversion in Cary 14</u> | <u>Thermal Return Half Life</u> |
|------------------------|--|------------------------------|--|---------------------------------|
| | <u>$\lambda_{max.}$ (mμ)</u> | <u>ϵ</u> | | |
| CH ₃ HgDz** | 470 | 31,500 | 100 | 50 min. |
| HgDz ₂ | 485 | 63,700 | 84 | 61 min. |
| ZnDz ₂ | 525 | ca. 90,000 | 60 | 8 sec. |
| CdDz ₂ | 515 | ca. 85,000 | 28 | Very fast |
| PbDz ₂ | 510 | 59,000 | 26 | Very fast |
| BiDz ₃ | 490 | 72,400 | 32 | Very fast |
| AgDz·H ₂ O | 460 | 30,900 | 50 | 36 sec. |
| PdDz ₂ | 445 | 35,300 | 100 | 19 sec. |
| | 635 | 31,800 | | |
| PtDz ₂ | 420 sh | 19,700 | 10 | Very fast |
| | 485 | 28,400 | | |
| | 720 | 23,600 | | |

*Compounds synthesized under previous Cyanamid sponsored research.

**Dz = C₁₃H₁₁N₄S

Brief examination of the data in Table II shows how unique Hg^{+2} is in conferring high conversion and slow thermal return rates to this photochromic system. The effects which the synthetic modifications had upon the properties of the metal dithizonate systems are presented below.

1. Spectra

a. Mercury Type

On the basis of electronic spectra, the photochromic metal dithizonates of Hg^{+2} , Zn^{+2} , Cd^{+2} , Bi^{+3} and Ag^{+} are all very similar. The essential features of these spectra (stable forms) are: (see Figures 1, 2, 3, 4, 6, 7, 8 and 9)

1. A single benzenoid absorption band at 260-290 $m\mu$ ($\epsilon = 5,000$ to $10,000$ per phenyl ring)
2. A weak shoulder in the 300-400 $m\mu$ region.
3. A broad (half-band width $>100 m\mu$) intense band ($\epsilon = 20,000$ - $50,000$ per dithizone ligand) appearing at 445-560 $m\mu$, depending upon the metal and the substituents in the phenyl rings.

Upon exposure to light which is absorbed in either the ultraviolet or visible absorption bands, the visible band shifts to longer wavelength (+100 to 165 $m\mu$) and, when 100% converted, absorbs with an intensity roughly one-half that of the stable form. The benzenoid band in the ultraviolet shows much smaller changes, usually shifting to longer wavelengths and absorbing more strongly in the metastable forms.

The substitution of groups in the ortho, meta and para positions of the phenyl rings in dithizone produced changes in location and intensity of the various bands (i.e., λ_{max} and ϵ_{max}), but the basic features of the spectra remained the same.

Four different chemical types of substituents were studied: alkyl, fluoroalkyl, alkoxy and halogen (see Table I). The complete range of ortho, meta and para substitution was studied with methoxy, chloro and fluoro groups. The effects which the various groups had on the spectral properties of the mercury type complexes can be seen from examination of the data in Table III. This table lists λ_{max} and ϵ_{max} values for the broad visible band (stable forms) of the various substituted bis complexes of mercury and zinc. Similar effects were observed for the other mercury type metals.

Table III

Effect of Phenyl Substituents on the Spectral
Properties of Mercury and Zinc Bisdithizonates in
"Dry" Methylene Chloride at Room Temperature

| <u>Substituent</u> | Mercury | | Zinc | |
|---------------------------|------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|
| | <u>$\lambda_{max.}$</u> | <u>$\epsilon_{max.}$</u> | <u>$\lambda_{max.}$</u> | <u>$\epsilon_{max.}$</u> |
| H | 485 | 63,700 | 525 | ca. 90,000 |
| <u>o</u> -Chloro | 485 | 49,000 | 530 | 75,000 |
| <u>o</u> -Ethyl | 475 | 44,100 | 515 | 77,200 |
| <u>o</u> -Fluoro | 485 | 52,800 | 527 | 84,100 |
| <u>o</u> -Methoxy | 510 | 46,100* | 558 | 95,100 |
| <u>o</u> -Trifluoromethyl | 445 | 53,000 | 500 | 72,500 |
| <u>m</u> -Chloro | 485 | 60,900 | 530 | 89,300 |
| <u>m</u> -Fluoro | 485 | 63,200 | 528 | 89,800 |
| <u>m</u> -Methoxy | 490 | 64,200 | 532 | 88,100 |
| <u>p</u> -Chloro | 495 | ** | 540 | 97,800 |
| <u>p</u> -Ethyl | 498 | 70,700 | 540 | 94,900 |
| <u>p</u> -Fluoro | 485 | 56,800 | 525 | 87,100 |
| <u>p</u> -Methoxy | 510 | 72,000 | 545 | 93,000 |

*Unanalyzed sample synthesized under previous Cyanamid sponsored research.

**Sample too insoluble in CH_2Cl_2 .

From the data in Table III, it is apparent that meta substituents have very little effect on the $\lambda_{max.}$ or $\epsilon_{max.}$ values of the complexes. In the para position, ethyl, chloro and methoxy groups caused small shifts toward longer wavelengths and small intensity increases. Para fluoro groups had essentially no effect.

The largest spectral changes were produced by ortho substituents. These groups generally decreased the intensity of absorption ($\epsilon_{max.}$). Chloro and fluoro groups had no effect on $\lambda_{max.}$ but ortho-ethyl and ortho-trifluoromethyl groups caused blue shifts, the latter being a particularly large 40 m μ shift (see Figure 3). Ortho-methoxy groups caused large red shifts with a small intensity increase (for zinc, see Figure 4).

The intensity decreases caused by most of the ortho groups are probably due to a steric inhibition of resonance effect whereby the phenyl rings of the complex are forced into a noncoplanar arrangement. This effect might also account for the blue shifts caused by ortho-ethyl and ortho-trifluoromethyl groups. With methoxy groups, resonance effects apparently predominate.

b. Palladium Type

In the case of palladium and platinum, the spectra of the stable forms (see Figures 5 and 10) consist of:

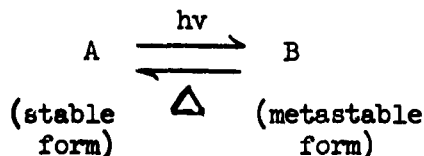
1. Benzenoid absorption at 260-390 $m\mu$ similar in intensity to that of the other metals, but comprised of more than one band.
2. Two or more bands in the visible appearing around 450 and 620 $m\mu$ ($\epsilon \cong 15,000$ per dithizone ligand).

Upon exposure to light, absorption in the ultraviolet band or in either of the two visible bands produces small changes in the ultraviolet band, while the short wavelength (+35 $m\mu$) with little change in intensity and the long wavelength visible peak shifts into the near infrared (750-850 $m\mu$) with a decrease in intensity.

The effects of substituents on the spectra of the palladium complexes were somewhat similar to those shown by the mercury type complexes. One notable exception was the ortho-trifluoromethyl group which produced a much smaller blue shift in the palladium spectrum. In general, the long wavelength peak in the spectrum of the palladium complexes was quite insensitive to the substituents.

2. Photochromism (Conversion and Return Rates)

Since the metal dithizonate system appears to conform to the simple model:



an adequate characterization of the photochromic properties is provided from determination of:

- a. The position of the photostationary conversion at a given light intensity, specified in this report as percent conversion from A to B.
- b. The thermal (dark) return rate ($B \rightarrow A$), specified in this report as the experimentally measured half life (or calculated half life assuming first order kinetics).

The data sheets (1-65) list measurements of these two photochromic properties for most of the synthesized substituted metal dithizonates. Because of the experimental difficulties involved in reproducibly measuring conversions and return rates (see Experimental), it is not possible to interpret these values rigorously; however, the following features are significant:

1. Mercury compounds consistently provide high conversions and slow thermal return rates.

2. In the mercury family, zinc seems to provide the closest approach to the mercury properties, while Cd^{+2} , Pb^{+2} , Bi^{+3} and Ag^{+} were consistently poor (i.e., fast return rates and low conversions).

3. The various substituents in the phenyl rings did not appear to exert a large influence on the conversions and return rates of the complexes. Ortho-methoxy groups did seem to cause decreases in return rate, but these changes were small compared to the difference in properties between mercury and the other metals.

4. Palladium compounds consistently showed high conversions and fairly fast return rates ($t_{1/2} < 1$ min.). Here also, substituents did not cause large changes in photochromism.

3. Stability Studies

a. Light Fastness

All compounds were examined for light fastness in solution-cast cellulose acetate films (see Experimental). In these films, the photochromic properties of all the compounds were reduced (i.e., lower conversions, faster return rates) compared to "dry" CH_2Cl_2 , since there was moisture in the films.

Some compounds were observed to be light unstable during evaluation of photochromic properties in the "dry" CH_2Cl_2 . In the case of compounds 6 (Figure 9), 10 (Figure 7) and 13 (Figure 8), irradiation in the Cary 14 caused some decomposition, indicated by lack of complete return to the stable form.

The light fastness results in cellulose acetate film do not show any systematic correlation with the type of substituent or its position. The limited solubility of some mercury and palladium dithizonates prevented obtaining as complete a series as desired with these compounds.

Table IV gives the available data on light fastness expressed as sun hours to 50% fade. Neither the bismuth nor silver dithizonates are included in the table since only a limited number were made. In addition, their light fastness was relatively poor.

Table IV

Light Fastness of Metal Dithizonates in Cellulose
Acetate Film (Sun Hours to 50% Fade)

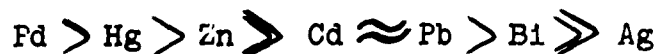
| Metal | Position | Substituent | | | | | |
|-----------|----------|-------------|-------|---------|-------------------|--------|--------|
| | | H | Ethyl | Methoxy | Tri-fluoro-methyl | Chloro | Fluoro |
| Mercury | ortho | 40 | 12 | 108 | 52 | * | * |
| | meta | 40 | - | 36 | - | 56 | NE |
| | para | 40 | 32 | 32 | - | * | NE |
| Zinc | ortho | | 8 | 36 | 24 | 20 | 24 |
| | meta | NE | - | 68 | - | 32 | NE |
| | para | | 56 | 44 | - | 32 | NE |
| Palladium | ortho | | 32 | >80 | >80 | >80 | NE |
| | meta | NE | - | * | - | * | NE |
| | para | | 48 | * | - | * | NE |
| Lead | ortho | | 4 | 20 | 32 | 28 | NE |
| | meta | NE | - | 16 | - | * | NE |
| | para | | 16 | 16 | - | * | NE |
| Cadmium | ortho | | 8 | 8 | 48 | * | NE |
| | meta | NE | - | - | - | NE | NE |
| | para | | 20 | - | - | * | NE |

- Compound not prepared.

* Compound too insoluble to evaluate.

NE - Not Evaluated.

In general, the metal dithizonates showed the following order of light stability with respect to metal:



With the one major exception of mercury bis-(o-methoxydithizonate), electron donating groups seemed to reduce the light stability of Hg, Cd and Pb complexes,

while electron withdrawing groups seemed to increase it. With the zinc complexes, the reverse was true. The reason for the exceptional light stability of the mercury bis-(o-methoxydithizonate) is not known at present.

b. Thermodynamic Stability

Some of the Pd compounds showed thermodynamic (dark) instability, particularly compounds 16 and 38. These changes were irreversible, indicating they were not merely partial conversion to the metastable forms.

4. Application Studies

a. Fiber Reactivity

This area was explored (for nylon only) by synthesis and evaluation of compounds 14 and 15. The dichlorotriazinyl group present in compound 15 is reactive toward hydroxyl and amino groups, and is used commercially for reactive dyes on cellulose.

Using compound 14 as the unreactive analog of 15, both were dyed on Spun Nylon 6 fabric and on samples of thermally resistant nylon received from Natick¹². Both compounds dyed easily from dispersion, 14 producing a red dyeing, while 15 was orange. Portions of each fabric were treated at the boil in:

1. Neutral soap solution
2. Dilute Na₂CO₃ solution (alkaline fixation)

All fabrics were then extracted with boiling propanol, a procedure used by Scott and Vickerstaff¹³ to show that Procinyl[®] dyes actually react with nylon. Estimations of percent dye remaining on the various fabrics were made from reflectance readings. Table V lists the fixation results on regular Nylon 6 fabric.

Table V

Fixation of Reactive Mercury Dithizonate on Nylon

| <u>Treatment</u> | <u>Relative % Compound 14</u> | <u>Relative % Compound 15</u> |
|---------------------------|-----------------------------------|-----------------------------------|
| Untreated, unextracted | 100 | 100 |
| Untreated, extracted | 26 | 61 |
| Soaped, extracted | 24 | 74 |
| Alkaline fixed, extracted | 20 | 69 |

[®] Registered trademark, Imperial Chemical Industries, Ltd.

The difference between these two sets of extraction values (14 vs. 15) is a good indication of reactivity of 15 toward nylon. Most of the fixation of 15 on the nylon appeared to occur during the neutral dyeing.

Reflectance measurements on the untreated, unextracted dyeing of 14 and the alkaline fixed, extracted dyeing of 15 showed the following photochromic properties (on regular Nylon 6 fabric):

Table VI

Photochromism of Reactive Mercury Dithizonate on Nylon

| <u>Compound</u> | <u>Estimated % Conversion in Full, Bright Sunlight</u> | <u>Thermal Return $t_{\frac{1}{2}}$</u> |
|-----------------|--|--|
| 14 | 15% | 9.4 min. |
| 15 | 36% | 5.4 min. |

The applications of 14 and 15 on thermally resistant nylon samples gave results quite similar to those found on regular Nylon 6 except that dyeings on the Ca-form fabric seemed to lead to precipitation at the fiber surface rather than solution in the fiber.

b. Disperse Dyeings

Some limited attempts were made to apply some of the nonmercury dithizonates to textile fabrics by disperse dyeing methods. Zinc dithizonates were successfully applied to give red shades on nylon, silk and wool, but these dyeings were not usefully photochromic.

Attempts to dye the very interesting palladium compounds on textile fibers were unsuccessful, apparently because of the lack of affinity for any of the fibers. It was possible to incorporate Pd compounds in solution-cast films (e.g., cellulose acetate, cyanoethylated cotton and acrylic polymers), but the photochromism in these polymer films was much less (i.e., conversions of about 20% and very rapid return rates) than that shown in "dry" CH_2Cl_2 .

IV. CONCLUSIONS AND RECOMMENDATIONS

The synthetic modifications of the metal dithizonate photochromic system described in this report brought about some large spectral shifts for the stable and metastable forms with the various r tals and some small increases in light fastness (e.g., ortho-methoxy and ortho-trifluoromethyl derivatives).

The photochromic properties—percent conversion and thermal return rate—were relatively insensitive to substitution in the phenyl rings. Any mechanism proposed to explain the photochromism of the metal dithizonate system must be compatible with this somewhat surprising result.

Of the mercury type complexes, mercury itself is by far the best metal for all-around performance. Only the zinc complexes approach the performance of mercury. The other mercury type metals, Cd^{+2} , Pb^{+2} , Bi^{+3} and Ag^{+} , are not satisfactory for one or more of the following reasons:

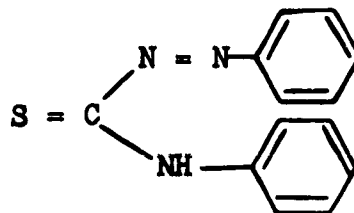
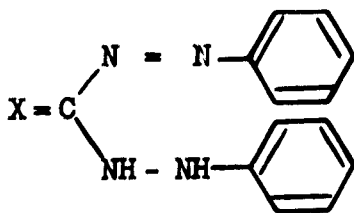
1. Very poor solubility
2. Poor photochromic properties
3. Poor light fastness

The palladium complexes exhibit very interesting properties in "dry" CH_2Cl_2 , but these properties are not presently obtainable in polymers. More application work will be necessary in this area.

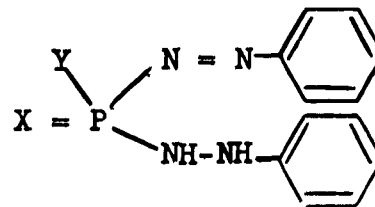
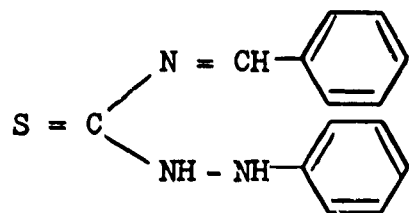
Fiber reactivity (toward nylon) has been achieved with a mercury dithizonate. The photochromic properties of the reacted mercury dithizonate appear to be unaffected by the covalent attachment to the fiber.

Since substitution in the phenyl rings of dithizone did not accomplish all of the specific objectives outlined in Section I, it is recommended that the synthetic effort during the second year of the present three-year contract be directed toward three areas: first, a more fundamental modification of the dithizonate system; second, a broader investigation of fiber reactivity; third, an intensified search for new photochromic systems. In order to show in a more specific manner the direction the work will take—in each of these areas, some examples of the systems to be studied are listed below.

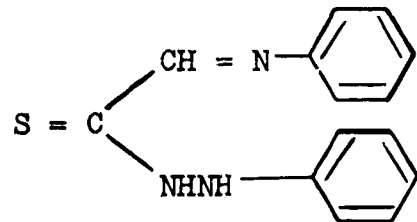
Modified dithizonate systems and their metal complexes: This, as indicated by the structures, involves the replacement of existing atoms or groups on the dithizone ligand with other atoms or groups.



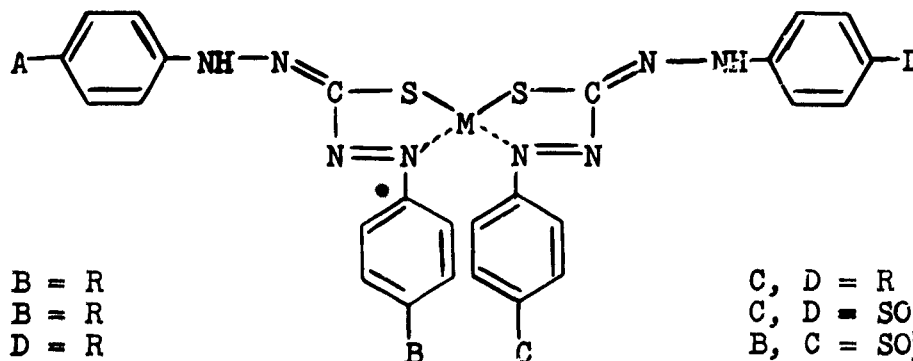
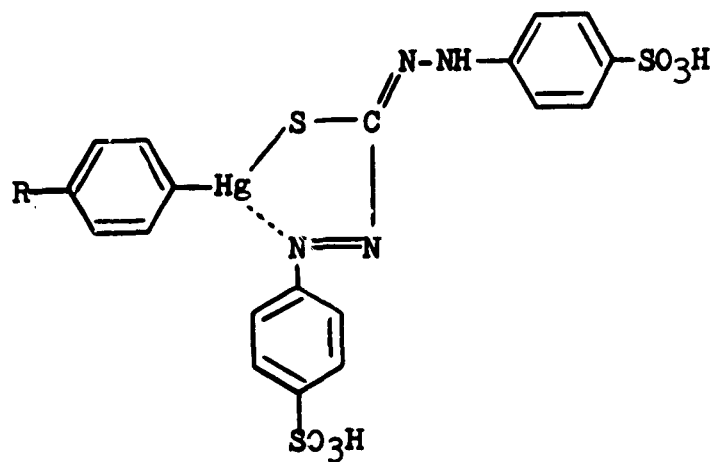
X = O, NR



X = S, O; Y = H, etc.



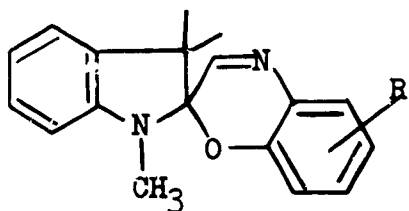
Fiber Reactivity: The continuation of fiber reactivity studies (including the preparation of water-soluble compounds) on the dithizonate system and the introduction of this property into any other promising systems found. Studies contemplated on the dithizonate system are summarized below. (R indicates fiber reactive group)



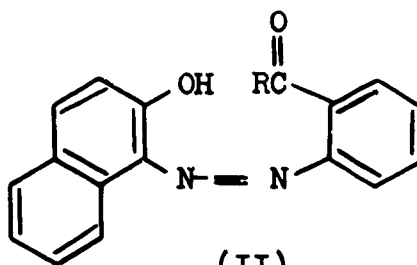
A, B = R
A, B = R
A, D = R

C, D = R
C, D = SO₃H
B, C = SO₃H

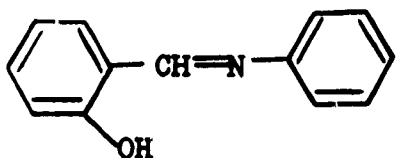
New Systems: This would include the study of modification of existing photochromic systems, other than the dithizonates, including pigment types, and studies into the preparation of entirely new systems. Examples would include modification of the spiropyran system (I) currently under investigation; the preparation of new potentially photochromic compounds such as (II); and the utilization of solid state photochromic systems such as anils (III) and nitrobenzylpyridines (IV) as pigments by direct formation on the fabric or by laking (precipitation of sulfonic acid derivatives with heavy metal salts).



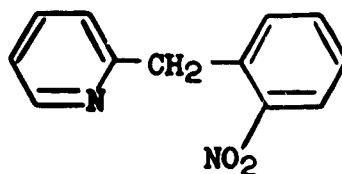
(I)



(II)



(III)



(IV)

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DATA SHEETS (Compounds 1-65)

The following data sheets summarize the experimental results obtained on the 65 compounds synthesized during the first year of the present three-year contract.

Infrared Spectra - The infrared spectrum for each compound is given at the top of the data sheet (except compounds 11 and 59, since these syntheses did not yield identifiable products). All of the spectra presented were obtained on Nujol mulls on the Perkin-Elmer Model 137 "Infracord" spectrophotometer.

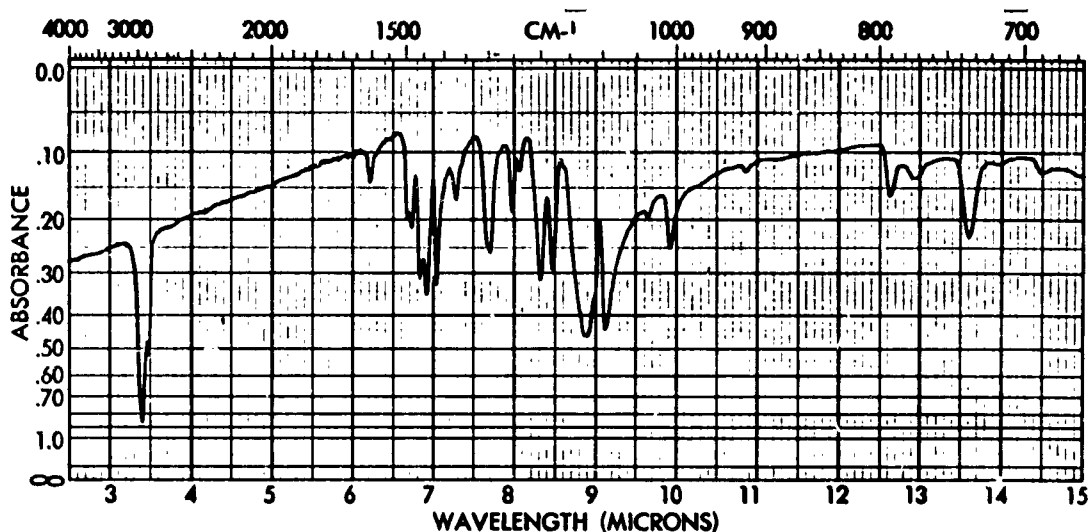
Synthesis - In the center of each data sheet are listed compound number, name, structural formula, molecular weight, melting point, appearance (of the solid), synthetic procedure (as described in Section II, pp. 3-10), % yield (not maximized, ligands varied in purity) and microanalytical data. In view of the complexity of the compounds, a maximum deviation of 0.5% was set as the general limit for an acceptable analysis. In a few cases where all of the elements except one deviated less than 0.3% from theory, the analysis was accepted even if that single element had a deviation of more than 0.5%. Any exceptions to this are noted on the data sheet.

Spectral Data - The ultraviolet-visible spectral data listed in the lower left of the data sheets were obtained on the Cary 14 spectrophotometer. The color specifications for the unirradiated and irradiated solutions are based on visual observation of the standard solution in CH_2Cl_2 as run on the Cary 14. These color specifications are quite subjective and will depend on concentration as well as conversion obtained with the light source used. The λ_{max} values are given in millimicrons. Shoulders on main absorption bands are indicated by (sh). The absorption intensity (at λ_{max}) is listed under ϵ , the molar absorptivity, this value having the units cm^{-1} (moles per liter) $^{-1}$.

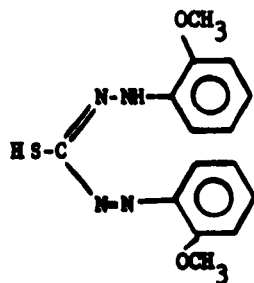
Photochromic Properties - The percent conversion values are in all cases (except for these compounds showing 100%) estimations assuming that the basic features of the spectra shown by the mercury and palladium complexes apply also to the other metal dithizonates. The conversion values listed are those obtained at room temperature during irradiation of an unstirred solution with visible light from the near-infrared source of the Cary 14. The thermal return half lives are taken from experimental measurements at room temperature from the % conversion listed to complete return to the stable form. In the case of the very slow mercury compounds, the half lives were extrapolated from first order rate plots.

Light Fastness - These results are based upon sunlight exposures of cellulose acetate films behind ultraviolet absorbing screens. The compound adopted as a standard, mercury bisdithizonate, required an average of 42 sun-hours to reach 50% fade.

Remarks - This section lists the solvent(s) used in the purification of the compound, the photochromic properties obtained in cellulose acetate film and observations of unusually poor solubility.



Compound No.: 1 Name: 1,5-Di(o-methoxyphenyl)thiocarbazono



Mol. Wt.: 316.38 M.P.: 174-175

Appearance: Green bronze needles

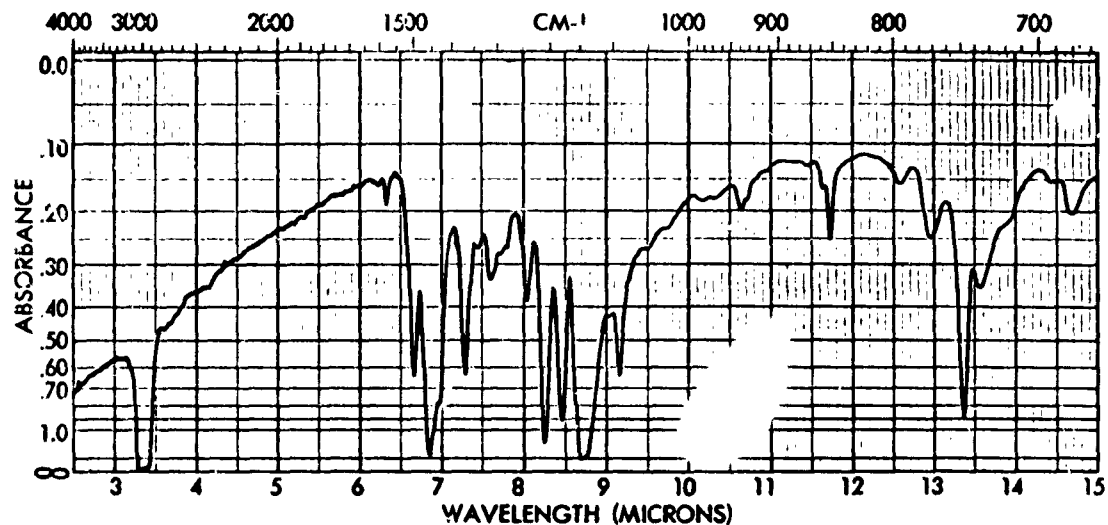
Synthetic Procedure: * % Yield: 56

Analysis: C H N S
 Found
 Calc.

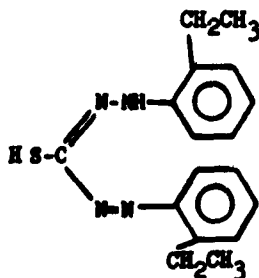
Spectral Data

| Color | λ Max. | ϵ | Thermal Return, Half Life: |
|--------------|----------------|------------|---|
| Unirradiated | 470 | 13,000 | % Conversion: (Cary 14 NIR Source) |
| | 640 | 54,400 | |
| Irradiated | | | Lightfastness in C.A. Film: 65 (Sun hours to 50% fade) |

Remarks: *Hubbard, D. M. and Scott, E. S.; J. Am. Chem. Soc. 65 2390 (1943).



Compound No.: 2 Name: 1,5-Di(o-ethylphenyl)thiocarbazono



Mol. Wt.: 312.36 M.P.: 141-141.5

Appearance: Bronze crystals

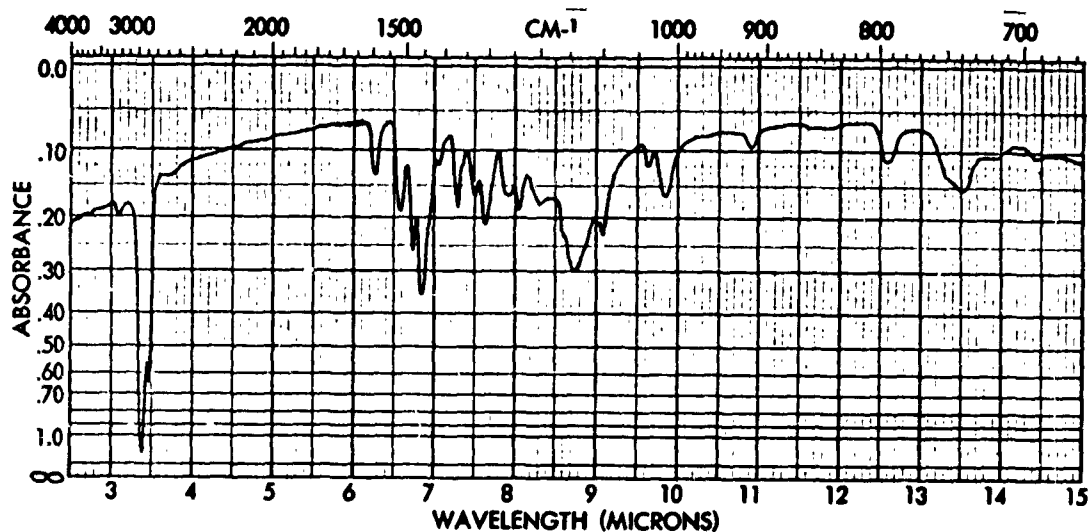
Synthetic Procedure: * % Yield: 61

Analysis: C H N S
Found
Calc.

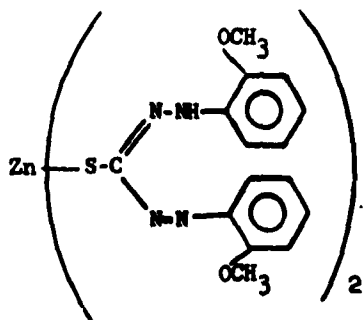
Spectral Data

| Color | λ_{Max} | Σ | Thermal Return, Half Life: |
|--------------|-----------------|----------|---|
| Unirradiated | 455 | 15,130 | % Conversion: (Cary 14 NIR Source) |
| | 620 | 46,100 | |
| Irradiated | | | Lightfastness in C.A. Film: 40 (Sun hours to 50% fade) |

Remarks: *Hubbard, D. M. and Scott, E. S.; J. Am. Chem. Soc. 65 2390 (1943).



Compound No.: 3 Name: Zinc bis[5-(4-methoxyphenyl)thiocarbazonate]



Mol. Wt.: 696.10 M.P.: 253-254 (d)

Appearance: Sparking maroon crystals.

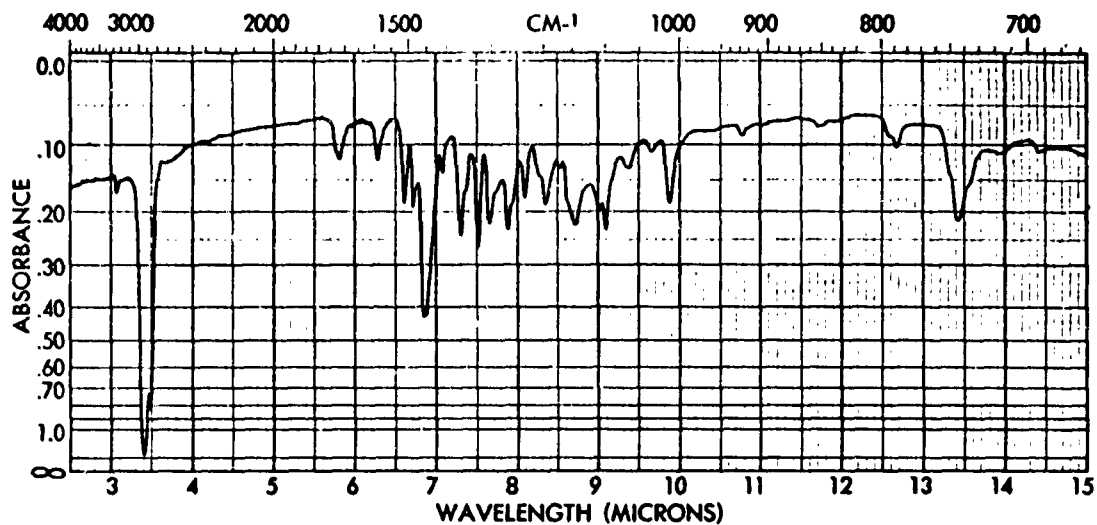
Synthetic Procedure: 1 % Yield: 70

| Analysis: | C | H | N | S | Zn |
|-----------|------|------|------|------|-------|
| Found | 51.6 | 4.33 | 15.6 | 8.95 | 10.12 |
| Calc. | 51.7 | 4.36 | 16.1 | 9.20 | 9.40 |

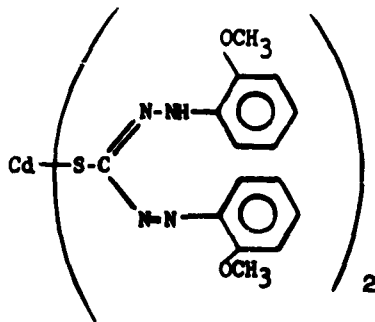
Spectral Data

| Color | λ_{Max} | ϵ | Thermal Return, Half Life: 44 sec. |
|--------------|-----------------|------------|------------------------------------|
| Unirradiated | | | % Conversion: 49 |
| Violet | 285 | 36,400 | (Cary 14 NIR Source) |
| | 390 (sh) | 12,870 | |
| | 558 | 95,100 | |
| Irradiated | | | Lightfastness in C.A. Film: 35 |
| Weak Violet | 720 | | (Sun hours to 50% fade) |

Remarks: Cellulose acetate film, % conversion 40-45%, thermal return, half life - ca. 20 sec. Purification solvent: chloroform-methanol.



Compound No.: 4 Name: Cadmium bis[1,5-di(o-methoxyphenyl)thiocarbazonate]



Mol. Wt.: 743.13 M.P.: 252-253

Appearance: Green iridescent crystals.

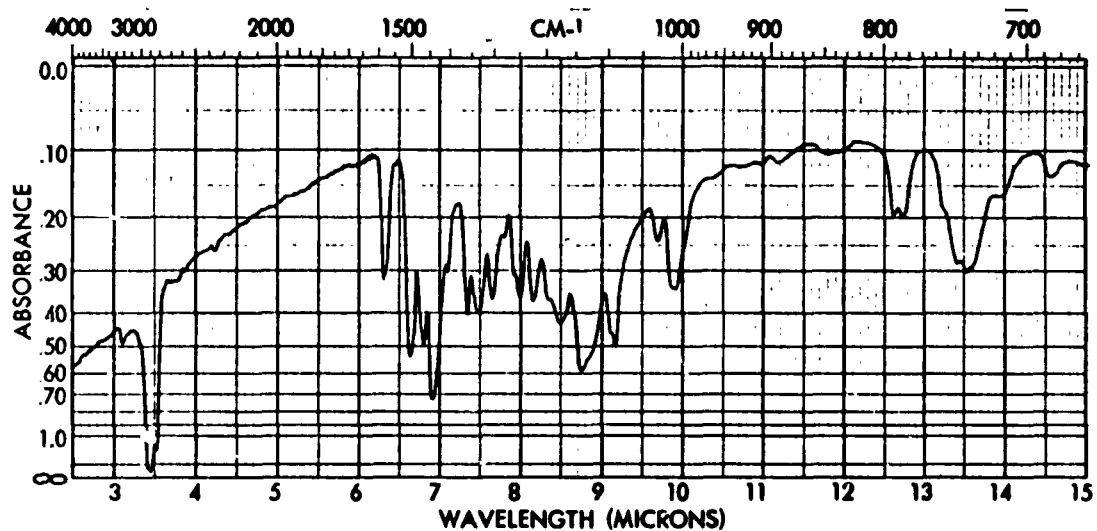
Synthetic Procedure: 1 % Yield: 96

| Analysis: | C | H | N | S | Cd |
|-----------|------|------|------|------|------|
| Found | 48.3 | 3.95 | 14.9 | 8.64 | 14.6 |
| Calc. | 48.5 | 4.07 | 15.1 | 8.63 | 15.1 |

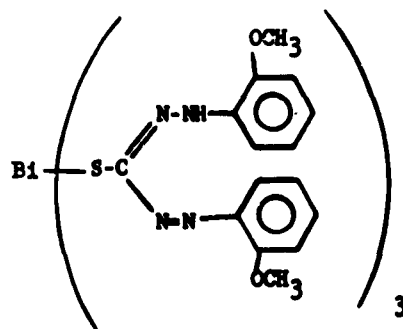
Spectral Data

| Color | λ_{Max} | ϵ | Thermal Return, Half Life: |
|---------------------|------------------------|------------|-------------------------------|
| Unirradiated Violet | 285 | 35,400 | 3.4 min. |
| | 375 (sh) | 10,500 | |
| | 550 | 83,900 | |
| Irradiated Blue | 710 | | % Conversion: 66 |
| | | | (Cary 14 NIR Source) |
| | | | Lightfastness in C.A. Film: 8 |
| | | | (Sun hours to 50% fade) |

Remarks: Cellulose acetate film - % conversion 30-35%, thermal return, half life - ca. 50 sec. Purification solvent: chloroform-methanol.



Compound No.: 5 Name: Bismuth tris[1,5-di(o-methoxyphenyl)thiocarbazonate]



Mol. Wt.: 155.09

M.P.: 206-1/2 -
207-1/2

Appearance: Brown iridescent crystals.

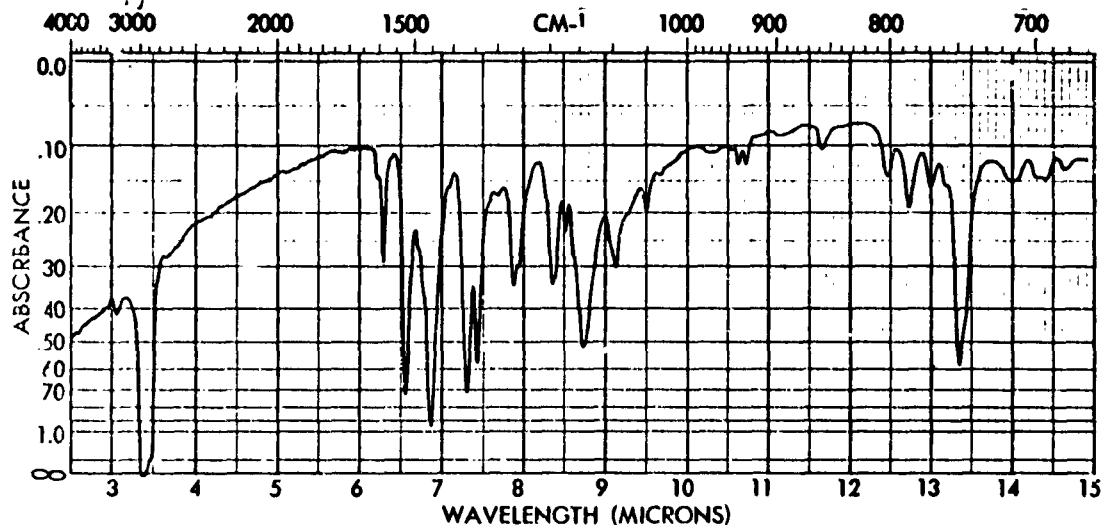
Synthetic Procedure: 1 % Yield: 60

| Analysis: | C | H | N | S | Bi |
|-----------|------|------|------|------|------|
| Found | 46.4 | 4.12 | 14.2 | 7.90 | 18.2 |
| Calc. | 46.8 | 3.93 | 14.6 | 8.34 | 18.1 |

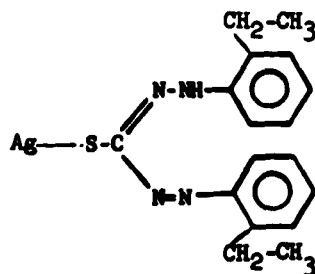
Spectral Data

| Color | λ Max. | ϵ | Thermal Return, Half Life: Less than 30 sec. |
|--------------|----------------|------------|--|
| Unirradiated | | | % Conversion: Low |
| Pink | 280 | 50,000 | (Cary 14 NIR Source) |
| | 520 | 77,200 | |
| | 640 (sh) | 13,800 | Lightfastness in C.A. Film: 26 |
| Irradiated | | | (Sun hours to 50% fade) |
| Bluish Pink | 640 | | |

Remarks: Cellulose acetate film - % conversion 20-25%, thermal return, half life - 4 min. 20 sec. Purification solvent: chloroform-methanol.



Compound No.: 6 Name: Silver [1,5-di(o-ethylphenyl)thiocarbazonate]



Mol. Wt.: 420.24 M.P.: 202-202-1/2 (d)

Appearance: Orange solid.

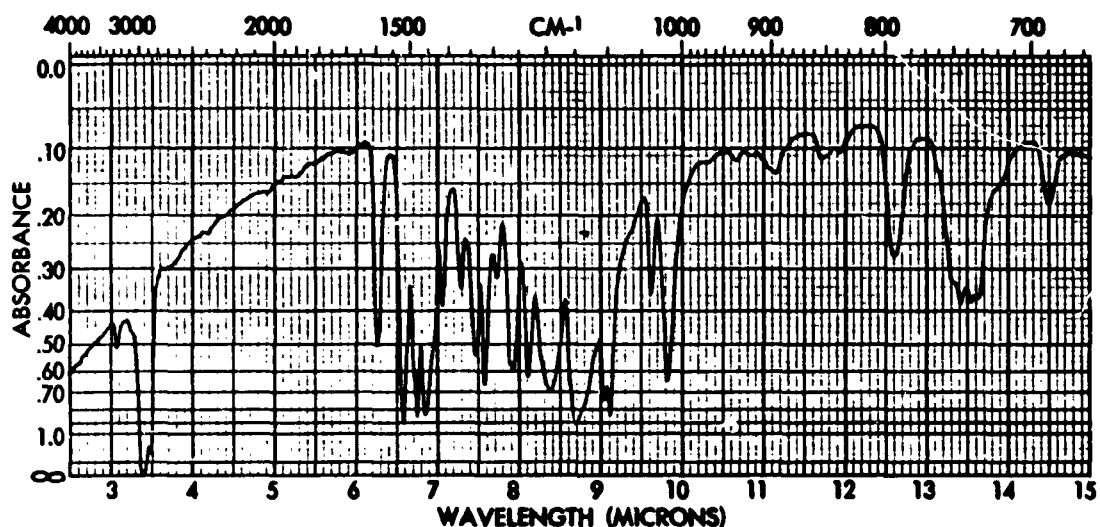
Synthetic Procedure: 2 % Yield: 51

| Analysis: | C | H | N | S |
|-----------|------|------|------|-----|
| Found | 48.6 | 4.45 | 13.5 | 7.5 |
| Calc. | 48.7 | 4.50 | 13.7 | 7.6 |

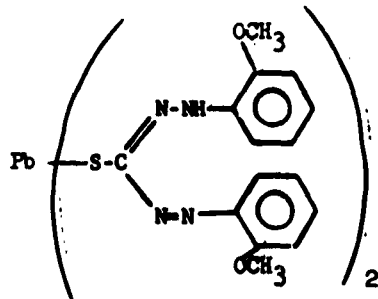
Spectral Data

| Color | λ Max. | ϵ | Thermal Return, Half Life: Less than 5 sec. |
|--------------|----------------|------------|---|
| Unirradiated | | | % Conversion: Low |
| Yellow | 265 | 15,600 | (Cary 14 NIR Source) |
| | 300 (sh) | 8,550 | |
| | 450 | 23,900 | Lightfastness in C.A. Film: 2 |
| Irradiated | 590 | | (Sun hours to 50% fade) |

Remarks: Decomposition occurred in solution on irradiation. Cellulose acetate film - % conversion 35-40%; thermal return, half life in excess of 25 min.
Purification solvent: chloroform-methanol.



Compound No.: 7 Name: Lead bis[1,5-di(o-methoxyphenyl)thiocarbazonate]



Mol. Wt.: 838.67 M.P.: 228-228-1/2 (d)

Appearance: Green iridescent solid.

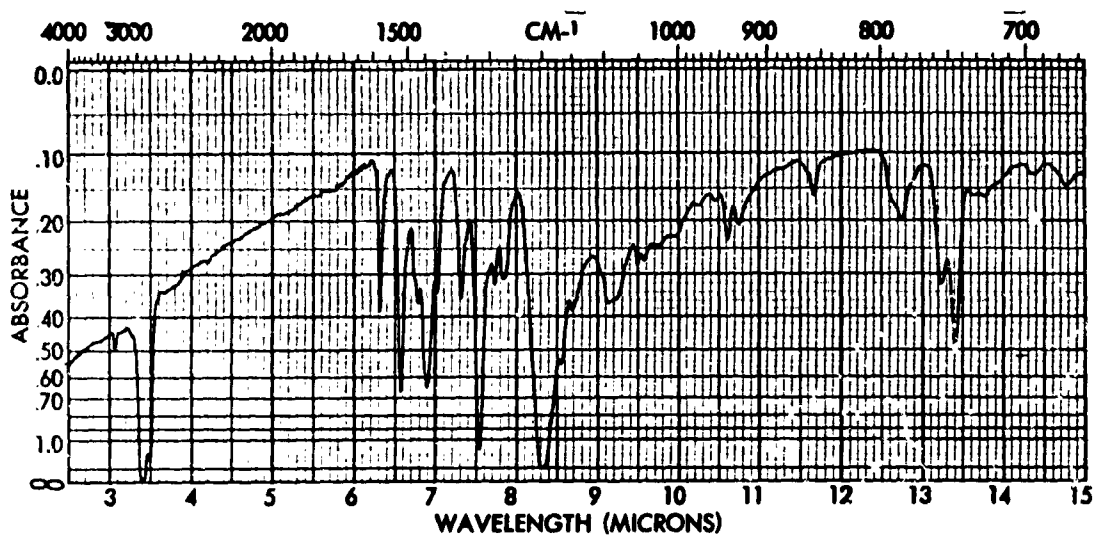
Synthetic Procedure: 1 % Yield: 76

| Analysis: | C | H | N | S | Pb |
|-----------|------|------|------|------|------|
| Found | 42.9 | 3.55 | 13.1 | 7.34 | 24.7 |
| Calc. | 43.0 | 3.61 | 13.4 | 7.65 | 24.7 |

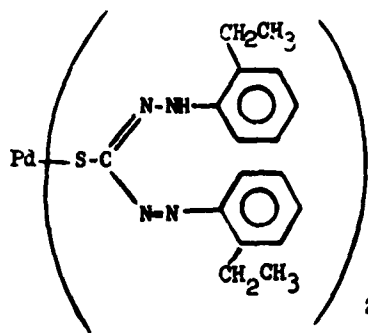
Spectral Data

| Color | λ Max. | ϵ | Thermal Return, Half Life: 15-30 sec. |
|--------------|----------------|------------|---------------------------------------|
| Unirradiated | | | % Conversion: 68 |
| Bluish Red | 285 | 35,100 | (Cary 14 NIR Source) |
| | 535 | 62,800 | |
| Irradiated | | | Lightfastness in C.A. Film: 19 |
| Blue | 680 | | (Sun hours to 50% fade) |

Remarks: Cellulose acetate film - 25-30% conversion, thermal return, half life - 1 min. 15 sec. Purification solvent: chloroform-methanol.



Compound No.: 8 Name: Palladium bis[1,5-di(o-ethylphenyl)thiocarbazonate]



Mol. Wt.: 729.42 M.P.: 236-236-1/2 (d)

Appearance: Black rods

Synthetic Procedure: \approx % Yield: 78

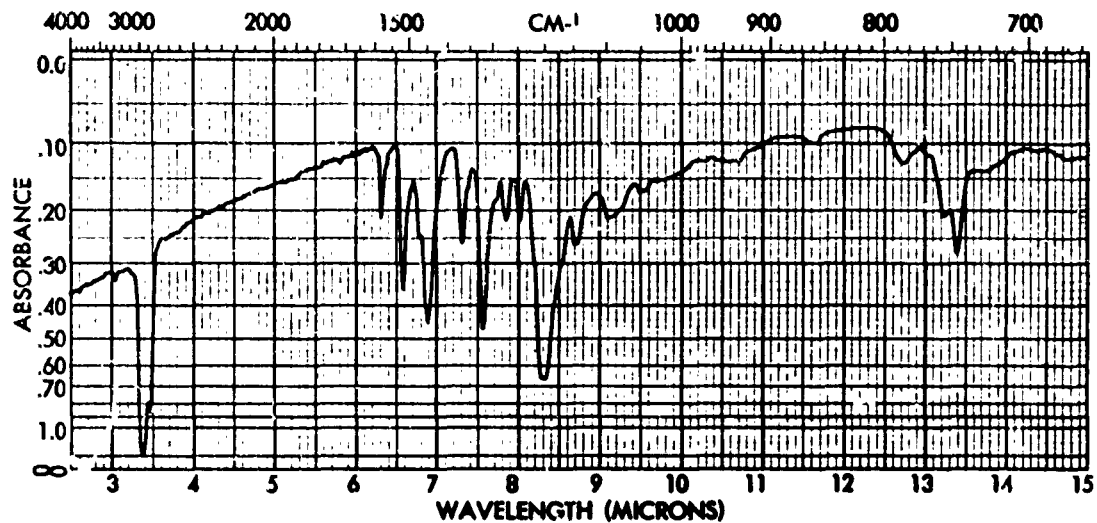
| Analysis: | C | H | N | S |
|-----------|------|------|------|------|
| Found | 56.1 | 5.12 | 15.4 | 8.60 |
| Calc. | 56.0 | 5.21 | 15.4 | 8.77 |

2

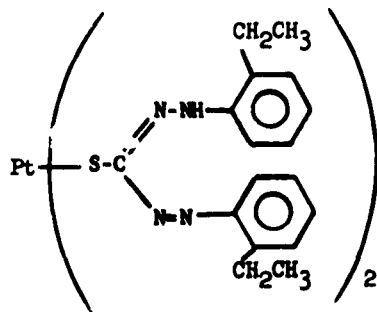
Spectral Data

| | Color | λ Max. | ϵ | Thermal Return, Half Life: Less than 60 sec. |
|--------------|--------|----------------|------------|---|
| Unirradiated | Green | 275 | 31,000 | % Conversion: 100 (Cary 14 NIR Source) |
| | | 305 | 26,300 | |
| | | 445 | 29,900 | |
| | | 630 | 38,400 | |
| Irradiated | Yellow | 480 | 27,700 | Lightfastness in C.A. Film: 30 (Sun hours to 50% fade) |
| | | 785 | 22,800 | |

Remarks: Cellulose acetate film - % conversion 50-60%; thermal return half life - less than 10". Purification solvent: chloroform-methanol.



Compound No.: 9 Name: Platinum bis[1,5-di(o-ethylphenyl)thiocarbazonate]



Mol. Wt.: 818.06

M.P.: 225-226

Appearance: Sparkling purple crystals.

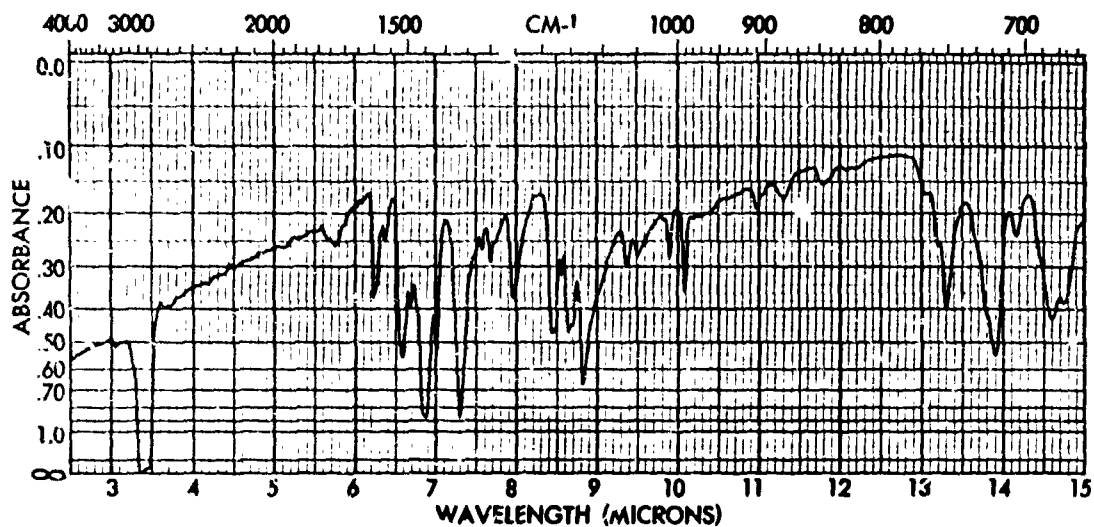
Synthetic Procedure: 1 % Yield: 50

| Analysis: | C | H | N | S | Pt |
|-----------|------|------|------|------|------|
| Found | 48.9 | 4.34 | 13.1 | 7.22 | 23.9 |
| Calc. | 49.9 | 4.68 | 13.7 | 7.83 | 24.9 |

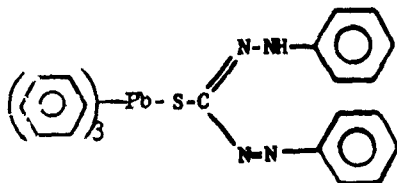
Spectral Data

| | Color | λ_{Max} | ϵ | Thermal Return, Half Life: Less than 5 sec. |
|--------------|-------------|-----------------|------------|--|
| Unirradiated | Dull Yellow | 405 | 19,000 | % Conversion: ~ 20 (Cary 14 NIR Source) |
| | | 485 | 22,300 | |
| | | 725 | 28,300 | |
| | | 830 | 1,320 | |
| Irradiated | Orange | | | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks: Analysis not satisfactory after two recrystallizations. Purification solvents used: chloroform-methanol; tetrahydrofuran-methanol.



Compound No.: 10 Name: Triphenyl lead(1,5-diphenylthiocarbazonate)



Mol. Wt.: 704.8 M.P.: 68-1/2-69-1/2

Appearance: Orange solid

Synthetic Procedure: 2 % Yield: 39

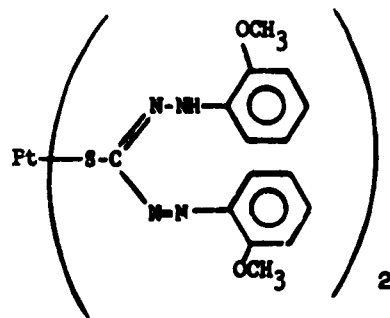
| Analysis: | C | H | N | S |
|-----------|------|------|------|------|
| Found | 53.4 | 3.60 | 8.07 | 4.77 |
| Calc. | 52.9 | 3.78 | 8.08 | 4.62 |

Spectral Data

| Color | λ Max. | ϵ | Thermal Return, Half Life: Less than 30 sec. |
|---------------------|----------------|------------|---|
| Unirradiated Yellow | 275 (sh) | 21,700 | % Conversion: Low - with decomposition. (Cary 14 NIR Source) |
| | 310 (sh) | 8,880 | |
| | 430 | 25,300 | |
| Irradiated | | | Lightfastness in C.A. Film: 11 (Sun hours to 50% fade) |
| Dull Yellow | 570 | | |

Remarks: Cellulose acetate film - % conversion 45-50%; thermal return, half life - 2 min. 45 sec. Purification solvent: methanol.

Compound No.: 11 Name: Platinum bis[1,5-di(o-methoxyphenyl)thiocarbazonate]



Mol. Wt.:

M.P.:

Appearance:

Synthetic Procedure:

% Yield:

Analysis: C H N S

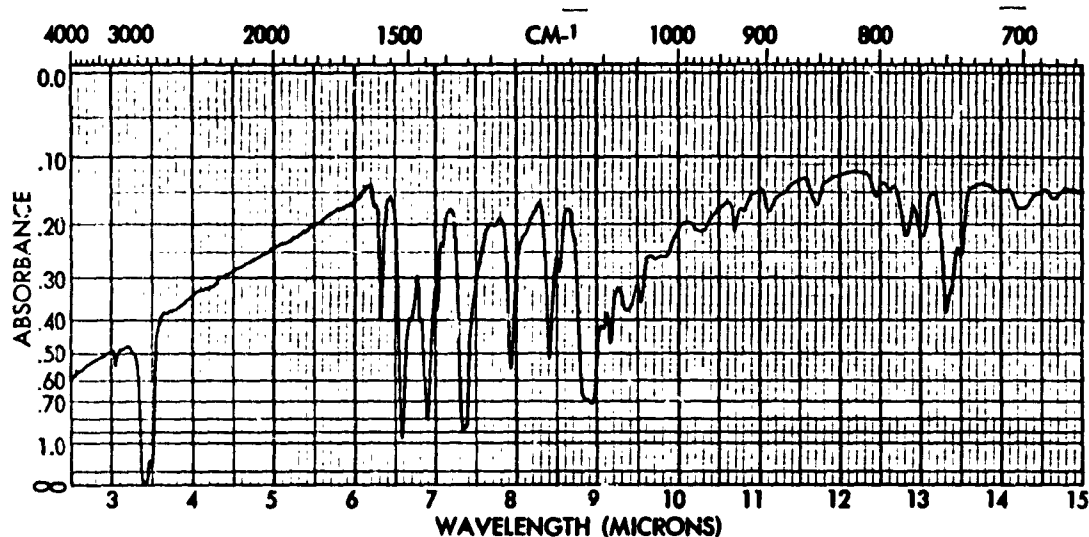
Found

Calc.

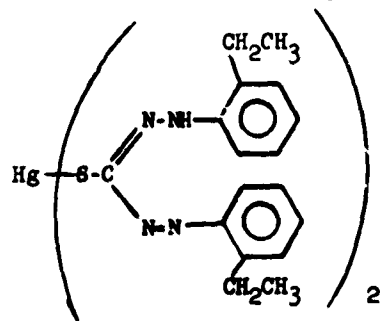
Spectral Data

| | Color | λ Max. | ϵ | Thermal Return, Half Life: |
|--------------|-------|----------------|------------|--|
| Unirradiated | | | | % Conversion: (Cary 14 NIR Source) |
| Irradiated | | | | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks: Attempts at preparation did not yield an identifiable product.



Compound No.: 12 Name: Mercury bis[1,5-di(o-ethylphenyl)thiocarbazonate]



Mol. Wt.: 833.33 M.P.: 144-145

Appearance: Sparkling red plates.

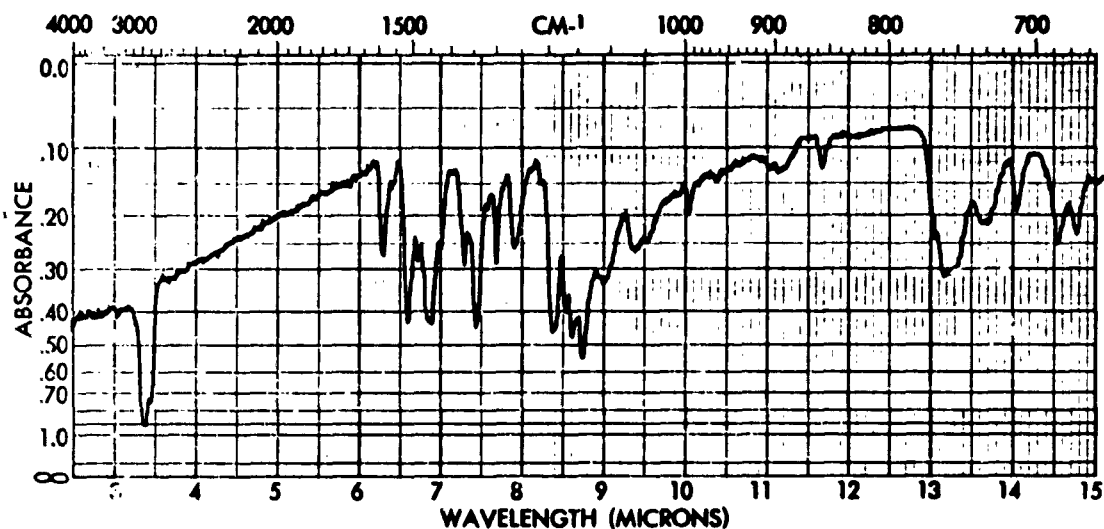
Synthetic Procedure: 1 % Yield: 50

| Analysis: | C | H | N | S | Hg |
|-----------|------|------|------|------|------|
| Found | 49.1 | 4.32 | 13.9 | 8.06 | 24.7 |
| Calc. | 49.6 | 4.62 | 13.6 | 7.78 | 24.4 |

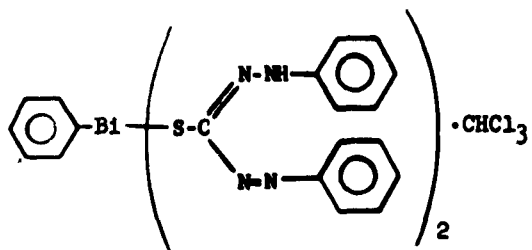
Spectral Data

| | Color | λ Max. | ϵ | Thermal Return, Half Life: | 12 min. |
|--------------|--------|----------------|------------------|-----------------------------|-------------------------------|
| Unirradiated | Yellow | 265 475 | 30,400 44,100 | % Conversion: | 94 (Cary 14 NIR Source) |
| Irradiated | Blue | 580 | | Lightfastness in C.A. Film: | 11 (Sun hours to 50% fade) |

Remarks: Cellulose acetate film - 80-90% conversion; thermal return, half life - 5 min. 15 sec. Purification solvent: tetrahydrofuran-methanol.



Compound No.: 13 Name: Phenyl bismuth bis(1,5-diphenylthiocarbazonate)



Mol. Wt.: 916.12 M.P.: 135-136
Rx from CHCl_3

Appearance: Green iridescent needles.

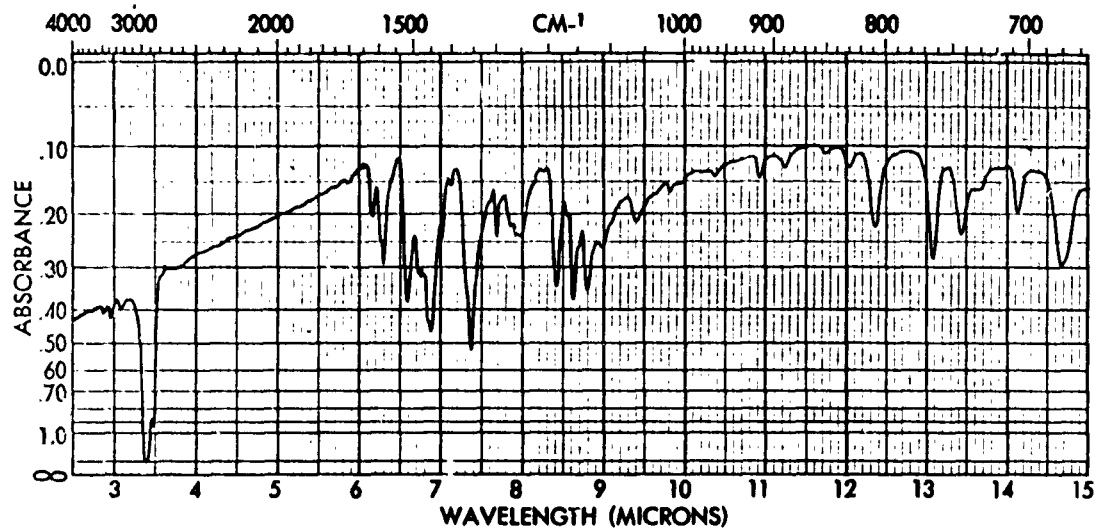
Synthetic Procedure: 2 % Yield: 47

| Analysis: | C | H | N | S | Bi | Cl |
|-----------|------|------|------|------|------|------|
| Found | 43.3 | 2.99 | 12.1 | 6.96 | 22.8 | 10.3 |
| Calc. | 43.2 | 3.08 | 12.2 | 7.00 | 22.8 | 11.5 |

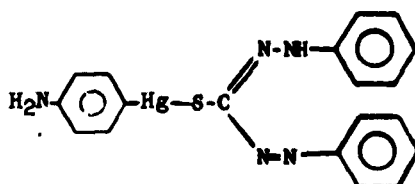
Spectral Data

| Color | λ_{Max} | ϵ | Thermal Return, Half Life: Less than 10 sec. |
|--------------|------------------------|------------|--|
| Unirradiated | | | % Conversion: 25-40% |
| Orange | 272 | 40,200 | (Cary 14 NIR Source) |
| | 490 | 48,700 | |
| Irradiated | | | Lightfastness in C.A. Film: 24 |
| Weak Orange | 600 | | (Sun hours to 50% fade) |

Remarks: The mole of solvent of crystallization changed with solvent of recrystallization.
Purification solvent: chloroform-methanol.



Compound No.: 14 Name: p-Aminophenyl mercury(1,5-diphenylthiocarbazonate)



Mol. Wt.: 549.05 M.P.: 192-1/2 -
193-1/2 (d)

Appearance: Orange crystals.

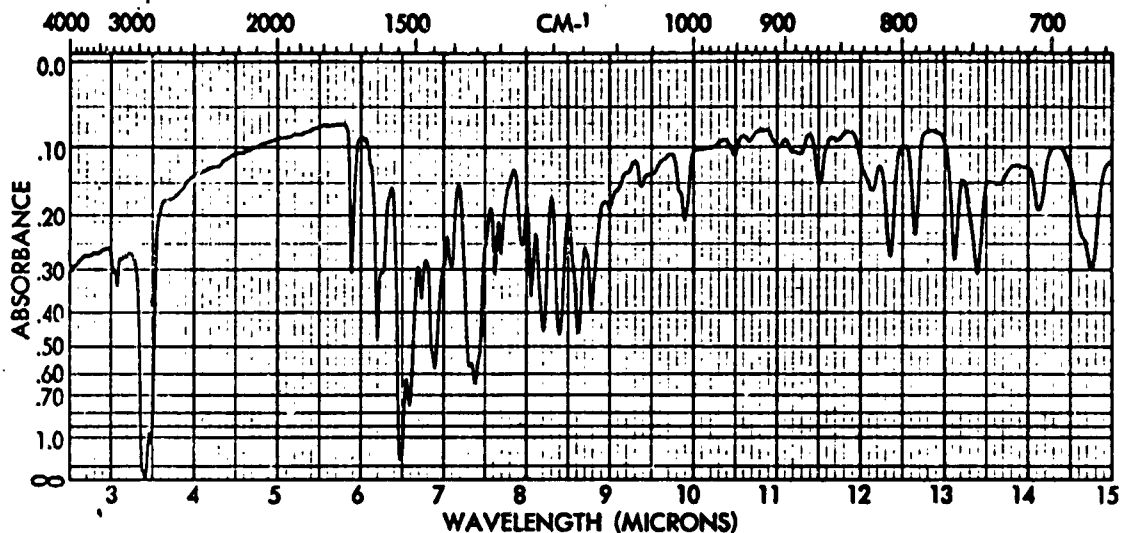
Synthetic Procedure: 2 % Yield: 56

| Analysis: | C | H | N | S | Hg |
|-----------|------|------|------|------|------|
| Found | 42.0 | 3.06 | 12.9 | 5.81 | 36.6 |
| Calc. | 41.6 | 3.13 | 12.8 | 5.85 | 36.6 |

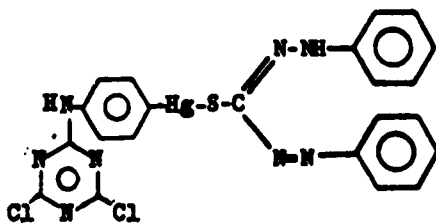
Spectral Data

| | Color | $\lambda_{Max.}$ | ϵ | Thermal Return, Half Life: 51.3 min. |
|--------------|--------|------------------|------------|---|
| Unirradiated | Yellow | 260 | 31,200 | % Conversion: 100 (Cary 14 NIR Source) |
| | | 470 | 31,600 | |
| Irradiated | Blue | 268 | 30,900 | Lightfastness in C.A. Film: Not evaluated. (Sun hours to 50% fade) |
| | | 585 | 16,400 | |

Remarks: Purification solvent: acetone.



Compound No.: 15 Name: p-[4,6-Dichloro-s-triazin-2-yl)amino]phenylmercury-(1,5-diphenylthiocarbazonate)



Mol. Wt.: 708.2 M.P.: 126-1/2 - 127-1/2 (d)

Appearance: Orange red plates

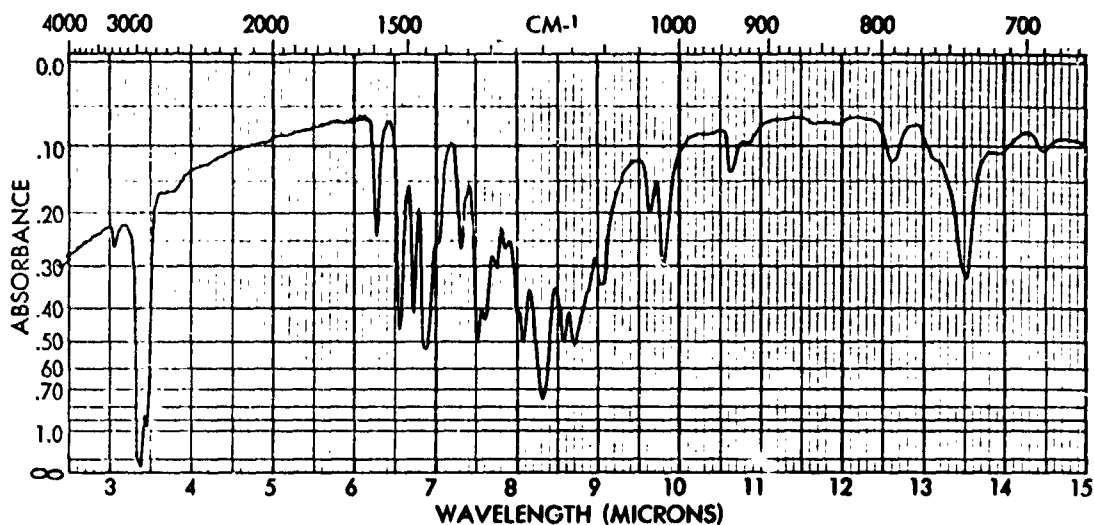
Synthetic Procedure: 3 % Yield: 83

| Analysis: | C | H | N | S | Cl | Hg |
|-----------|------|------|------|------|------|------|
| Found | 37.9 | 2.17 | 16.6 | 4.41 | 9.84 | 28.5 |
| Calc. | 38.0 | 2.32 | 16.1 | 4.61 | 10.2 | 28.8 |

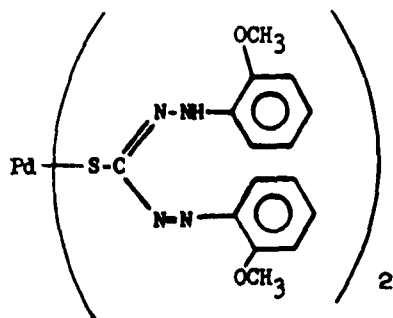
Spectral Data

| | Color | λ Max. | ϵ | Thermal Return, Half Life: 23.9 min. |
|--------------|--------|----------------|------------|---|
| Unirradiated | Yellow | 275 | 37,600 | % Conversion: 100 (Cary 14 NIR Source) |
| | | 470 | 31,100 | |
| Irradiated | Blue | 280 | 42,400 | Lightfastness in C.A. Film: 30 (Sun hours to 50% fade) |
| | | 590 | 16,200 | |

Remarks: Cellulose acetate film - % conversion 80%; thermal return, half life, 30 min.
Purification solvent: acetone.



Compound No.: 16 Name: Palladium bis[1,5-di(o-methoxyphenyl)thiocarbazonate]



Mol. Wt.: 737.46

M.P.: 134 (d)

Appearance: Purple solid

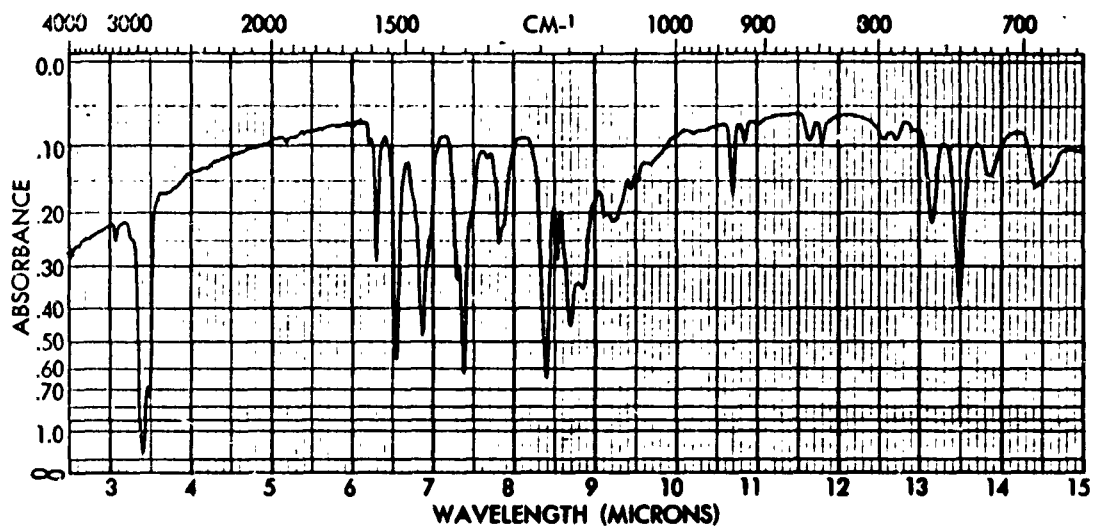
Synthetic Procedure: 2 % Yield: 69

| Analysis: | C | H | N | S | Pd |
|-----------|------|------|------|------|------|
| Found | 48.5 | 4.51 | 15.3 | 8.79 | 14.4 |
| Calc. | 48.9 | 4.10 | 15.2 | 8.70 | 14.4 |

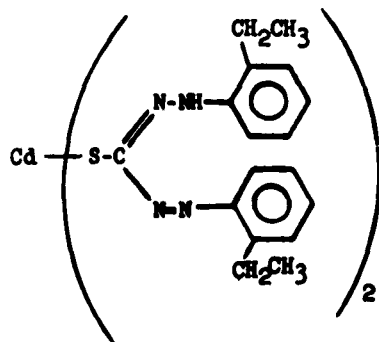
Spectral Data

| | Color | λ_{Max} | ϵ | Thermal Return, Half Life: Less than 10 sec. |
|--------------|--------|-----------------|------------|---|
| Unirradiated | Green | 282 | 29,800 | % Conversion: 100 (Cary 14 NIR Source) |
| | | 460 | 26,600 | |
| | | 640 | 30,000 | |
| Irradiated | Yellow | 495 | 25,100 | Lightfastness in C.A. Film: In excess of 50. (Sun hours to 50% fade) |
| | | 775 | 18,400 | |

Remarks: Cellulose acetate film - % conversion 90-100%; thermal return, half life - less than 10 sec. Purification solvent: chloroform-methanol. Solutions in CH_2Cl_2 showed thermal (dark) instability.



Compound No.: 17 Name: Cadmium bis[1,5-di(o-ethylphenyl)thiocarbazonate]



Mol. Wt.: 735.24 M.P.: 176-177 (d)

Appearance: Maroon prisms.

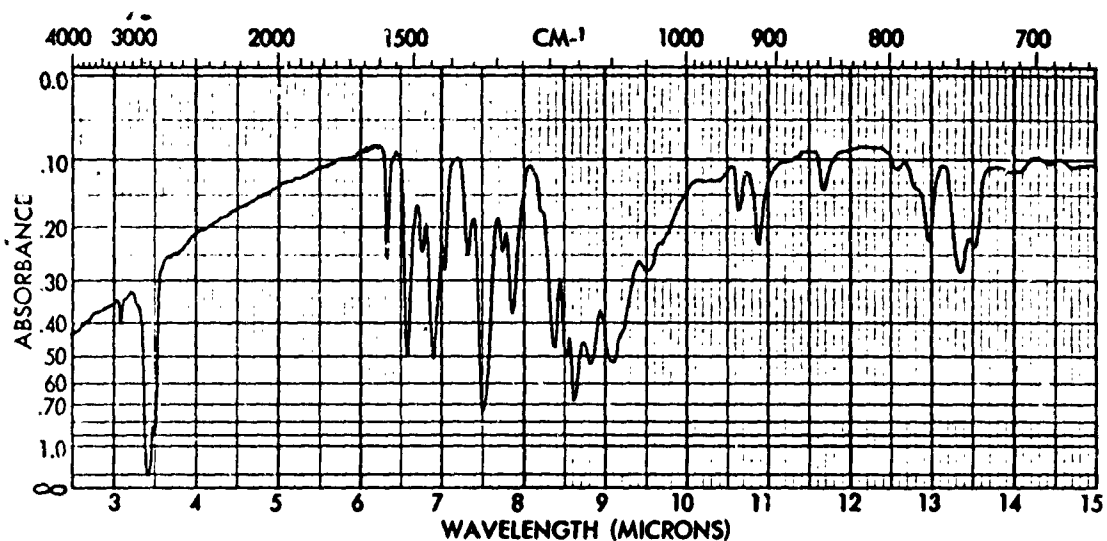
Synthetic Procedure: 1 % Yield: 78

| Analysis: | C | H | N | S |
|-----------|------|------|------|------|
| Found | 55.5 | 5.23 | 14.9 | 8.33 |
| Calc. | 55.5 | 5.21 | 15.2 | 8.72 |

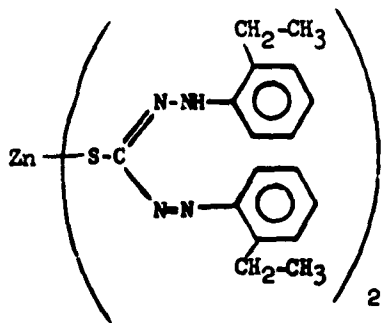
Spectral Data

| | Color | λ Max. | ϵ | Thermal Return, Half Life: 12 sec. |
|--------------|-----------|----------------|------------|--|
| Unirradiated | Orange | 273 | 29,350 | % Conversion: 46 (Cary 14 NIR Source) |
| | | 505 | 69,600 | |
| Irradiated | Dull Blue | 640 | | Lightfastness in C.A. Film: 9 (Sun hours to 50% fade) |
| | | | | |

Remarks: Cellulose acetate film - % conversion 20%, thermal return, half life - 45 sec.
Purification solvent: benzene-methanol.



Compound No.: 18 Name: Zinc bis[1,5-di(o-ethylphenyl)thiocarbazonate]



Mol. Wt.: 688.10 M.P.: 163-164

Appearance: Green iridescent needles.

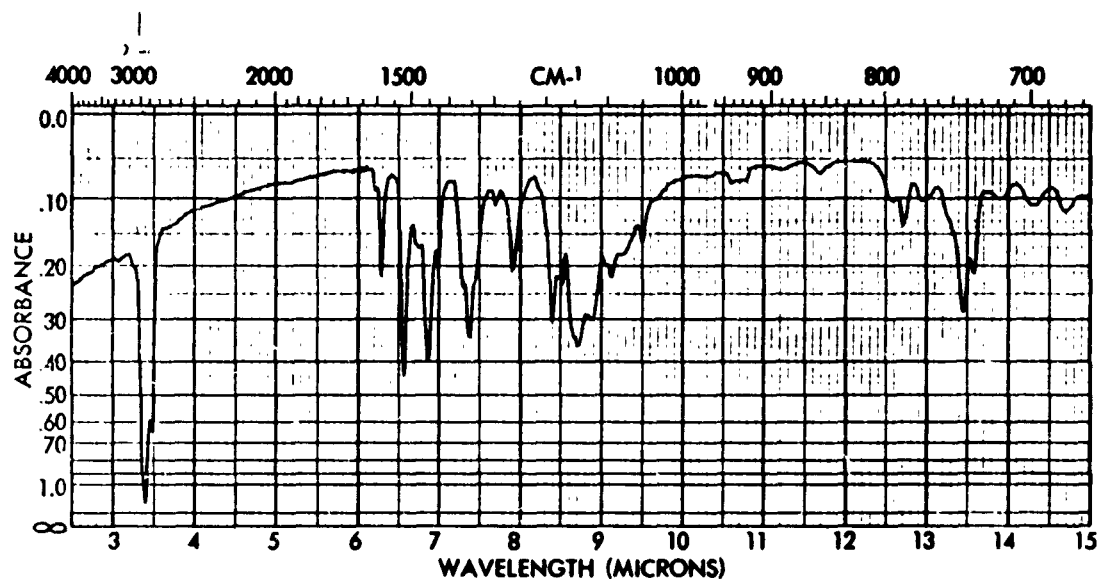
Synthetic Procedure: 1 % Yield: 93

| Analysis: | C | H | N | S |
|-----------|------|------|------|------|
| Found | 59.0 | 5.67 | 16.1 | 9.29 |
| Calc. | 59.3 | 5.57 | 16.3 | 9.32 |

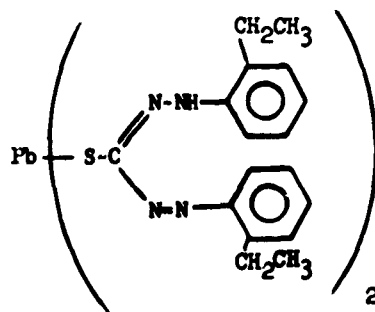
Spectral Data

| Color | λ_{Max} | ϵ | Thermal Return, Half Life: Less than 15 sec. |
|--------------|-----------------|------------|--|
| Unirradiated | | | % Conversion: Est. 62 |
| Pink | 275 | 29,300 | (Cary 14 NIR Source) |
| | 345 (sh) | 8,600 | |
| | 515 | 77,200 | |
| Irradiated | | | Lightfastness in C.A. Film: 7 |
| Pinkish Blue | 660 | | (Sun hours to 50% fade) |

Remarks: Cellulose acetate film - 30% conversion, thermal return, half life - less than 15 sec. Purification solvent: benzene-methanol.



Compound No.: 19 Name: Lead bis[1,5-di(o-ethylphenyl)diocarbazonate]



Mol. Wt.: 831.63 M.P.: 173-1/2 - 174-1/2

Appearance: Brown microcrystals

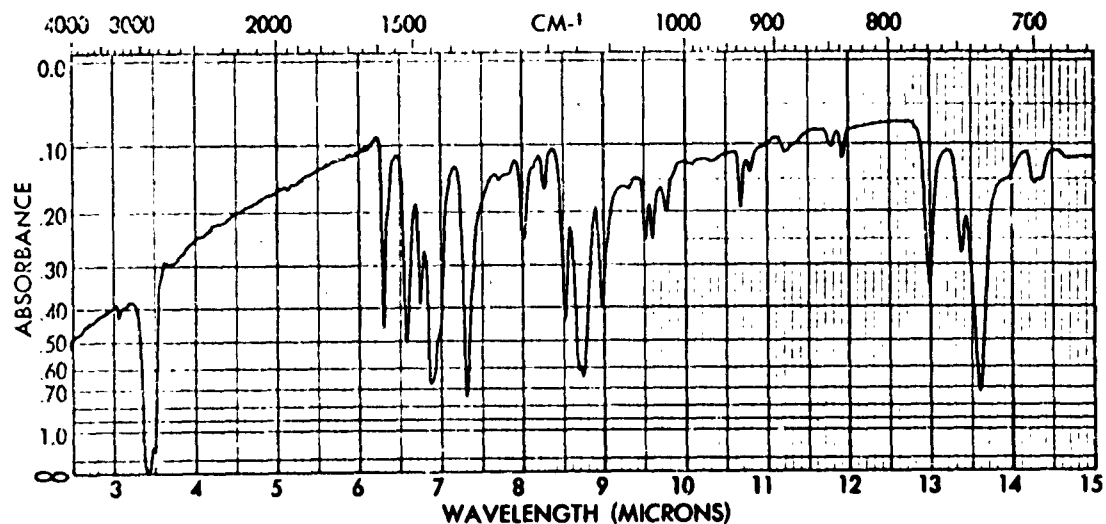
Synthetic Procedure: 1 % Yield: 92.5

| Analysis: | C | H | N | S |
|-----------|------|------|------|------|
| Found | 49.2 | 4.58 | 13.3 | 7.76 |
| Calc. | 49.2 | 4.61 | 13.5 | 7.73 |

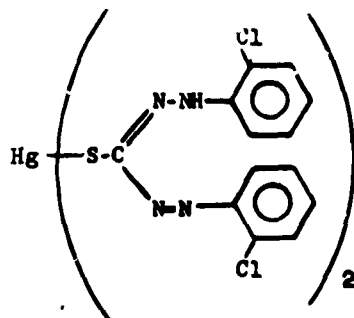
Spectral Data

| | Color | λ Max. | ϵ | Thermal Return, Half Life: Less than 10 sec. |
|--------------|--------|----------------|------------|--|
| Unirradiated | Orange | 268 | 32,400 | % Conversion: Low (Cary 14 NIR Source) |
| | | 345 (sh) | 11,800 | |
| | | 500 | 51,400 | |
| Irradiated | | 620 | | Lightfastness in C.A. Film: 5 (Sun hours to 50% fade) |

Remarks: Cellulose acetate film - est. 15% conversion, thermal return, half life - too fast to measure. Purification solvent: benzene-methanol.



Compound No.: 20 Name: Mercury bis[1,5-di(o-chlorophenyl)thiocarbazonate]



Mol. Wt.: 848.89 M.P.: 276-278-1/2 (u)

Appearance: Light orange needles.

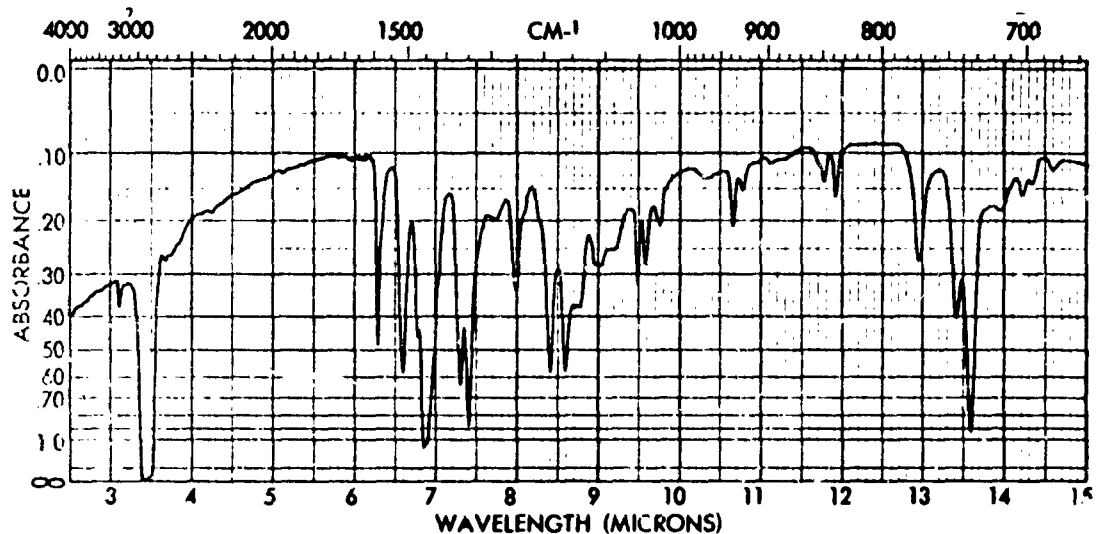
Synthetic Procedure: 1 % Yield: 75

| Analysis: | C | H | N | S | Cl | Hg |
|-----------|------|------|------|------|------|-------|
| Found | 37.1 | 2.19 | 13.2 | 7.56 | 16.8 | 23.03 |
| Calc. | 36.8 | 2.14 | 13.2 | 7.55 | 16.7 | 23.6 |

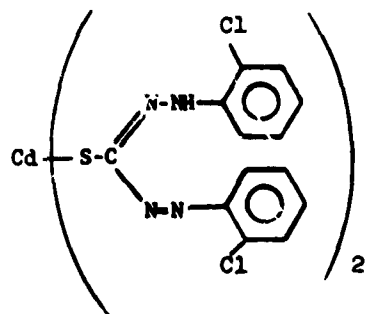
Spectral Data

| | Color | λ_{Max} | ϵ | Thermal Return, Half Life: 12 min. |
|--------------|--------|-----------------|------------------|--|
| Unirradiated | Orange | 270 485 | 31,600 49,000 | % Conversion: 86 (Cary 14 NIR Source) |
| Irradiated | Blue | 600 | | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks: Compound too insoluble in cellulose acetate film to evaluate.
Purification solvent: chlorobenzene.



Compound No.: 21 Name: Cadmium bis[1,5-di(o-chlorophenyl)thiocarbazonate]



Mol. Wt.: 760.82

M.P.: 279-280

Appearance: Orange microneedles.

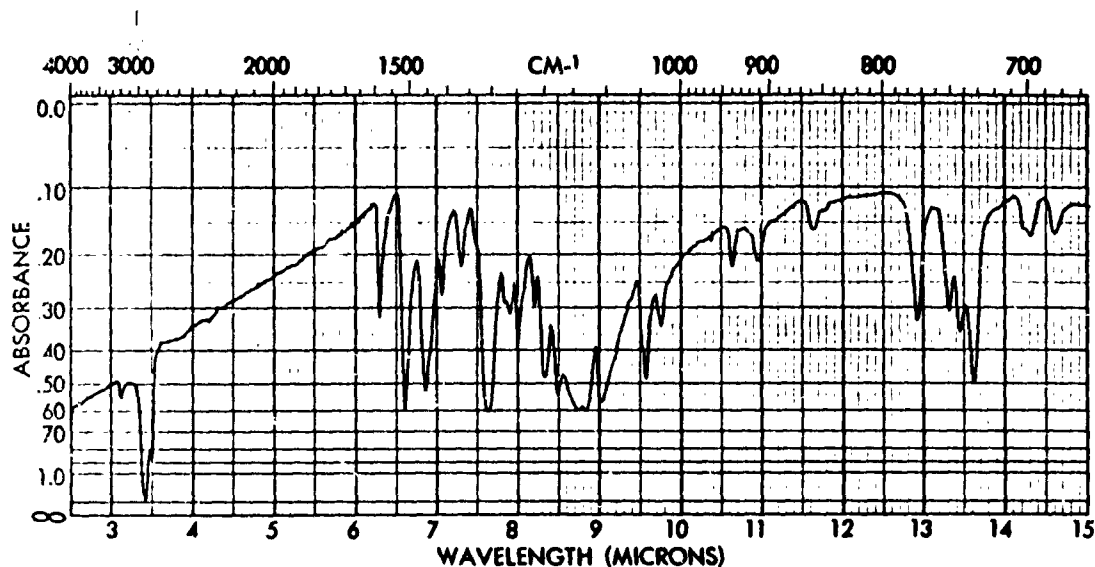
Synthetic Procedure: 1 % Yield. 20

| Analysis: | C | H | N | S |
|-----------|------|------|------|---|
| Found | 40.1 | 2.29 | 14.8 | |
| Calc. | 41.0 | 2.28 | 14.8 | |

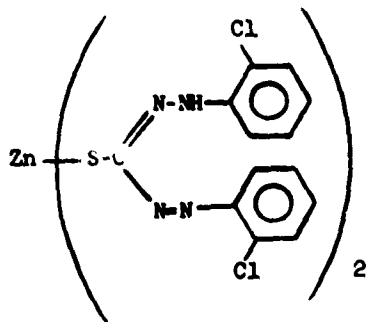
Spectral Data

| | Color: | λ_{Max} | ϵ | Thermal Return, Half Life: 9 sec. |
|--------------|--------|-----------------|------------|--|
| Unirradiated | | 520 | | % Conversion: Est. 48% (Cary NIR Source) |
| Irradiated | | 670 | | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks: Poor solubility in CH_2Cl_2 , insoluble in cellulose acetate film.
Difficult to purify. Purification solvent: tetrahydrofuran.



Compound No.: 22 Name: Zinc bis[1,5-di(o-chlorophenyl)thiocarbazonate]



Mol. Wt.: 713.66

M.P.: 241-1/2 -
242-1/2 (d)

Appearance: Green iridescent crystals.

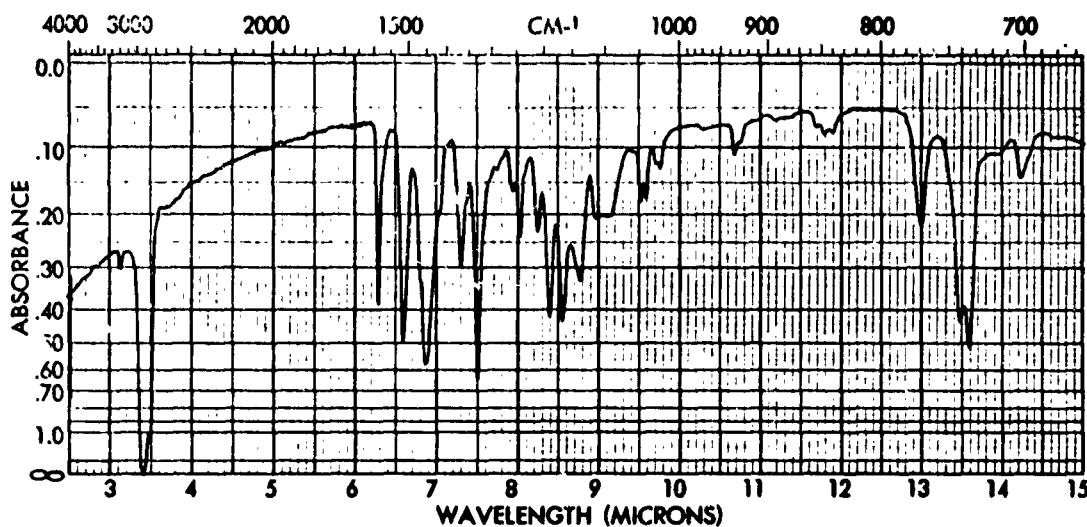
Synthetic Procedure: 1 % Yield: 67

| Analysis: | C | H | N | S | Cl | Zn |
|-----------|------|------|------|------|------|------|
| Found | 44.0 | 2.60 | 15.8 | 8.82 | 19.9 | 9.17 |
| Calc. | 43.8 | 2.54 | 15.7 | 8.98 | 19.9 | 9.16 |

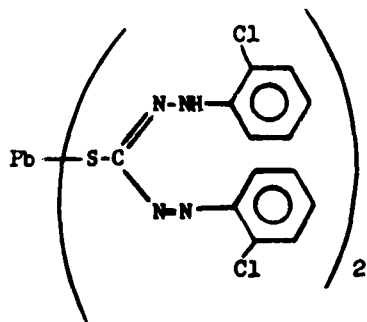
Spectral Data

| Color | λ_{Max} | ϵ | Thermal Return, Half Life: 16 sec, 33 sec. |
|----------------------------|------------------------|----------------------------|--|
| Unirradiated Pink | 280 370 (sh) 530 | 30,100 11,600 75,000 | % Conversion: 73 (Cary 14 NIR Source) |
| Irradiated Pinkish Blue | 685 | | Lightfastness in C.A. Film: 19 hrs. (Sun hours to 50% fade) |

Remarks: Cellulose acetate film - 10% conversion, thermal return, too fast to measure.
Purification solvent: chloroform-methanol.



Compound No.: 23 Name: Lead bis[1,5-di(o-chlorophenyl)thiocarbazonate]



Mol. Wt.: 856.19 M.P.: 261-1/2 - 262-1/2

Appearance: Brown maroon crystals.

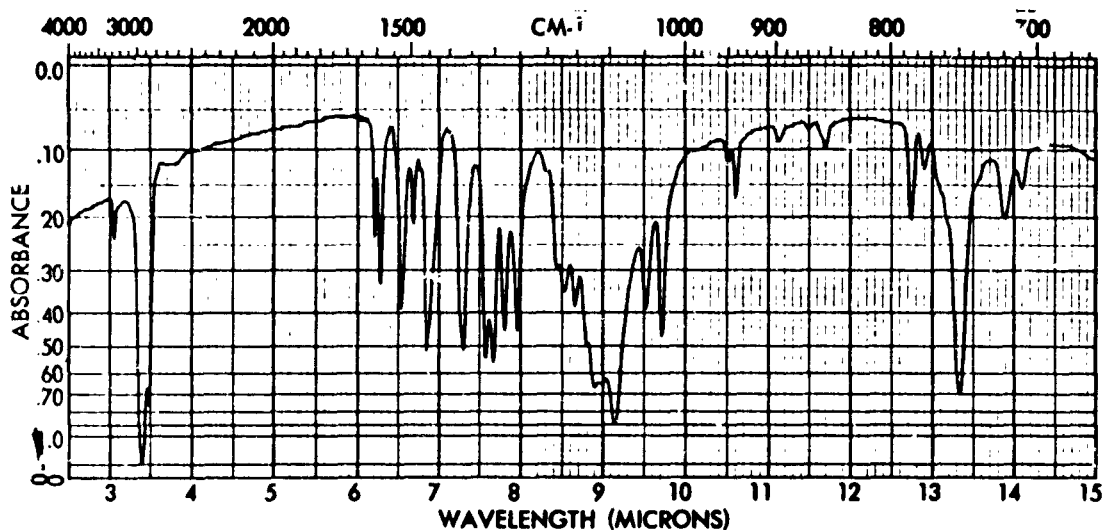
Synthetic Procedure: 1 % Yield: 76

| Analysis: | C | H | N | S | Cl | Pb |
|-----------|------|------|------|------|------|------|
| Found | 36.7 | 1.80 | 13.4 | 7.45 | 17.0 | 24.4 |
| Calc. | 36.5 | 2.12 | 13.1 | 7.50 | 16.6 | 24.2 |

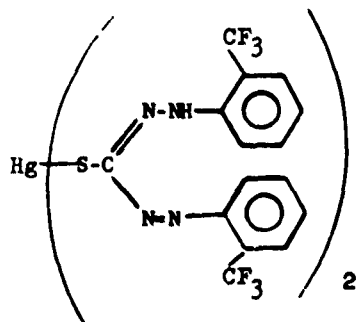
Spectral Data

| Color | λ Max. | ϵ | Thermal Return, Half Life: Less than 10 sec. |
|--------------|----------------|------------------|---|
| Unirradiated | 280 510 | 20,100 30,700 | % Conversion: Low 9-10% (Cary 14 NIR Source) |
| Irradiated | | | Lightfastness in C.A. Film: 29 (Sun hours to 50% fade) |

Remarks: Cellulose acetate film - ca. 4% conversion; thermal return not measurable.
Purification solvent: chlorobenzene.



Compound No.: 24 Name: Mercury bis[1,5-di(o-trifluoromethylphenyl)thiocarbazonate]



Mol. Wt.: 983.13 M.P.: 215-216 (d)

Appearance: Pale orange needles.

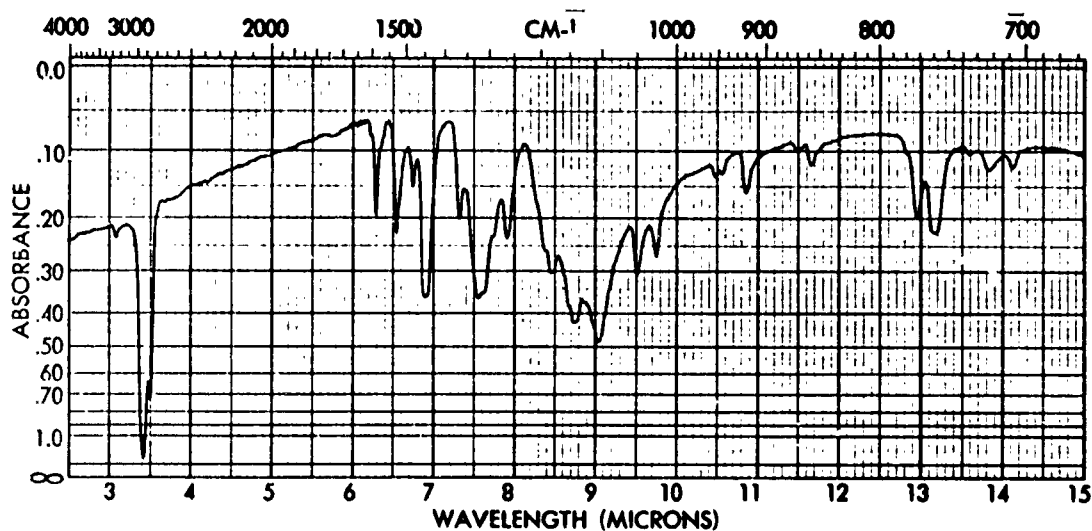
Synthetic Procedure: 1 % Yield: 68

| Analysis: | C | H | N | S | F | Hg |
|-----------|------|------|------|------|------|------|
| Found | 36.5 | 2.17 | 11.3 | 6.72 | 23.1 | 20.7 |
| Calc. | 36.7 | 1.85 | 11.4 | 6.52 | 23.2 | 20.4 |

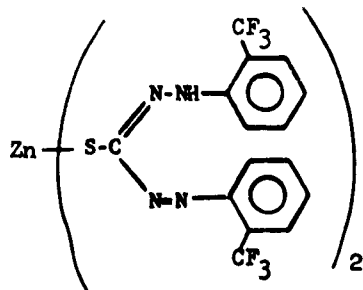
Spectral Data

| | Color | λ_{Max} | ϵ | Thermal Return, Half Life: 1.7 min., 6 min. |
|--------------|--------|-----------------|------------|---|
| Unirradiated | Yellow | 265 | 37,600 | % Conversion: 72 (Cary 14 NIR Source) |
| | | 445 | 53,000 | |
| Irradiated | Red | 550 | | Lightfastness in C.A. Film: 52 (Sun hours to 50% fade) |

Remarks: Cellulose acetate film - 57% conversion; thermal return, half life - 7 min.
Purification solvent: chloroform-methanol.



Compound No.: 25 Name: Zinc bis[1,5-di(o-trifluoromethylphenyl)thiocarbazonate]



Mol. Wt.: 847

M.P.: 167-168

Appearance: Orange crystals, green iridescence.

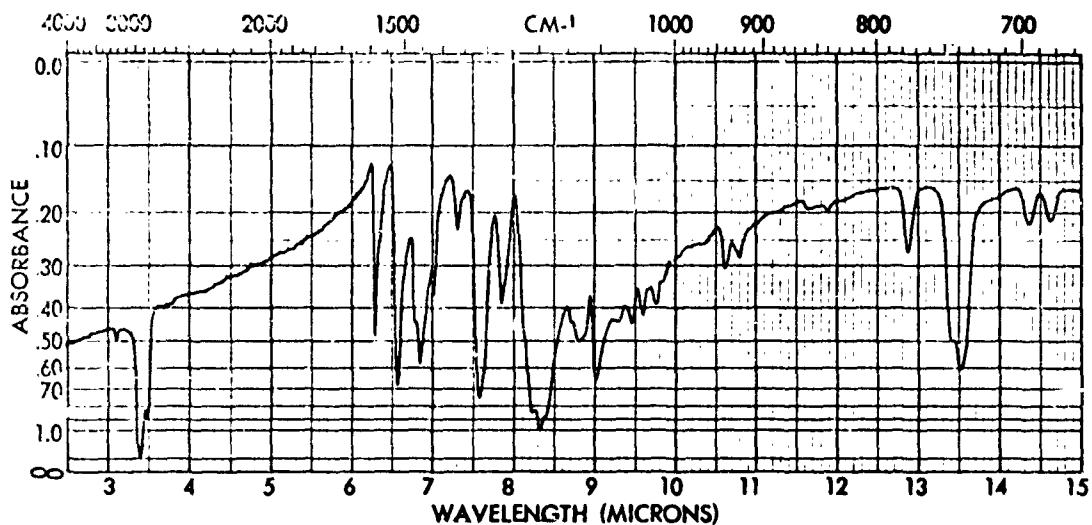
Synthetic Procedure: 1 % Yield: 92

| Analysis: | C | H | N | S | F | Zn |
|-----------|------|------|------|------|------|------|
| Found | 42.7 | 2.06 | 13.4 | 7.06 | 27.1 | 7.25 |
| Calc. | 42.5 | 2.14 | 13.2 | 7.56 | 26.9 | 7.71 |

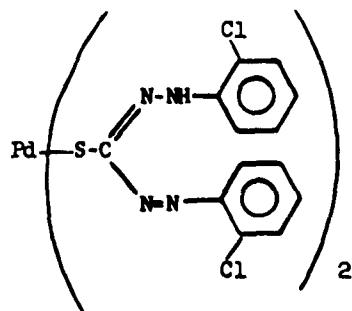
Spectral Data

| | Color | λ_{Max} | ϵ | Thermal Return, Half Life: ca. 10 sec. |
|--------------|--------|-----------------|------------|---|
| Unirradiated | Orange | 270 | 33,700 | % Conversion: 63 (Cary 14 NIR Source) |
| | | 350 (sh) | 10,630 | |
| | | 500 | 72,500 | |
| Irradiated | Green | 645 | | Lightfastness in C.A. Film: 26 (Sun hours to 50% fade) |

Remarks: Cellulose acetate film - 13% conversion; thermal return, half life - less than 5 sec. Purification solvent: ethanol-water.



Compound No.: 26 Name: Palladium bis[1,5-di(o-chlorophenyl)thiocarbazonate]



Mol. Wt.: 753.17

M.P.: 293-293-1/2

Appearance: Dark blue crystals.

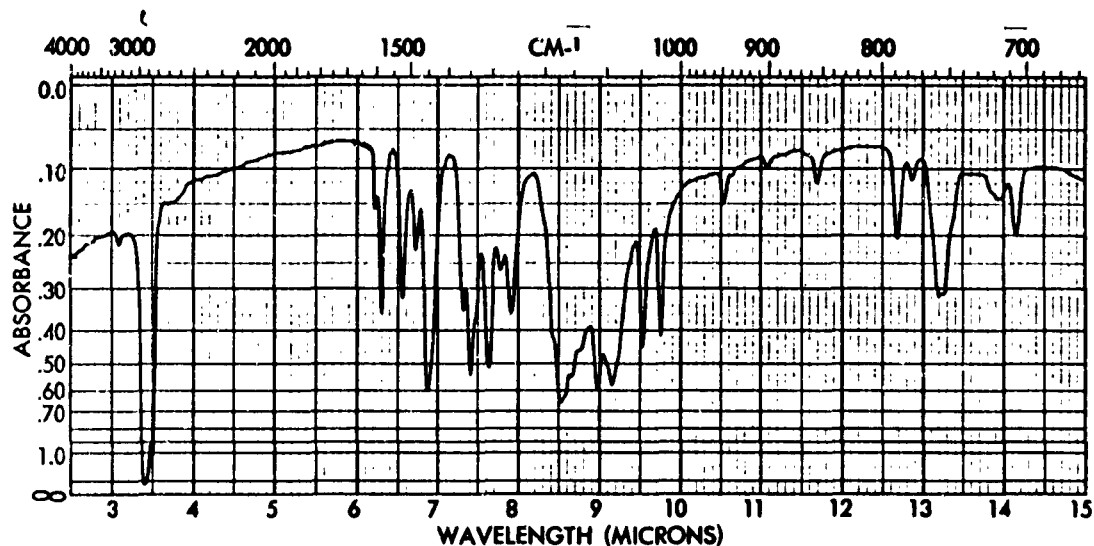
Synthetic Procedure: 2 % Yield: 60

| Analysis: | C | H | N | S | Cl | Pd |
|-----------|------|------|------|------|------|------|
| Found | 41.9 | 2.15 | 15.1 | 8.21 | 18.5 | 13.9 |
| Calc. | 41.4 | 2.40 | 14.8 | 8.50 | 18.8 | 14.1 |

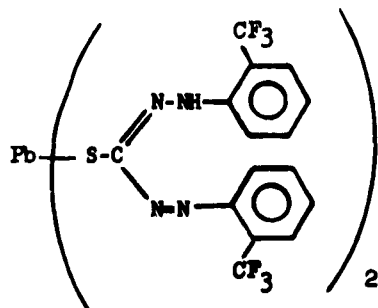
Spectral Data

| | Color | $\lambda_{Max.}$ | ϵ | Thermal Return, Half Life: 22 sec. |
|--------------|--------|------------------|------------|---|
| Unirradiated | Green | 280 | 31,100 | % Conversion: 100 (Cary 14 NIR Source) |
| | | 305 (sh) | 22,100 | |
| | | 450 | 31,100 | |
| | | 645 | 32,500 | |
| Irradiated | Orange | 480 | 26,600 | Lightfastness in C.A. Film: More than (Sun hours to 50% fade) 80 hours |
| | | 800 | 19,700 | |

Remarks: Cellulose acetate film, 5-10% conversion, thermal return too fast to measure. Purification solvent: chlorobenzene.



Compound No.: 27 Name: Lead bis[1,5-di(o-trifluoromethylphenyl)thiocarbazonate]



Mol. Wt.: 989.83 M.P.: 210-211 (d)

Appearance: Sparking red crystals.

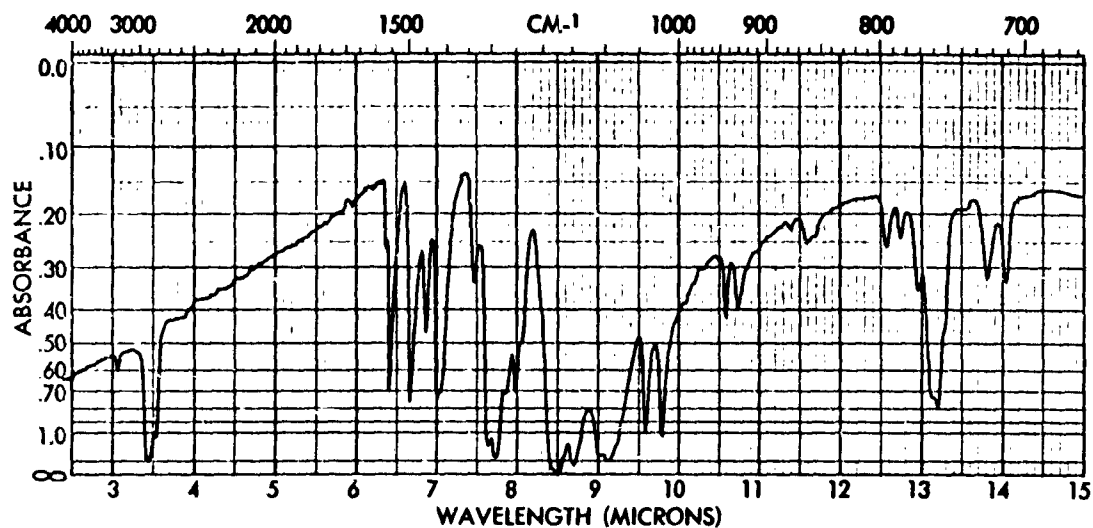
Synthetic Procedure: 1 % Yield: 67

| Analysis: | C | H | N | S | F | Pb |
|-----------|------|------|------|------|------|------|
| Found | 36.6 | 1.88 | 11.9 | 6.61 | 23.5 | 21.1 |
| Calc. | 36.4 | 1.83 | 11.4 | 6.48 | 23.1 | 21.0 |

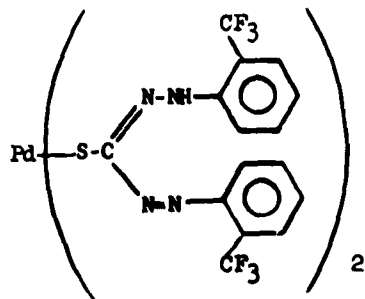
Spectral Data

| Color | λ Max. | ϵ | Thermal Return, Half Life: Less than 10 sec. |
|---------------------|----------------|------------|---|
| Unirradiated Yellow | 260 | 32,200 | % Conversion: Less than 10. (Cary 14 NIR Source) |
| | 340 (sh) | 13,700 | |
| | 480 | 43,400 | |
| Irradiated | 600 (?) | | Lightfastness in C.A. Film: 31 (Sun hours to 50% fade) |

Remarks: Purification solvent: chloroform-methanol.



Compound No.: 28 Name: Palladium bis[1,5-di(o-trifluoromethylphenyl)thiocarbazonate]



Mol. Wt.: 713.2 M.P.: 293-1/2 - 294-1/2

Appearance: Purple crystals

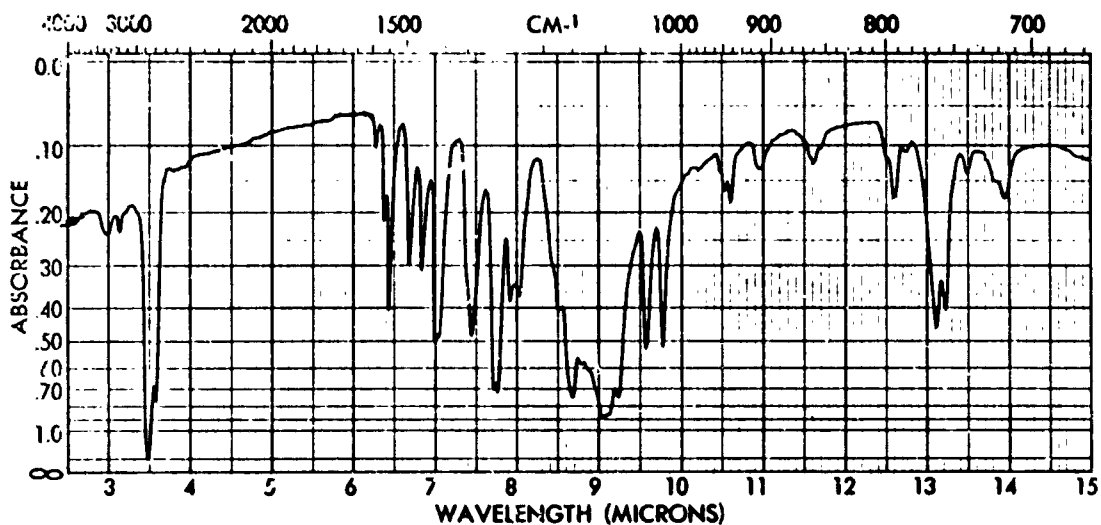
Synthetic Procedure: 2 % Yield: 71

| Analysis: | C | H | N | S | F | Pd |
|-----------|------|------|------|------|------|------|
| Found | 40.4 | 2.23 | 12.6 | 7.32 | 25.7 | 11.9 |
| Calc. | 40.5 | 2.04 | 12.6 | 7.21 | 25.6 | 12.0 |

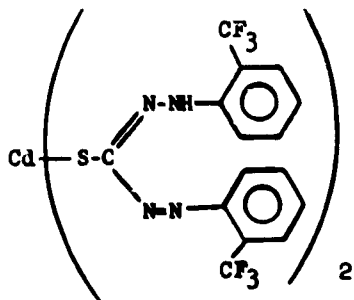
Spectral Data

| | Color | λ Max. | Σ | Thermal Return, Half Life: Less than 10 sec. |
|--------------|--------|----------------|----------|---|
| Unirradiated | Green | 280 | 34,400 | % Conversion: 100 (Cary 14 NIR Source) |
| | | 308 | 31,800 | |
| | | 437 | 36,400 | |
| | | 640 | 35,400 | |
| Irradiated | Yellow | 470 | 30,400 | Lightfastness in C.A. Film: More than 80 (Sun hours to 50% fade) |
| | | 795 | 25,200 | |
| | | | | |

Remarks: Cellulose acetate film - 25-30% conversion, thermal return, half life - less than 20 sec. Purification solvent: chloroform-methanol.



Compound No.: 29 Name: Cadmium bis[1,5-di(o-trifluoromethylphenyl)thiocarbazonate]⁷



Mol. Wt.: 895.05 M.P.: 234-235 (d)

Appearance: Red orange crystals.

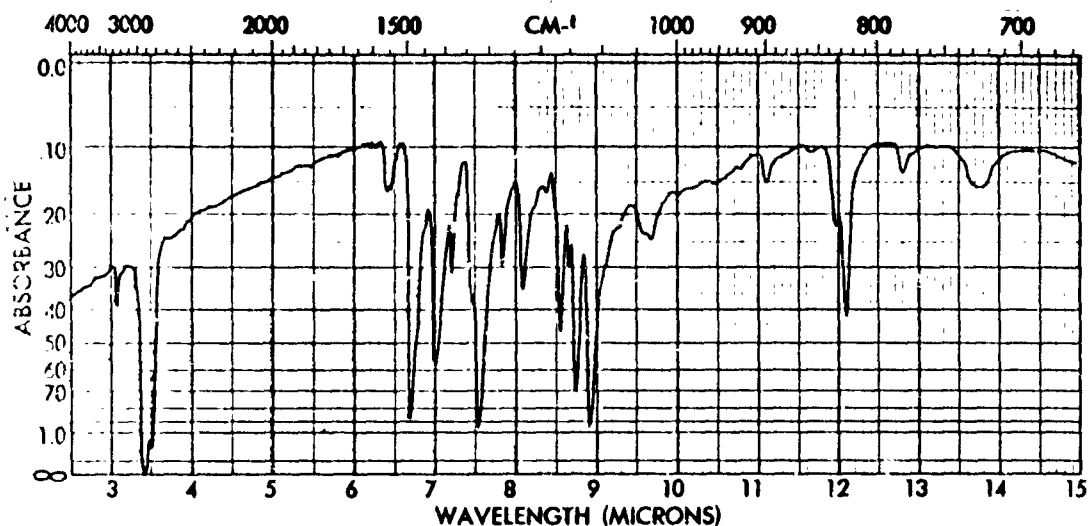
Synthetic Procedure: 1 % Yield: 79

| Analysis: | C | H | N | S | F | Cd |
|-----------|------|------|------|------|------|------|
| Found | 39.9 | 2.05 | 12.9 | | 26.1 | 12.9 |
| Calc. | 40.3 | 2.03 | 12.5 | 7.17 | 25.5 | 12.6 |

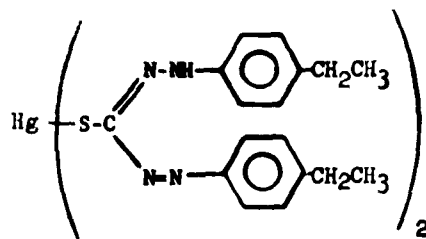
Spectral Data

| Color | λ_{Max} | ϵ | Thermal Return, Half Life: Less than 10 sec. |
|---------------------|-----------------|------------|---|
| Unirradiated Orange | 270 | 33,900 | % Conversion: 24 (Cary 14 NIR Source) |
| | 340 (sh) | 9,950 | |
| | 490 | 64,700 | |
| Irradiated | 630 | | Lightfastness in C.A. Film: 48 (Sun hours to 50% fade) |

Remarks: Cellulose acetate film - 20% conversion, thermal return, half life - ca. 45 sec. Purification solvent: ethanol-water.



Compound No.: 30 Name: Mercury bis[1,5-di(p-ethylphenyl)thiocarbazonate]



Mol. Wt.: 833.33 M.P.: 234-235 (d)

Appearance: Orange red needles

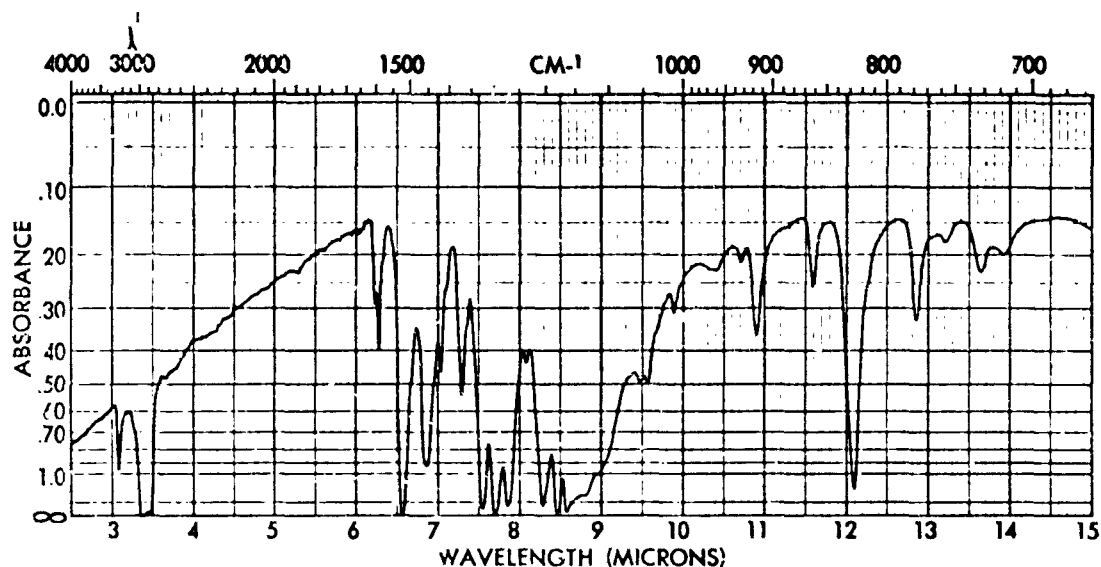
Synthetic Procedure: 1 % Yield: 15

| Analysis: | C | H | N | S | Hg |
|-----------|------|------|------|------|------|
| Found | 49.8 | 4.25 | 13.9 | 7.85 | 24.4 |
| Calc. | 49.6 | 4.65 | 13.6 | 7.79 | 24.4 |

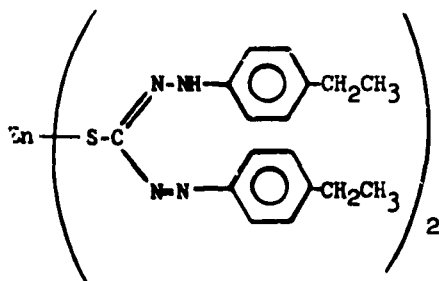
Spectral Data

| | Color | λ_{Max} | ϵ | Thermal Return, Half Life: 5.3 min. |
|--------------|--------|------------------------|------------|---|
| Unirradiated | Orange | 270 | 36,000 | % Conversion: 84 (Cary 14 NIR Source) |
| | | 498 | 70,700 | |
| Irradiated | Blue | 610 | | Lightfastness in C.A. Film: 31 (Sun hours to 50% fade) |

Remarks: Cellulose acetate film - 51% conversion; thermal return, half life - 13 min.
Purification solvent: chloroform-methanol.



Compound No. 31 Name: Zinc bis[1,5-di(p-ethylphenyl)thiocarbazonate]



Mol. Wt.: 689.10

M.P.: 282-283

Appearance: Purple solid, green iridescence.

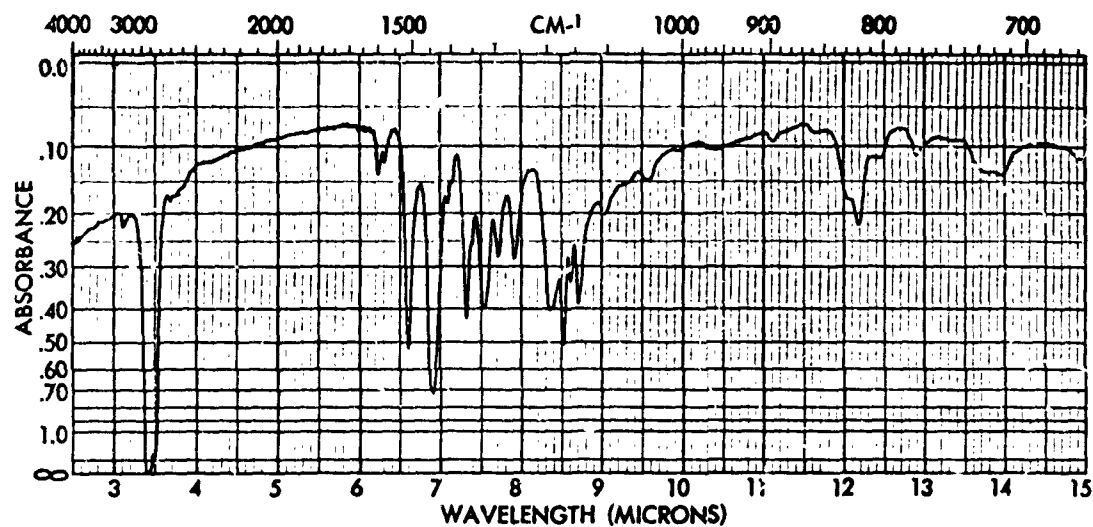
Synthetic Procedure: 1 % Yield: 100

| Analysis: | C | H | N | S | Zn |
|-----------|------|------|------|------|------|
| Found | 59.3 | 5.40 | 16.2 | 9.67 | 9.30 |
| Calc. | 59.3 | 5.57 | 16.3 | 9.32 | 9.50 |

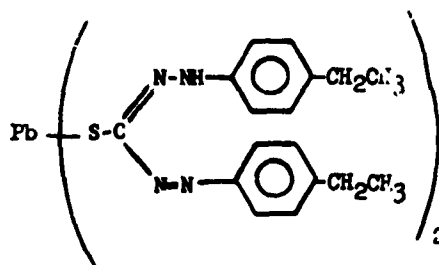
Spectral Data

| | Color | λ_{Max} | ϵ | Thermal Return, Half Life: 30 sec. |
|--------------|-------------|-----------------|------------|---|
| Unirradiated | Bluish Red | 280 | 30,700 | % Conversion: 66 (Cary 14 NIR Source) |
| | | 365 (sh) | 10,950 | |
| | | 540 | 94,900 | |
| Irradiated | Weak Violet | 690 | | Lightfastness in C.A. Film: 57 (Sun hours to 50% fade) |

Remarks: Cellulose acetate film - 45% conversion; thermal return, half life - 10 to 20 sec. Purification solvent: chloroform-methanol.



Compound No.: 32 Name: Lead bis[1,5-di(p-ethylphenyl)thiocarbazonate]



Mol. Wt.: 830.63 M.P.: 196-197 (d)

Appearance: Maroon needles

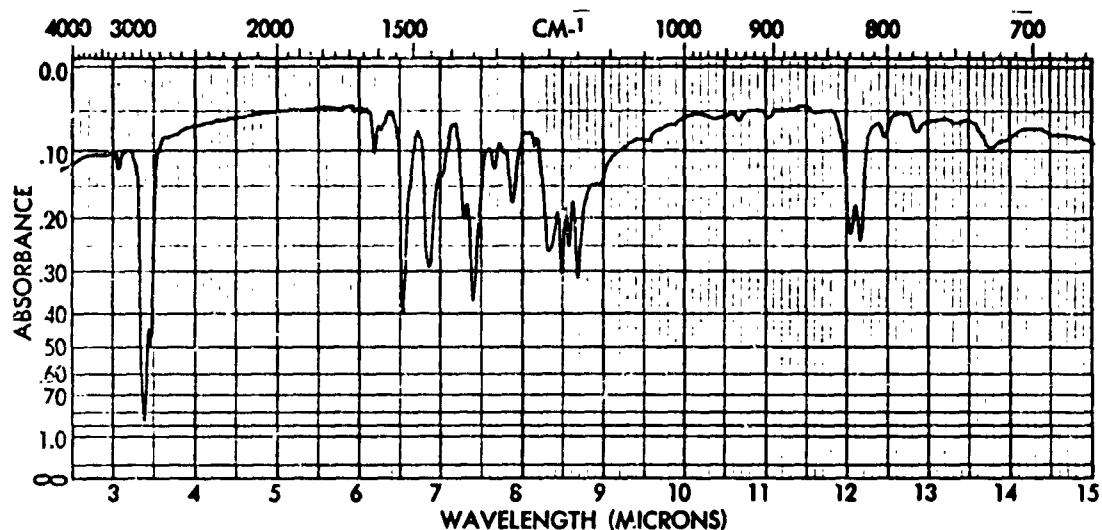
Synthetic Procedure: 1 % Yield: 15

| Analysis: | C | H | N | S | Pb |
|-----------|------|------|------|------|------|
| Found | 48.7 | 4.21 | 13.3 | 8.20 | 25.1 |
| Calc. | 49.2 | 4.62 | 13.5 | 7.73 | 25.0 |

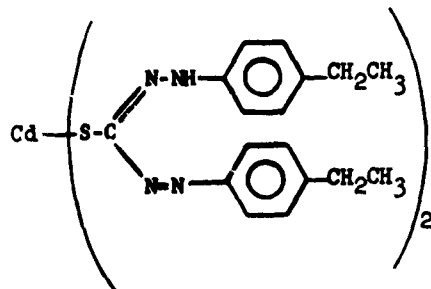
Spectral Data

| Color | λ_{Max} | ϵ | Thermal Return, Half Life: Less than 10 sec. |
|--------------|-----------------|------------|--|
| Unirradiated | | | % Conversion: 29 |
| Red | 270 | 37,300 | (Cary 14 NIR Source) |
| | 355 (sh) | 15,100 | |
| | 525 | 69,000 | Lightfastness in C.A. Film: 18 |
| Irradiated | | | (Sun hours to 50% fade) |
| Weak violet | 660 | | |

Remarks: Purification solvent: chloroform-methanol.



Compound No.: 33 Name: Cadmium bis[1,5-di(p-ethylphenyl)thiocarbazonate]



Mol. Wt.: 735.24

M.P.: 237-238

Appearance: Orange-red solid.

Synthetic Procedure: 1

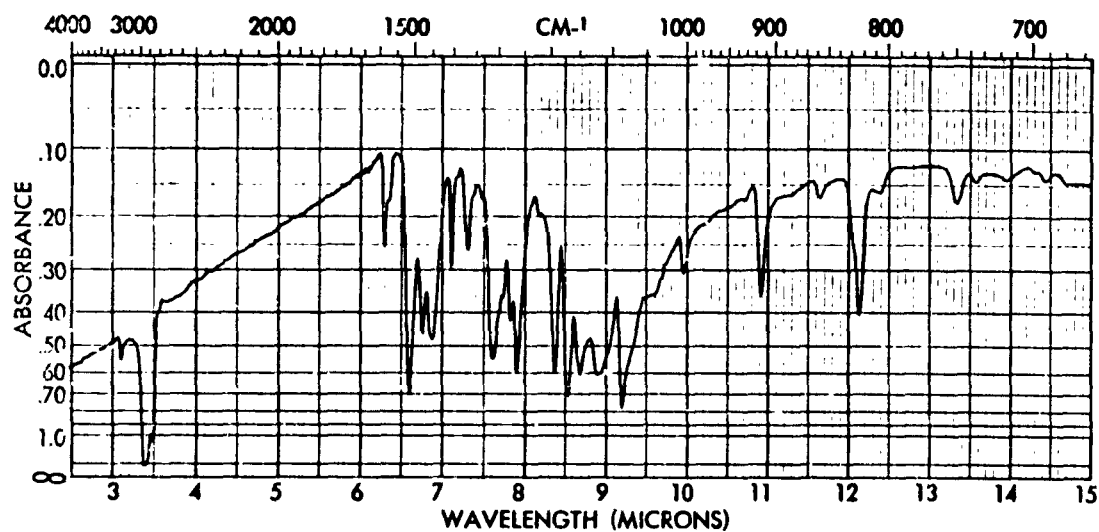
% Yield: 21

| Analysis: | C | H | N | S | Cl |
|-----------|------|------|------|------|------|
| Found | 55.3 | 5.25 | 15.2 | 8.52 | 15.2 |
| Calc. | 55.5 | 5.21 | 15.2 | 8.72 | 15.3 |

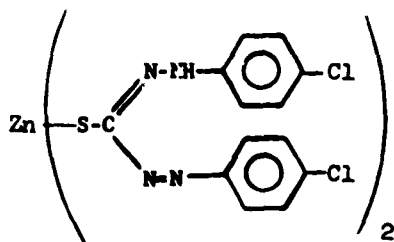
Spectral Data

| Color | λ_{Max} | ϵ | Thermal Return, Half Life: 7.4 sec. |
|--------------|-----------------|------------|-------------------------------------|
| Unirradiated | | | % Conversion: 56 |
| Red | 278 | 36,600 | (Cary 14 NIR Source) |
| | 345 (sh) | 12,850 | |
| | 525 | 96,000 | |
| Irradiated | | | Lightfastness in C.A. Film: 22 |
| Weak Violet | 665 | | (Sun hours to 50% fade) |

Remarks: Purification solvent: chloroform-methanol.



Compound No.: 34 Name: Zinc bis[1,5-di(p-chlorophenyl)thiocarbazonate]

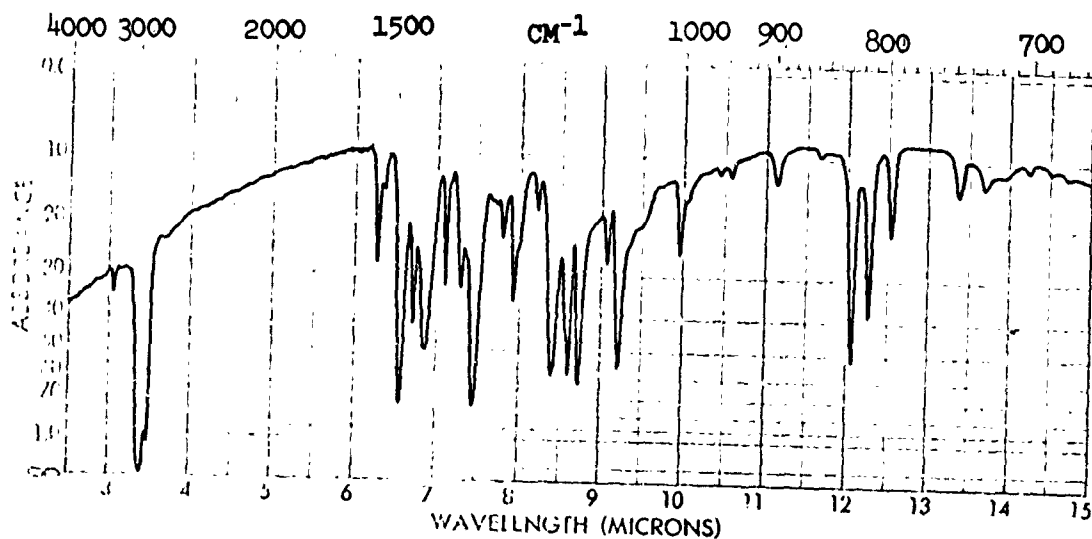


Mol. Wt.: 713.66 M.P.: 284-285 (d)
 Appearance: Purple solid, green iridescence.
 Synthetic Procedure: 1 % Yield: 83
 Analysis: C H N S Cl Zn
 Found 43.5 2.50 15.9 9.27 20.0 9.40
 Calc. 43.8 2.54 15.7 8.98 19.9 9.16

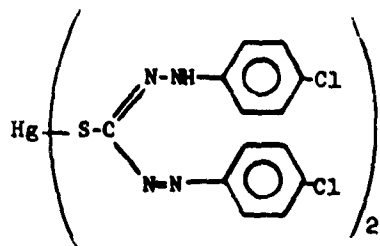
Spectral Data

| | Color | $\lambda_{Max.}$ | ϵ | Thermal Return, Half Life: 28 sec. |
|--------------|------------|------------------|------------|---|
| Unirradiated | Bluish Red | 280 | 33,100 | % Conversion: 64 (Cary 14 NIR Source) |
| | | 370 | 11,850 | |
| | | 540 | 97,800 | |
| Irradiated | Violet | 685 | | Lightfastness in C.A. Film: 35 (Sun hours to 50% fade) |

Remarks: Purification solvent: chloroform-methanol.



Compound No.: 35 Name: Mercury bis[1,5-di(p-chlorophenyl)thiocarbazonate]



Mol. Wt.: 848.89 M.P.: 259-260

Appearance: Red microcry tals

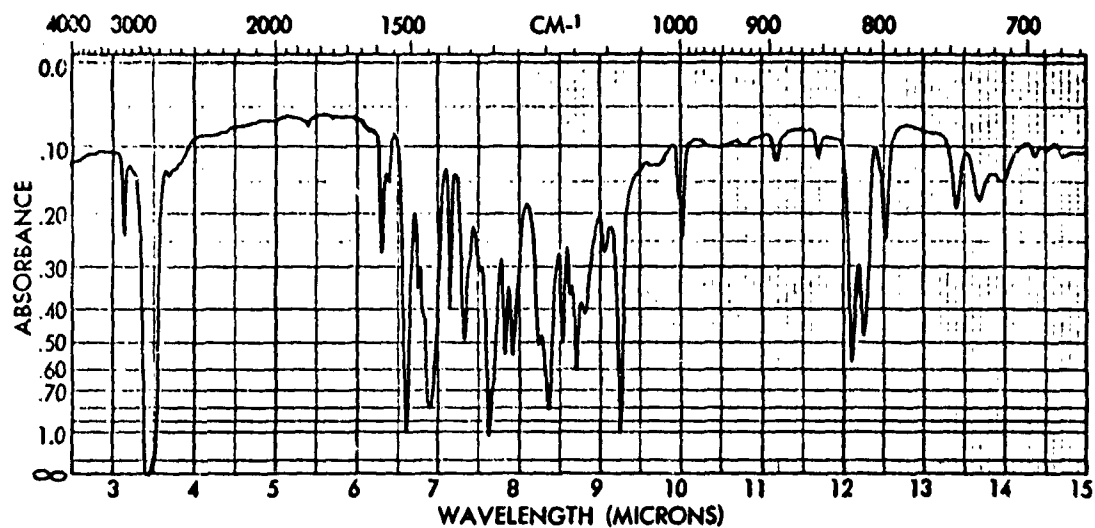
Synthetic Procedure: 1 % Yield: 55

| Analysis: | C | H | N | S | Hg |
|-----------|------|------|------|------|------|
| Found | 36.7 | 2.22 | 13.0 | 7.10 | 23.7 |
| Calc. | 36.8 | 2.14 | 13.2 | 7.55 | 23.6 |

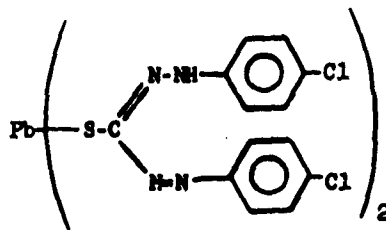
Spectral Data

| | Color | λ_{Max} | ϵ | Thermal Return, Half Life: 6 min. |
|--------------|--------|-----------------|------------|--|
| Unirradiated | Orange | 495 | ? | % Conversion: 90 (Cary 14 NIR Source) |
| Irradiated | Blue | 610 | | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks: Poor solubility in CH_2Cl_2 , insoluble in cellulose acetate film.
Purification solvent: tetrahydrofuran-methanol.



Compound No.: 36 Name: Lead bis[1,5-di(p-chlorophenyl)thiocarbazonate]



Mol. Wt.: 855.63 M.P.: 268-269 (d)

Appearance: Red-brown iridescent powder.

Synthetic Procedure: 1 % Yield: 50

| Analysis: | C | H | N | S | Cl | Pb |
|-----------|------|------|------|------|------|------|
| Found | 36.1 | 1.94 | 13.2 | 7.67 | 16.7 | 24.0 |
| Calc. | 36.5 | 2.12 | 13.1 | 7.49 | 16.6 | 24.2 |

Spectral Data

Color $\lambda_{Max.}$ ξ

Unirradiated

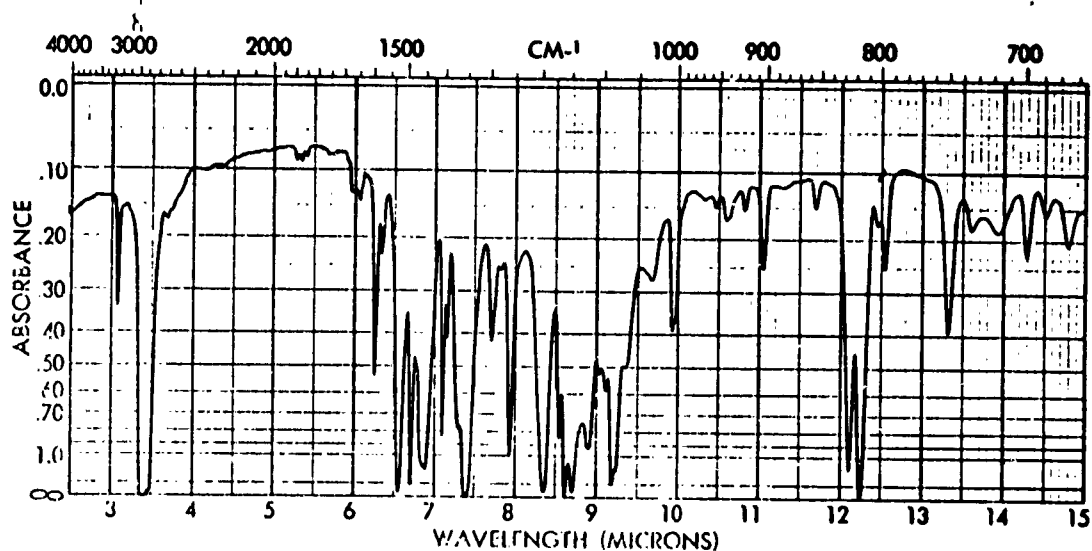
Irradiated

Thermal Return, Half Life:

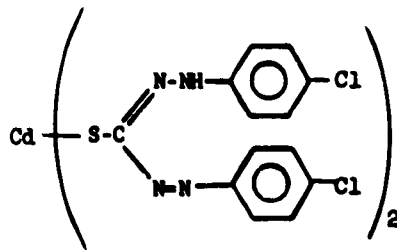
% Conversion:
(Cary 14 NIR Source)

Lightfastness in C.A. Film:
(Sun hours to 50% fade)

Remarks: Too insoluble to evaluate in CH_2Cl_2 . Washed with acetone for purification.



Compound No.: 37 Name: Cadmium bis[1,5-di(p-chlorophenyl)thiocarbazonate]



Mol. Wt.: 760.82

M.P.: 294 (d)

Appearance: Orange solid

Synthetic Procedure: 1 % Yield: 61

| Analysis: | C | H | N | S | Cl | Cd |
|-----------|------|------|------|------|------|------|
| Found | 41.1 | 2.36 | 14.7 | 8.91 | 18.8 | 14.8 |
| Calc. | 41.0 | 2.38 | 14.2 | 8.32 | 18.7 | 14.8 |

Spectral Data

Color λ_{Max} ξ

Thermal Return, Half Life:

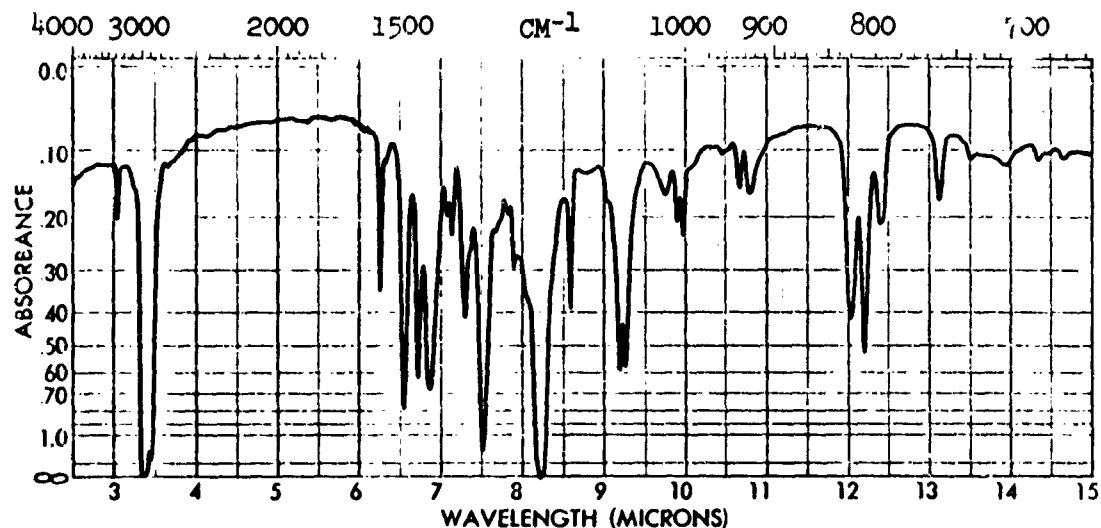
Unirradiated

% Conversion:
(Cary 14 NIR Source)

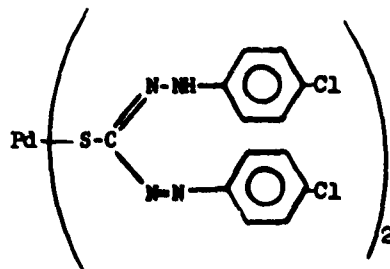
Irradiated

Lightfastness in C.A. Film:
(Sun hours to 50% fade)

Remarks: Too insoluble to evaluate in CH_2Cl_2 or cellulose acetate film.
Purification solvent: dimethylformamide.



Compound No.: 38 Name: Palladium bis[1,5-di(p-chlorophenyl)thiocarbazonate]



Mol. Wt.: 750.12 M.P.: 305-306 (d)

Appearance: Gray-black powder

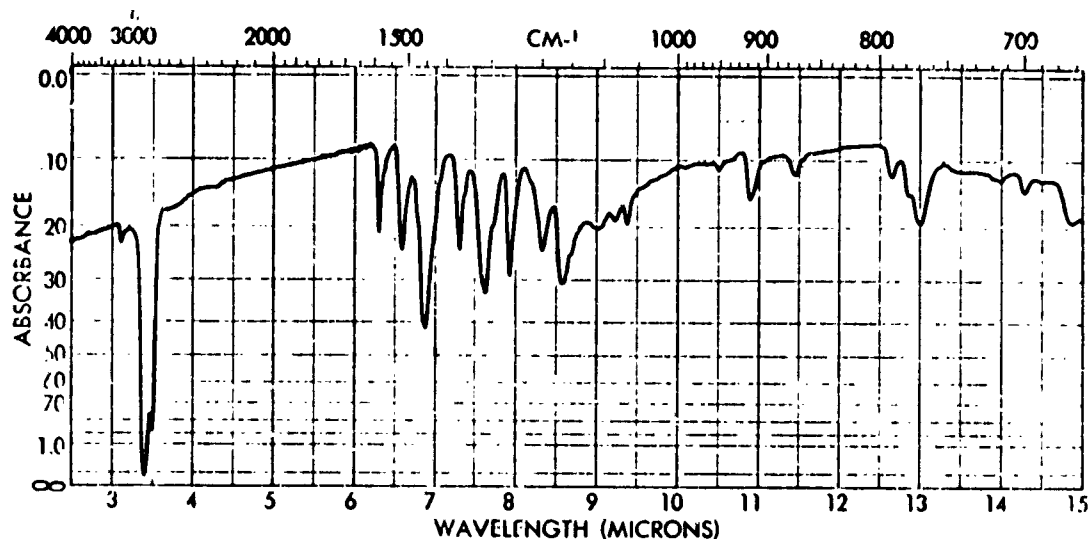
Synthetic Procedure: 2 % Yield: 87

| Analysis: | C | H | N | S | Cl | Pd |
|-----------|------|------|------|------|------|------|
| Found | 41.0 | 2.39 | 14.8 | 8.50 | 19.1 | 13.5 |
| Calc. | 41.3 | 2.41 | 14.9 | 8.50 | 18.8 | 14.2 |

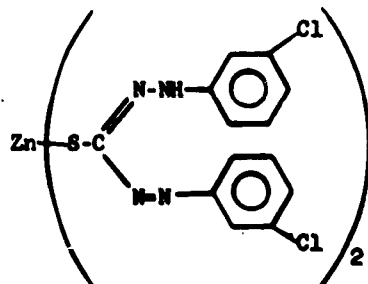
Spectral Data

| | Color | λ Max. | ϵ | Thermal Return, Half Life: Very fast. |
|--------------|--------|-----------------|------------|--|
| Unirradiated | Violet | 510 560 (sh) | | % Conversion: Est. 5% (Cary 14 NIR Source) |
| Irradiated | | | | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks: Poor solubility in CH_2Cl_2 , insoluble in cellulose acetate film.
Purification: slurried with acetone.



Compound No.: 39 Name: Zinc bis[1,5-di(m-chlorophenyl)thiocarbazonate]



Mol. Wt.: 713.66 M.P.: 258-258-1/2

Appearance: Maroon iridescent crystals,

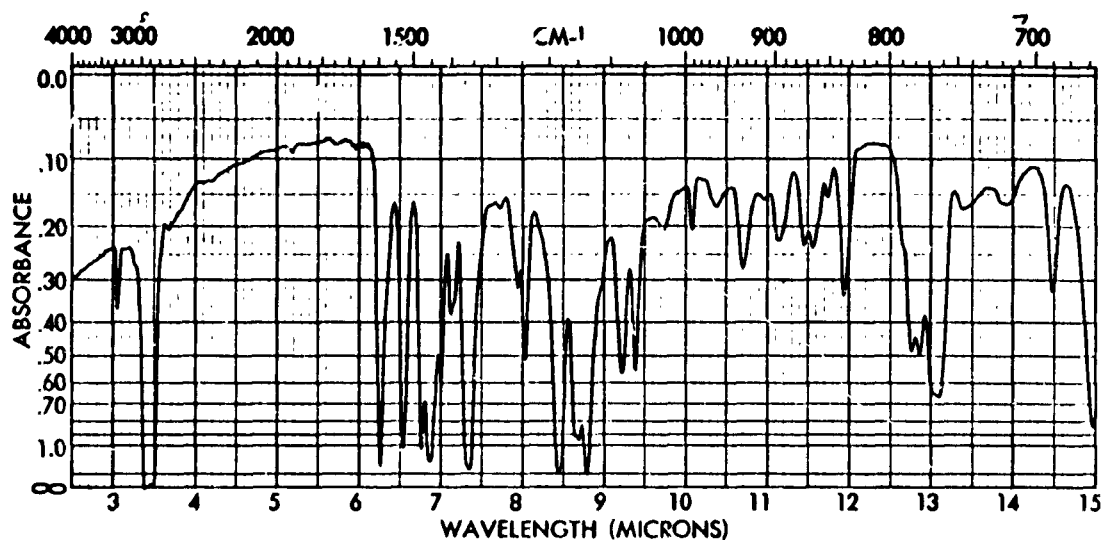
Synthetic Procedure: 1 % Yield: 55

| Analysis: | C | H | N | S | Cl | Zn |
|-----------|------|------|------|------|------|------|
| Found | 44.1 | 2.87 | 15.9 | 8.59 | 20.0 | 8.90 |
| Calc. | 43.8 | 2.54 | 15.7 | 8.98 | 19.9 | 9.16 |

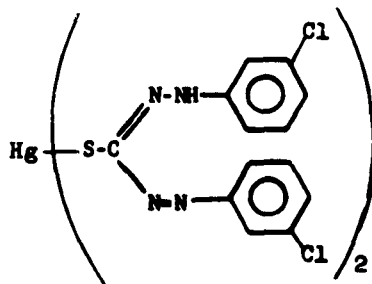
Spectral Data

| | Color | λ_{Max} | ϵ | Thermal Return, Half Life: 22-23 sec. |
|--------------|--------|-----------------|------------|---|
| Unirradiated | Red | 280 | 34,500 | % Conversion: (Cary 14 NIR Source) 59 |
| | | 365 | 11,050 | |
| | | 530 | 89,300 | |
| Irradiated | Violet | 680 | | Lightfastness in C.A. Film: 32 (Sun hours to 50% fade) |

Remarks: Purification solvent: tetrahydrofuran-methanol.



Compound No.: 40 Name: Mercury bis[1,5-di(m-chlorophenyl)thiocarbazonate]



Mol. Wt.: 848.89 M.P.: 242-243 (d)

Appearance: Orange crystals

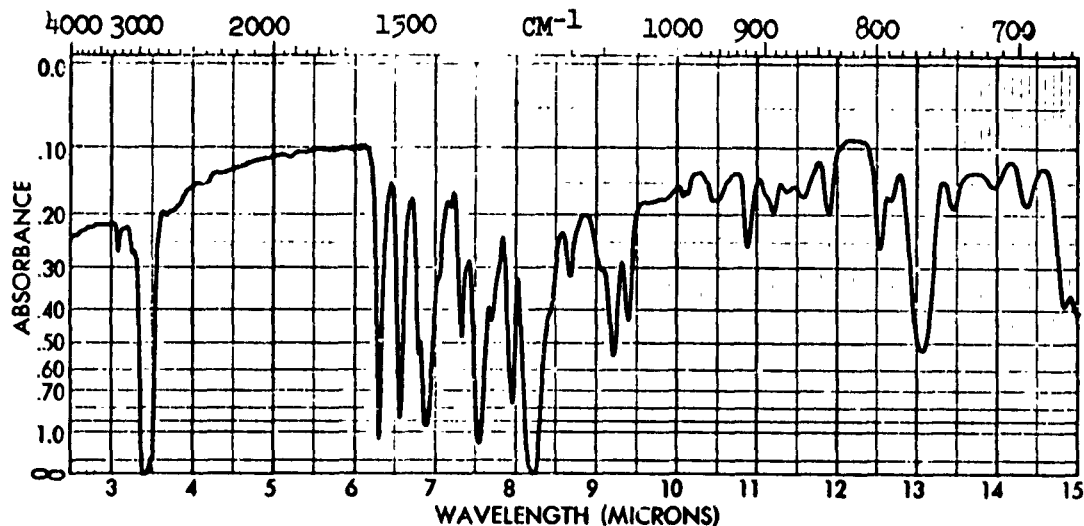
Synthetic Procedure: 1 % Yield: 60%

| Analysis: | C | H | N | S | Cl | Hg |
|-----------|------|------|------|------|------|------|
| Found | 36.6 | 2.56 | 13.3 | 7.20 | 16.5 | 23.5 |
| Calc. | 36.8 | 2.14 | 13.2 | 7.55 | 16.4 | 23.6 |

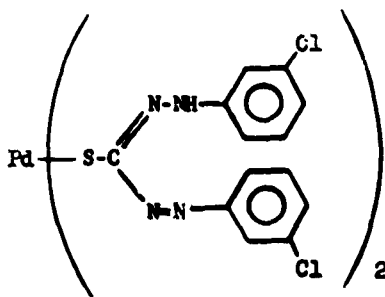
Spectral Data

| | Color | λ Max. | ϵ | Thermal Return, Half Life: |
|--------------|--------|----------------|------------|---|
| Unirradiated | Orange | 270 | 27,200 | % Conversion: 87 (Cary 14 NIR Source) |
| | | 305 (sh) | 14,300 | |
| | | 485 | 60,900 | |
| Irradiated | Blue | 600 | | Lightfastness in C.A. Film: 56 (Sun hours to 50% fade) |

Remarks: Purification solvent: benzene.



Compound No.: 41 Name: Palladium bis[1,5-di(m-chlorophenyl)thiocarbazonate]



Mol. Wt.: 753.12 M.P.: 277-278 (d)

Appearance: Black solid

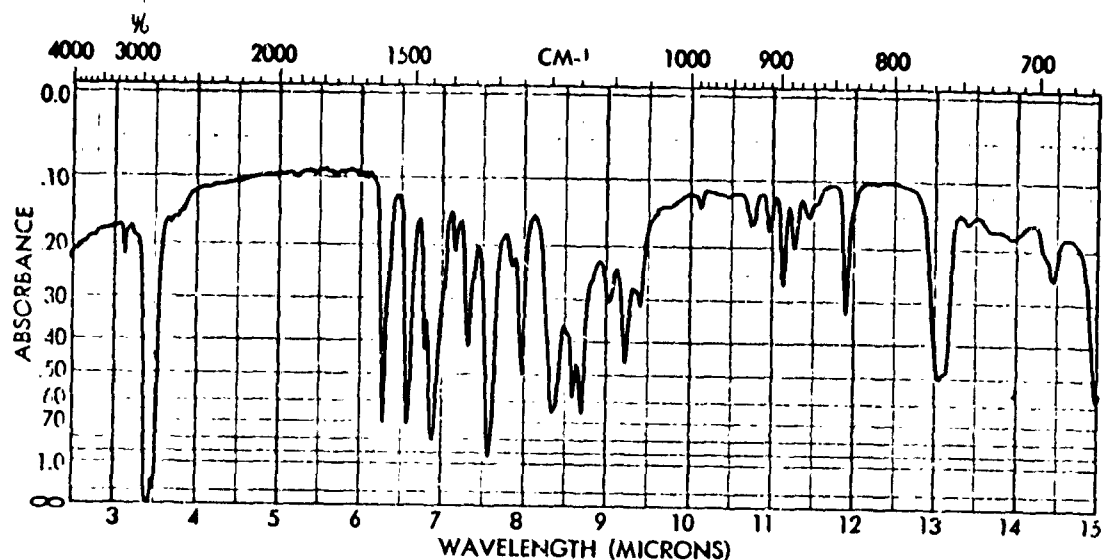
Synthetic Procedure: 2 % Yield: 40

| Analysis: | C | H | N | S | Cl | Pd |
|-----------|------|------|------|------|------|------|
| Found | 41.7 | 2.61 | 14.9 | 8.75 | 19.0 | 14.2 |
| Calc. | 41.4 | 2.41 | 14.9 | 8.51 | 18.9 | 14.2 |

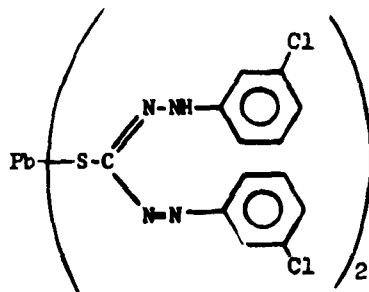
Spectral Data

| | Color | $\lambda_{\text{Max.}}$ | ϵ | Thermal Return, Half Life: Very fast |
|--------------|--------|-------------------------|------------|--|
| Unirradiated | Green | 280 452 640 | | % Conversion: Est. 56% (Cary 14 NIR Source) |
| Irradiated | Orange | | | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks: Poor solubility in CH_2Cl_2 , insoluble cellulose acetate film. Purification solvent: tetrahydrofuran.



Compound No.: 42 Name: Lead bis[1,5-di(m-chlorophenyl)thiocarbazonate]



Mol. Wt.: 855.63 M.P.: 241-242 (d)

Appearance: Bronze microneedles

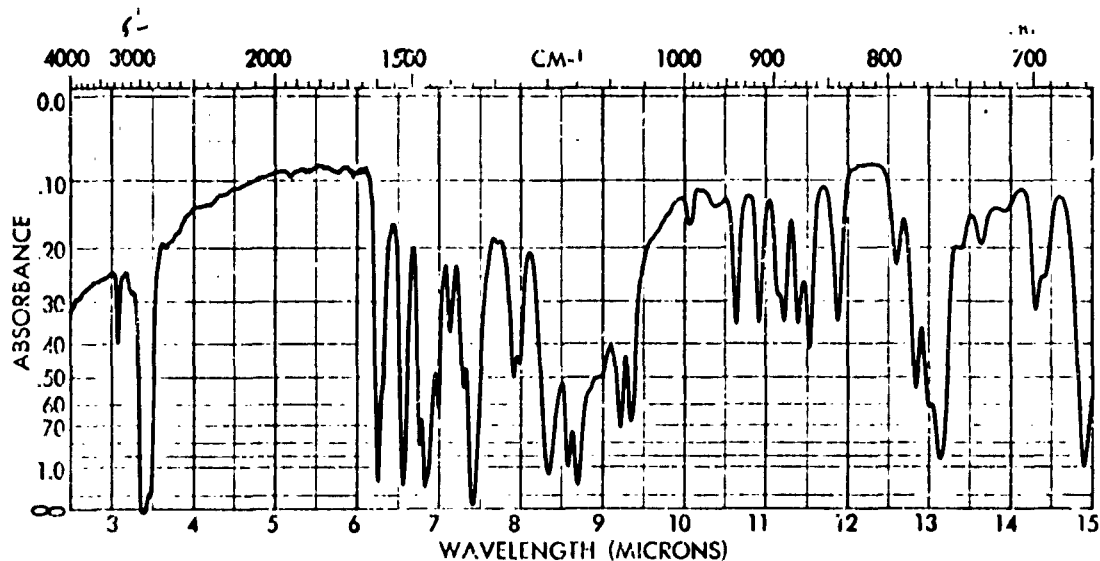
Synthetic Procedure: 1 % Yield: 35

| Analysis: | C | H | N | S | Cl | Pb |
|-----------|------|------|------|------|------|------|
| Found | 37.1 | 2.38 | 12.2 | 7.43 | 15.8 | 23.8 |
| Calc. | 36.5 | 2.12 | 13.1 | 7.49 | 16.6 | 24.2 |

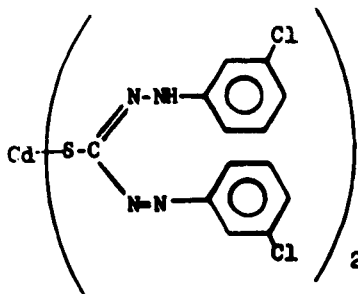
Spectral Data

| | |
|---|--|
| <p>Color $\lambda_{Max.}$ \leq</p> <p>Unirradiated Pale pink - sat. solution.</p> <p>Irradiated</p> | <p>Thermal Return, Half Life:</p> <p>% Conversion: (Cary 14 NIR Source)</p> <p>Lightfastness in C.A. Film: (Sun hours to 50% fade)</p> |
|---|--|

Remarks: Too insoluble to evaluate in CH_2Cl_2 . Purification solvent: tetrahydrofuran.



Compound No.: 43 Name: Cadmium bis[1,5-di(m-chlorophenyl)thiocarbazonate]



Mol. Wt.: 760.82 M.P.: 288-289 (d)

Appearance: Orange solid

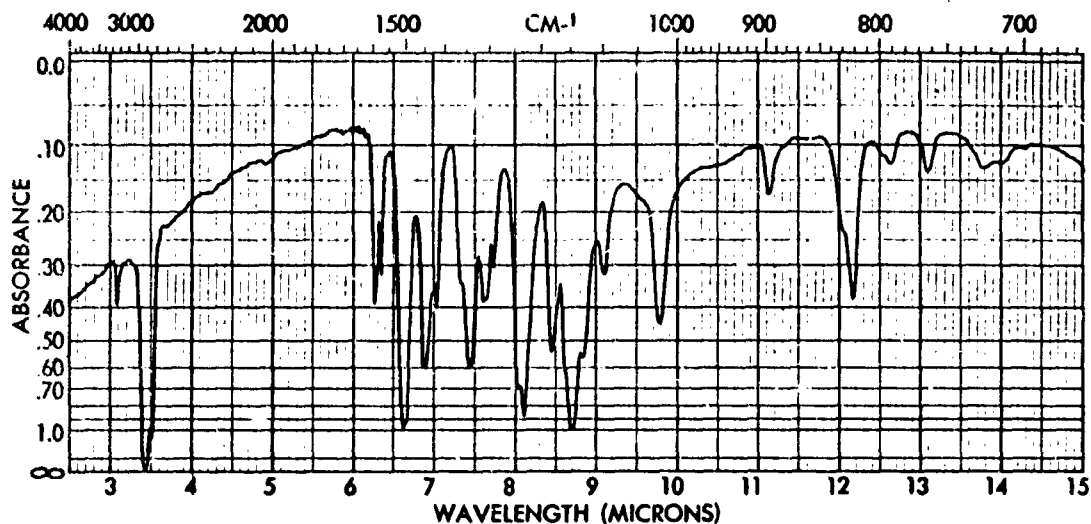
Synthetic Procedure: 1 % Yield: 37

| Analysis: | C | H | N | S | Cl | Cd |
|-----------|------|------|------|------|------|------|
| Found | 40.9 | 2.40 | 14.4 | 8.26 | 18.5 | 14.3 |
| Calc. | 41.0 | 2.38 | 14.8 | 8.32 | 18.7 | 14.8 |

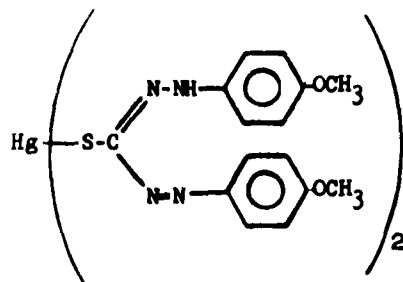
Spectral Data

| | | | |
|--------------|-----------------|------------|--|
| Color | λ_{Max} | ϵ | Thermal Return, Half Life: |
| Unirradiated | | | % Conversion: (Cary 14 NIR Source) |
| Irradiated | | | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks: Poor solubility in CH_2Cl_2 . Purification solvent: tetrahydrofuran-methanol.



Compound No.: 44 Name: Mercury bis[1,5-di(p-methoxyphenyl)thiocarbazonate]



Mol. Wt.: 831.37 M.P.: 211-212 (d)

Appearance: Dark red micro needles.

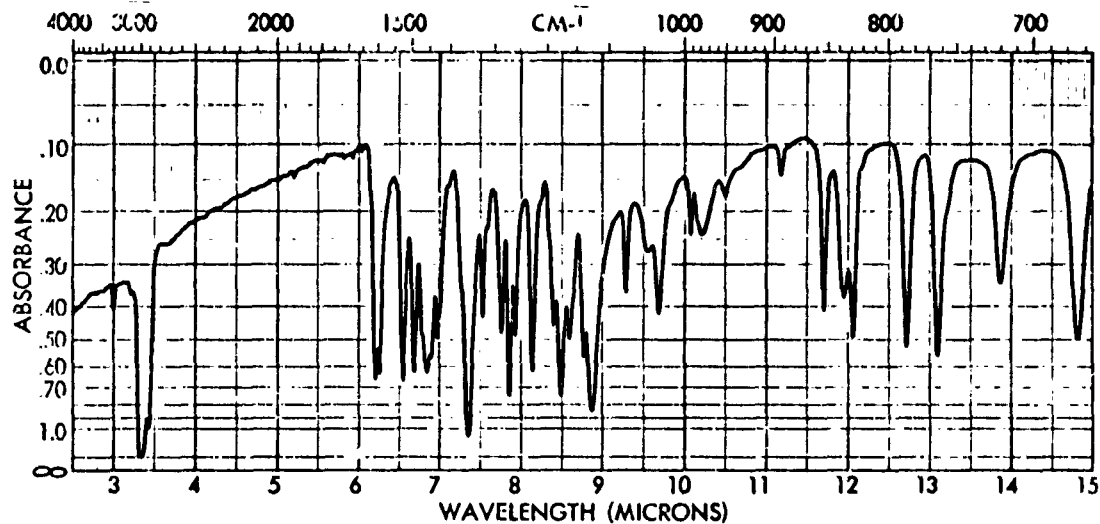
Synthetic Procedure: 1 % Yield: 66

| Analysis: | C | H | N | S | Hg |
|-----------|------|------|------|------|------|
| Found | 42.6 | 3.52 | 13.5 | 8.05 | 24.4 |
| Calc. | 43.3 | 3.64 | 13.5 | 7.72 | 24.1 |

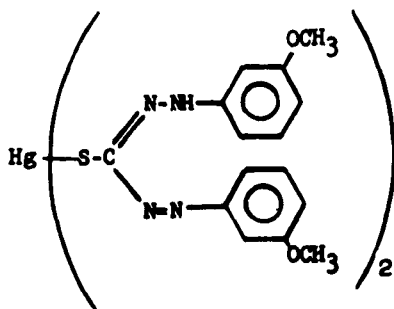
Spectral Data

| | Color | λ_{Max} | Σ | Thermal Return, Half Life: |
|--------------|--------------|-----------------|----------|---|
| Unirradiated | Pinky Orange | 270 | 29,200 | % Conversion: 86 (Cary 14 NIR Source) |
| | | 320 (sh) | 21,500 | |
| | | 510 | 72,000 | |
| Irradiated | Blue | 620 | | Lightfastness in C.A. Film: 30 (Sun hours to 50% fade) |

Remarks: Purification solvent: benzene.



Compound No.: 45 Name: Mercury bis[1,5-di(m-methoxyphenyl)thiocarbazonate]



Mol. Wt.: 831.37 M.P.: 190-191 (d)

Appearance: Red needles

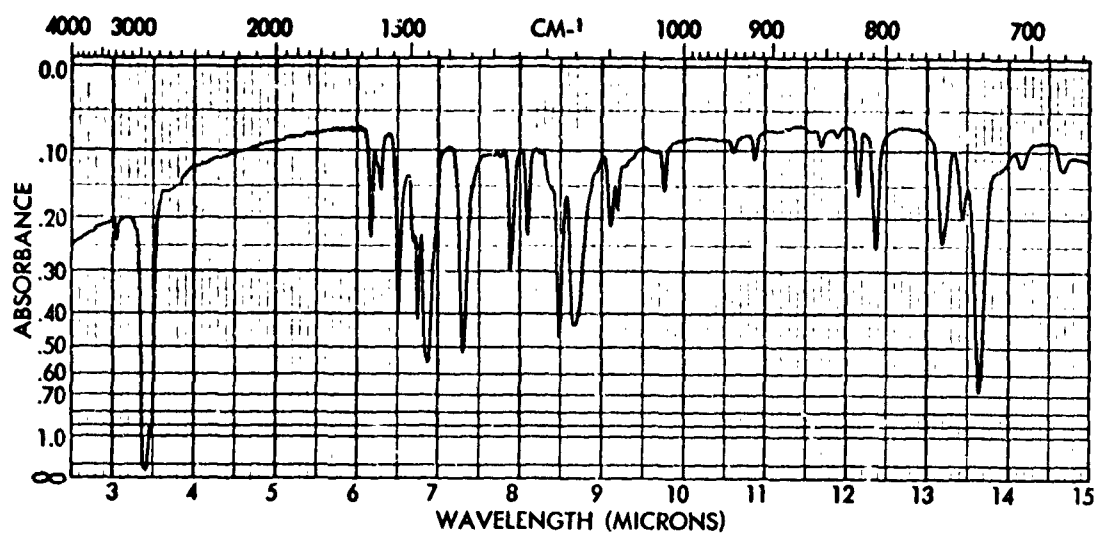
Synthetic Procedure: 1 % Yield: 40

| Analysis: | C | H | N | S | Hg |
|-----------|------|------|------|------|------|
| Found | 42.9 | 3.52 | 13.3 | 7.70 | 24.6 |
| Calc. | 43.3 | 3.64 | 13.5 | 7.71 | 24.1 |

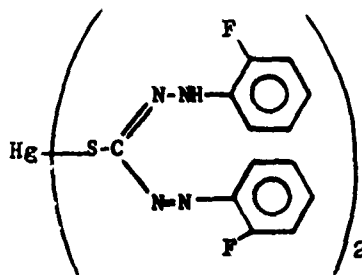
Spectral Data

| | Color | λ_{Max} | ϵ | Thermal Return, Half Life: |
|--------------|--------|-----------------|------------|---|
| Unirradiated | Orange | 270 | 31,200 | % Conversion: 83 (Cary 14 NIR Source) |
| | | 320 (sh) | 12,450 | |
| | | 490 | 64,200 | |
| Irradiated | Blue | 600 | | Lightfastness in C.A. Film: 37 (Sun hours to 50% fade) |

Remarks: Purification solvent: benzene.



Compound No.: 46 Name: Mercury bis[1,5-di(o-fluorophenyl)thiocarbazonate]



Mol. Wt.: 783.06 M.P.: 240-240-1/2 (a)

Appearance: Fine orange needles.

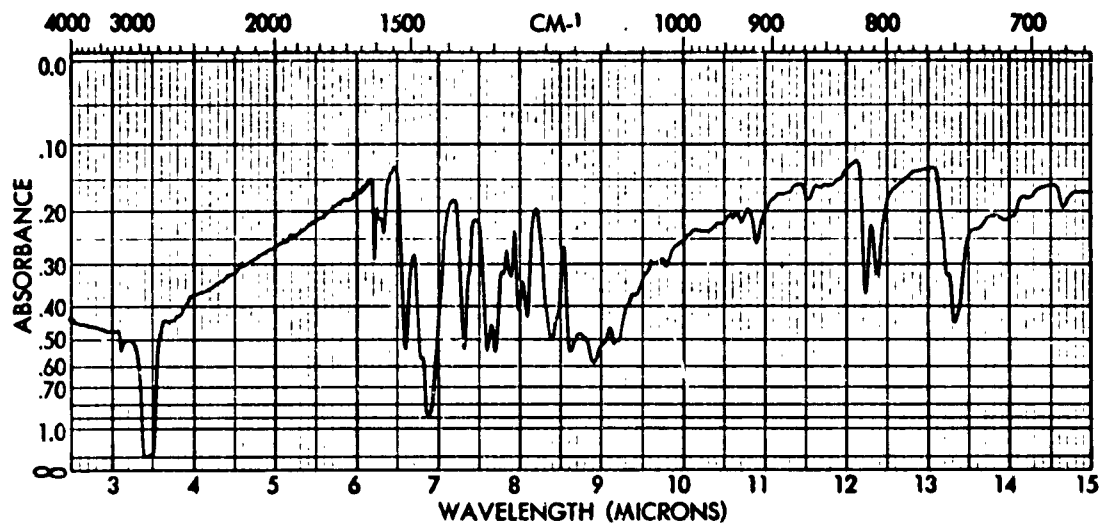
Synthetic Procedure: 1 % Yield: 80

| Analysis: | C | H | N | S | F | Hg |
|-----------|------|------|------|------|------|------|
| Found | 39.9 | 2.44 | 14.4 | 8.68 | 9.70 | 25.3 |
| Calc. | 39.9 | 2.32 | 14.3 | 8.18 | 9.70 | 25.6 |

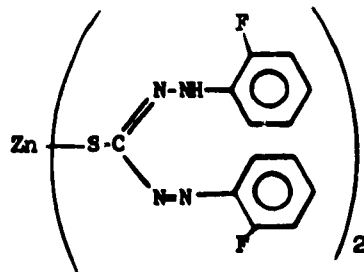
Spectral Data

| Color | λ_{Max} | ϵ | Thermal Return, Half Life: 62 min. |
|---------------------|-----------------|------------------|--|
| Unirradiated Orange | 260 485 | 34,600 52,800 | % Conversion: 90-95 (Cary 14 NIR Source) |
| Irradiated Blue | 590 | | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks: Insoluble in cellulose acetate film. Purification solvent: tetrahydrofuran.



Compound No.: 47 Name: Zinc bis[1,5-di(o-fluorophenyl)thiocarbazonate]



Mol. Wt.: 648.83 M.P.: 240-241 (d)

Appearance: Green iridescent needles.

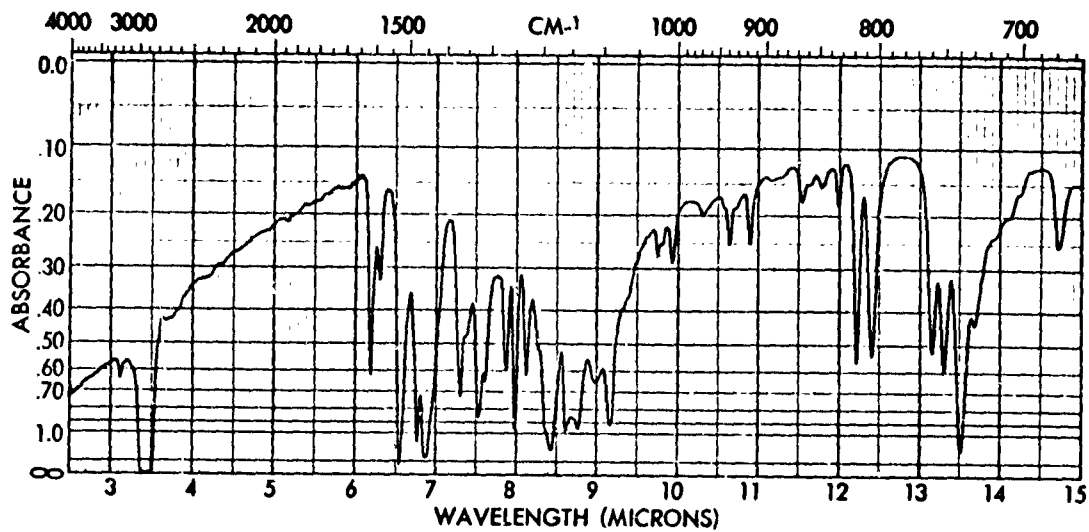
Synthetic Procedure: 1 % Yield: 90

| Analysis: | C | H | N | S | F | Zn |
|-----------|------|------|------|------|------|------|
| Found | 47.7 | 3.04 | 17.1 | 9.95 | 11.7 | 9.85 |
| Calc. | 48.2 | 2.80 | 17.3 | 9.98 | 11.7 | 10.1 |

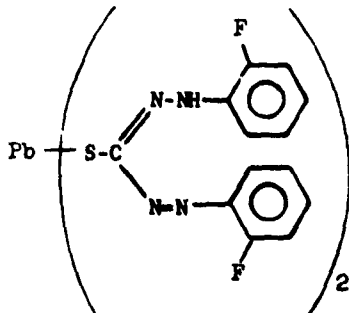
Spectral Data

| Color | λ Max. | ϵ | Thermal Return, Half Life: 33 sec. |
|----------------------------|----------------|------------|--|
| Unirradiated Bluish Red | 275 | 28,340 | % Conversion: 63 (Cary 14 NIR Source) |
| | 370 | 12,500 | |
| | 527 | 84,100 | |
| Irradiated Violet | 680 | | Lightfastness in C.A. Film: 26' (Sun hours to 50% fade) |

Remarks: 'fication solvent: chloroform-methanol.



Compound No.: 48 Name: Lead bis[1,5-di(o-fluorophenyl)thiocarbazonate]



Mol. Wt.: 790.36 M.P.: 208-209

Appearance: Reddish-brown iridescent micro crystals.

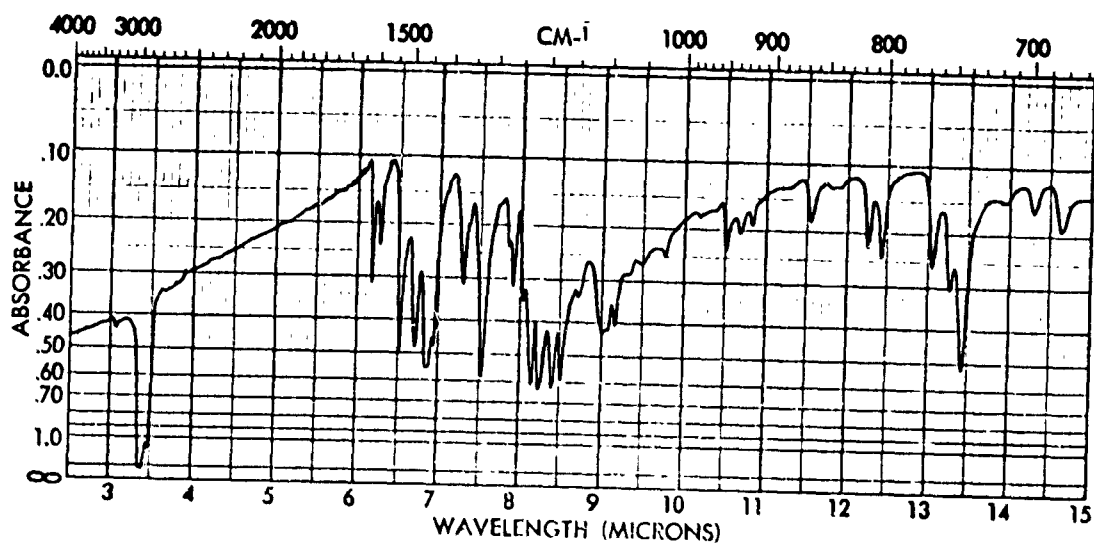
Synthetic Procedure: 1 % Yield: 25

| Analysis: | C | H | N | S | F | Pb |
|-----------|------|------|------|------|-----|------|
| Found | 39.9 | 2.30 | 13.9 | 8.30 | 9.3 | 26.5 |
| Calc. | 39.5 | 2.30 | 14.2 | 8.12 | 9.6 | 26.2 |

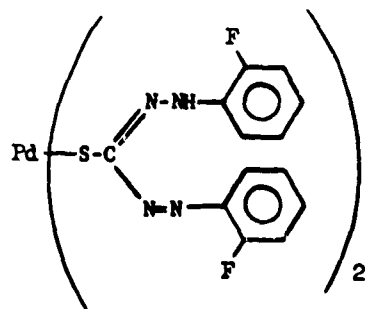
Spectral Data

| | Color λ Max. μ | Thermal Return, Half Life: |
|--------------|----------------------------|--|
| Unirradiated | Red | % Conversion: (Cary 14 NIR Source) |
| Irradiated | Sl. Bluish-Red | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks: Purification solvent: chlorobenzene.



Compound No.: 49 Name: Palladium bis[1,5-di(o-fluorophenyl)thiocarbazonate]



Mol. Wt.: 689.15 M.P.: 285-286 (d)

Appearance: Purple iridescent microcrystals.

Synthetic Procedure: 2 % Yield: 27

| Analysis: | C | H | N | S | F | Pd |
|-----------|------|------|------|------|------|------|
| Found | 45.1 | 2.56 | 16.5 | 9.34 | 11.3 | 15.4 |
| Calc. | 45.3 | 2.63 | 16.3 | 9.31 | 11.0 | 15.4 |

Spectral Data

Color λ_{Max} ξ
 Unirradiated
 Yellowish Green

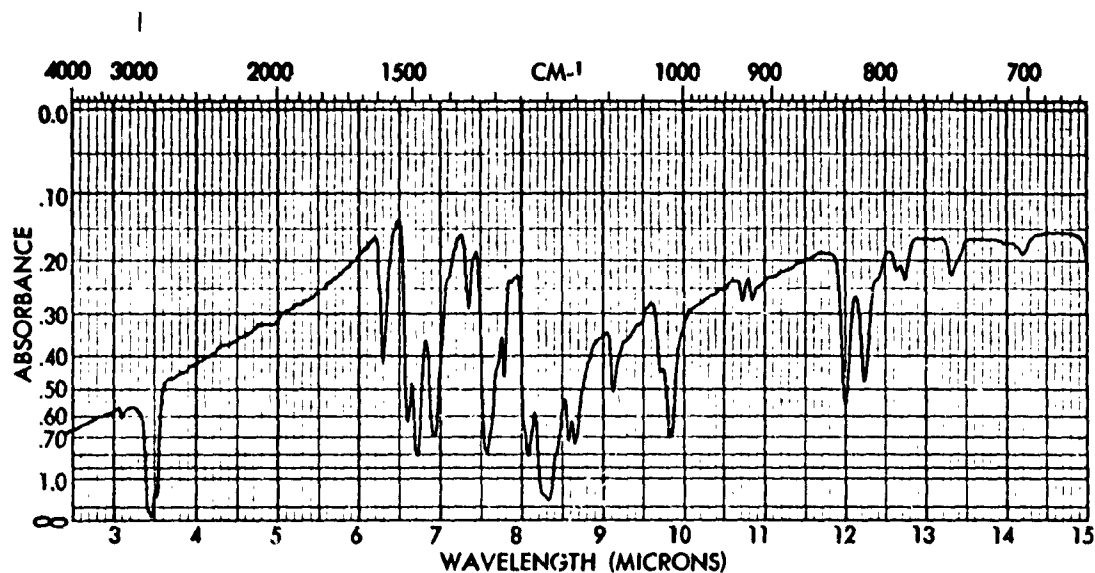
Irradiated

Thermal Return, Half Life:

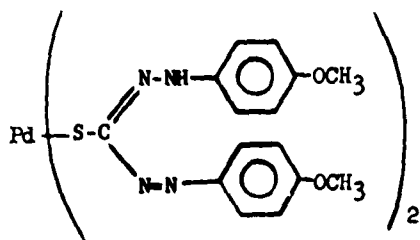
% Conversion:
 (Cary 14 NIR Source)

Lightfastness in C.A. Film:
 (Sun hours to 50% fade)

Remarks: Poor solubility in CH_2Cl_2 . Purification solvent: chlorobenzene.



Compound No.: 50 Name: Palladium bis[1,5-di(p-methoxyphenyl)thiocarbazonate]



Mol. Wt.: 737.46 M.P.: 254-255 (d)

Appearance: Purple iridescent plates.

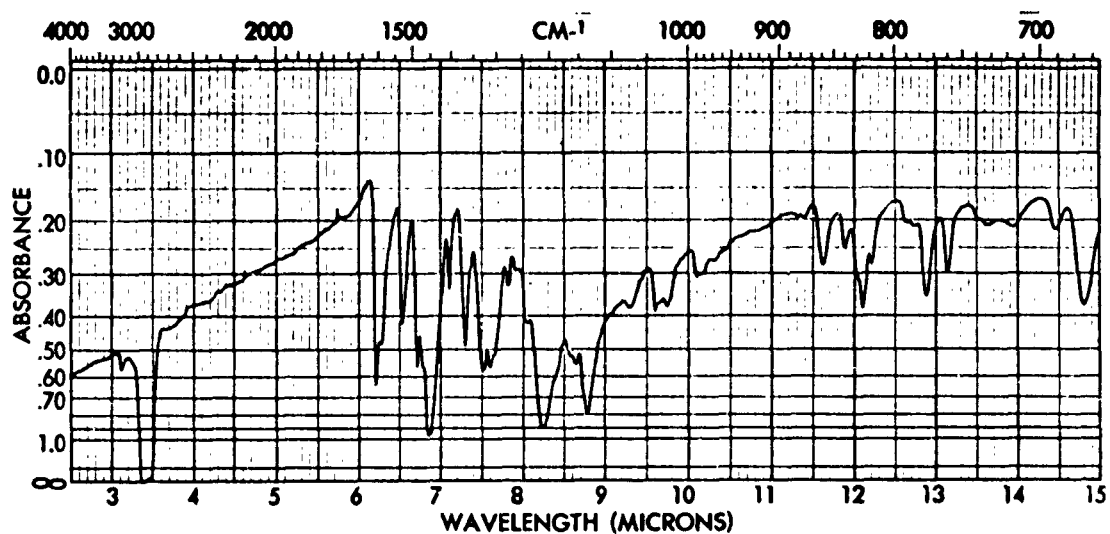
Synthetic Procedure: 2 % Yield: 50

| Analysis: | C | H | N | S | Pd |
|-----------|------|------|------|------|------|
| Found | 48.9 | 4.11 | 15.1 | 8.79 | 14.7 |
| Calc. | 49.0 | 4.11 | 15.3 | 8.72 | 14.5 |

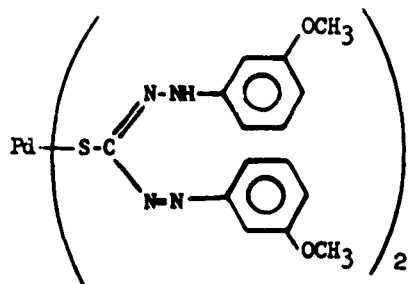
Spectral Data

| | Color | λ_{Max} | Σ | Thermal Return, Half Life: |
|--------------|--------|-----------------|----------|--|
| Unirradiated | Green | 275 | 34,850 | % Conversion: 100 (Cary 14 NIR Source) |
| | | 475 | 25,600 | |
| | | 565 | 33,100 | |
| | | 650 | 35,900 | |
| Irradiated | Orange | 510 | 35,200 | Lightfastness in C.A. Film: (Sun hours to 50% fade) |
| | | 800 | 24,300 | |
| | | | | |

Remarks: Insoluble in cellulose acetate film. Purification solvent: tetrahydrofuran-methanol.



Compound No.: 51 Name: Palladium bis[1,5-di(m-methoxyphenyl)thiocarbazonate]



Mol. Wt.: 737.46 M.P.: 251-252 (d)

Appearance: Purple iridescent plates.

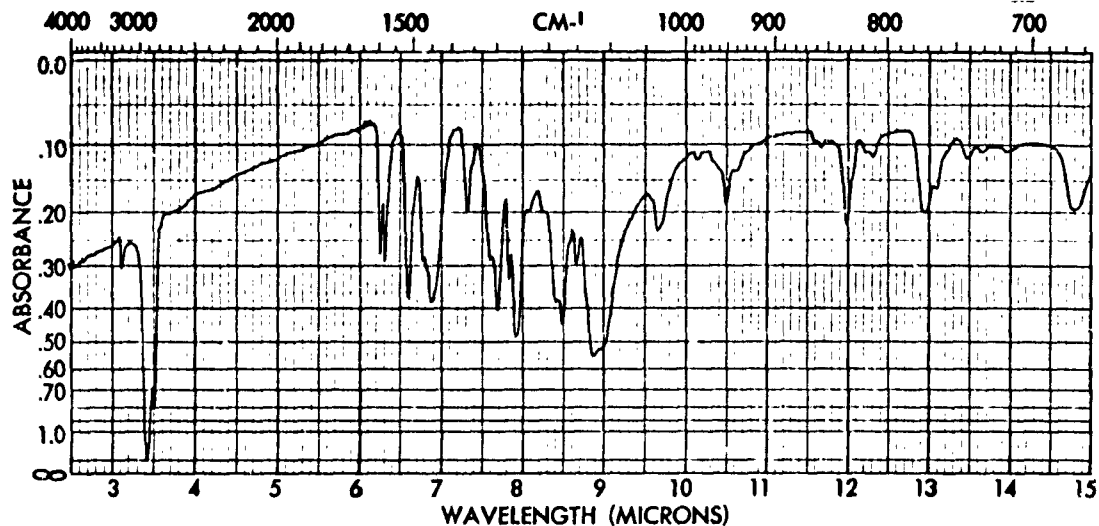
Synthetic Procedure: 2 % Yield: 26

| Analysis: | C | H | N | S | Pd |
|-----------|------|------|------|------|------|
| Found | 49.2 | 4.09 | 15.2 | 8.67 | 14.7 |
| Calc. | 49.0 | 4.11 | 15.3 | 8.72 | 14.5 |

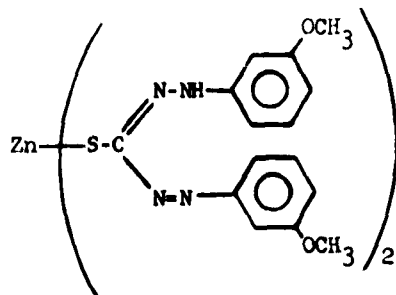
Spectral Data

| Color | λ_{Max} | Σ | Thermal Return, Half Life: |
|--------------------|-----------------|----------|--|
| Unirradiated Green | 285 | 38,600 | % Conversion: 100 (Cary 14 NIR Source) |
| | 455 | 32,900 | |
| | 640 | 32,300 | |
| Irradiated Yellow | 490 | 29,800 | Lightfastness in C.A. Film: (Sun hours to 50% fade) |
| | 790 | 20,800 | |

Remarks: Insoluble in cellulose acetate film. Purification solvent: tetrahydrofuran-methanol.



Compound No.: 52 Name: Zinc bis[1,5-di(m-methoxyphenyl)thiocarbazonate]



Mol. Wt.: 696.10

M.P.: 202-203 (d)

Appearance: Green iridescent microcrystals.

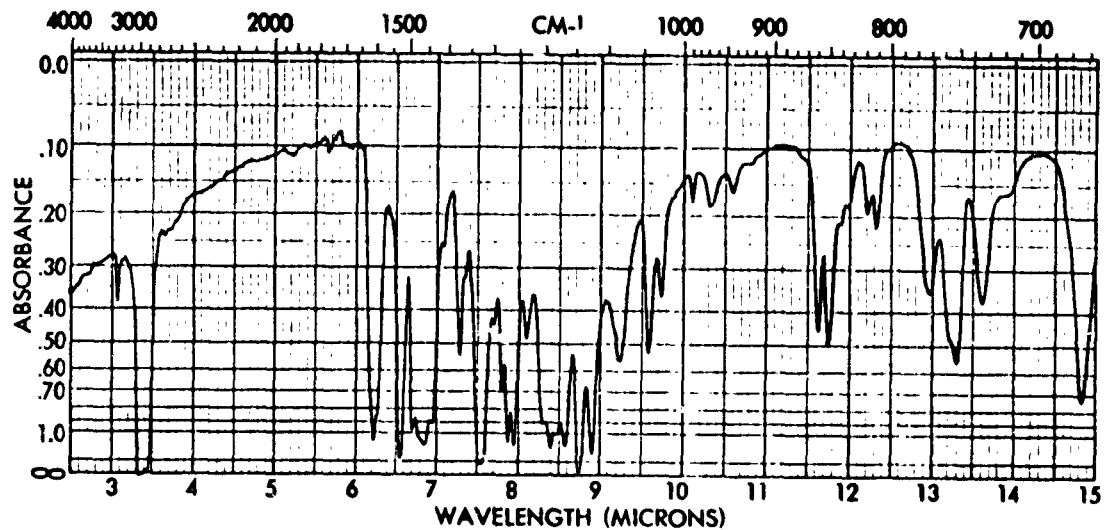
Synthetic Procedure: 1 % Yield: 67

| Analysis: | C | H | N | S | Zn |
|-----------|------|------|------|------|------|
| Found | 51.9 | 4.45 | 16.4 | 9.18 | 8.99 |
| Calc. | 51.7 | 4.34 | 16.1 | 9.21 | 9.40 |

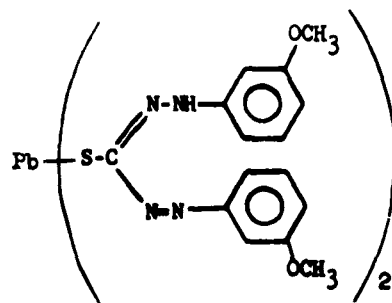
Spectral Data

| | Color | λ_{Max} | ϵ | Thermal Return, Half Life: 18 sec. |
|--------------|------------|-----------------|------------|---|
| Unirradiated | Red | 282 | 30,000 | % Conversion: 64 (Cary 14 NIR Source) |
| | | 350 | 12,000 | |
| | | 532 | 88,100 | Lightfastness in C.A. Film: 69 (Sun hours to 50% fade) |
| Irradiated | Bluish Red | 680 | | |

Remarks: Purification solvent: chloroform-methanol.



Compound No.: 53 Name: Lead bis[1,5-di(m-methoxyphenyl)thiocarbazonate]



Mol. Wt.: 838.67 M.P.: 207-209 (d)

Appearance: Maroon micro crystals.

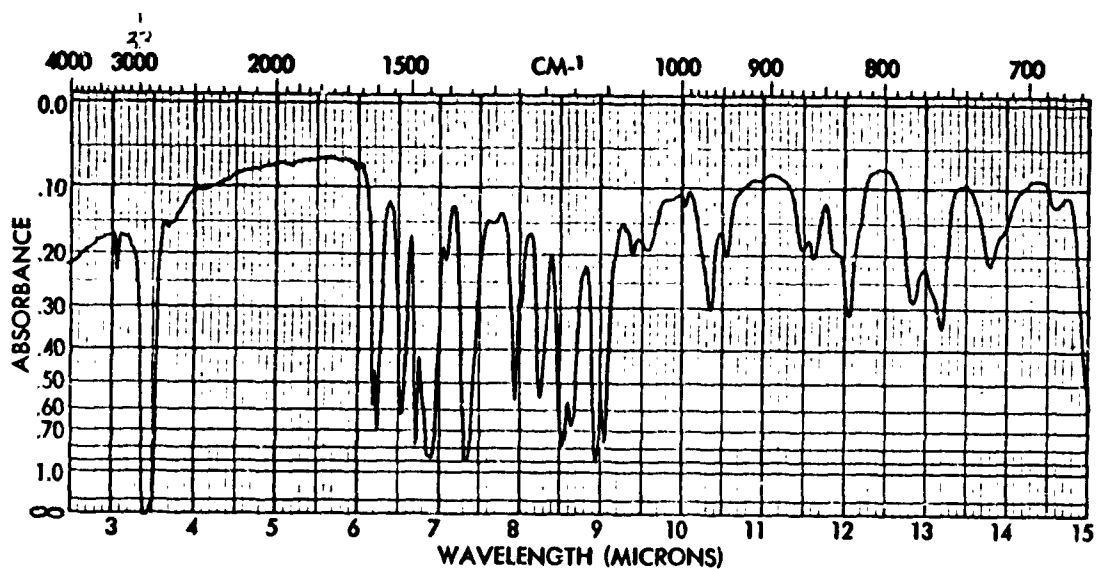
Synthetic Procedure: 1 % Yield: 56

| Analysis: | C | H | N | S | Pb |
|-----------|------|------|------|------|------|
| Found | 41.9 | 3.20 | 13.2 | 7.72 | 23.7 |
| Calc. | 43.0 | 3.61 | 13.4 | 7.65 | 24.7 |

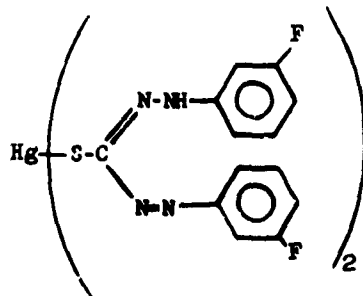
Spectral Data

| Color | λ_{Max} | ϵ | Thermal Return, Half Life: |
|-------------------|-----------------|------------|---|
| Unirradiated Pink | 280 | 33,600 | % Conversion: 22 (Cary 14 NIR Source) |
| | 340 | 14,400 | |
| | 520 | 62,700 | |
| Irradiated | 650 | | Lightfastness in C.A. Film: 15 (Sun hours to 50% fade) |

Remarks: Recrystallized from chloroform-methanol and chlorobenzene. Analysis did not change.



Compound No.: 54 Name: Mercury bis[1,5-di(m-fluorophenyl)thiocarbazonate]



Mol. Wt.: 783.06

M.P.: 236-237

Appearance: Orange solid

Synthetic Procedure: 1

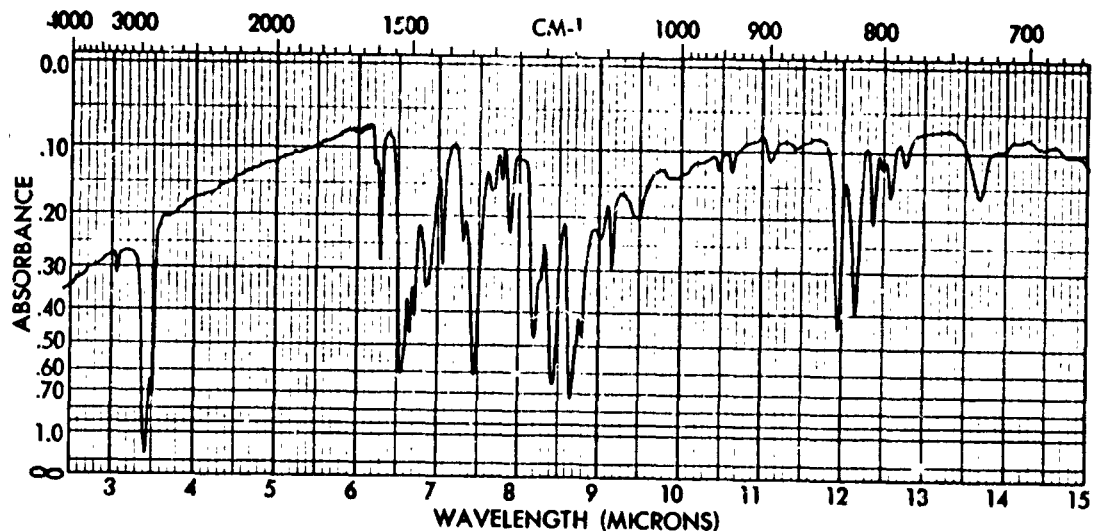
% Yield: 65

| Analysis: | C | H | N | S | F | Hg |
|-----------|------|------|------|------|------|------|
| Found | 40.2 | 2.30 | 14.3 | 8.19 | 9.92 | 25.6 |
| Calc. | 39.9 | 2.32 | 14.3 | 8.19 | 9.70 | 25.6 |

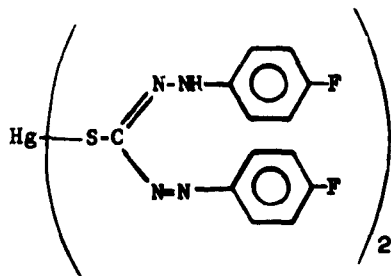
Spectral Data

| | Color | λ_{Max} | ϵ | Thermal Return, Half Life: |
|--------------|--------|-----------------|------------------|--|
| Unirradiated | Orange | 270 485 | 36,300 63,200 | % Conversion: 86 (Cary 14 NIR Source) |
| Irradiated | Blue | 595 | | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks: Purification solvent: tetrahydrofuran-methanol.



Compound No.: 55 Name: Mercury bis[1,5-di(p-fluorophenyl)thiocarbazonate]



Mol. Wt.: 783.06

M.P.: 245-246

Appearance: Red micro crystals.

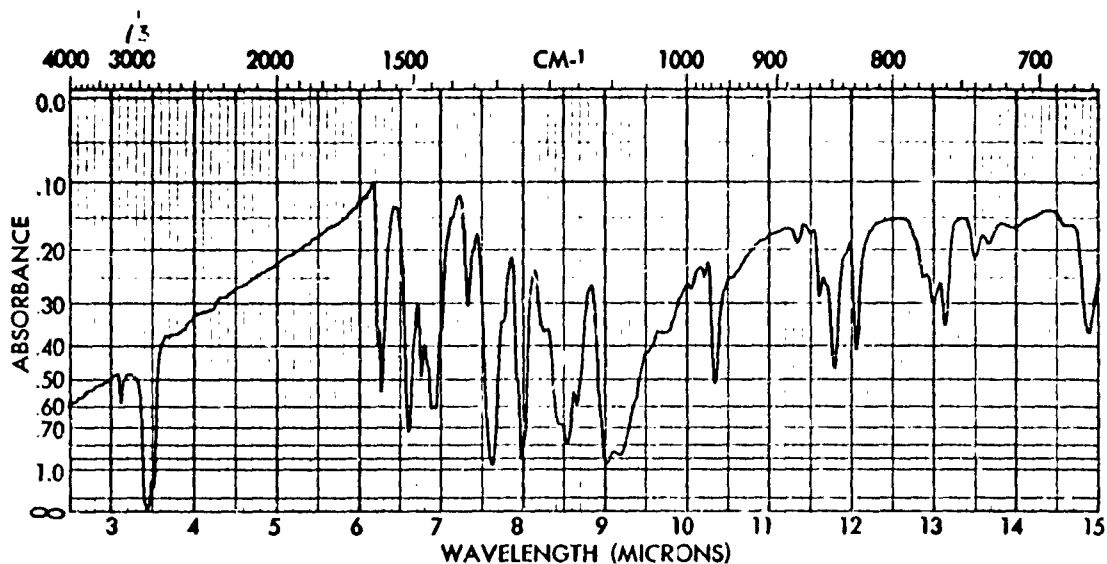
Synthetic Procedure: 1 % Yield: 38

| Analysis: | C | H | N | S | Hg |
|-----------|------|------|------|------|------|
| Found | 39.7 | 2.14 | 14.1 | 7.77 | 25.9 |
| Calc. | 39.9 | 2.32 | 14.3 | 8.19 | 25.6 |

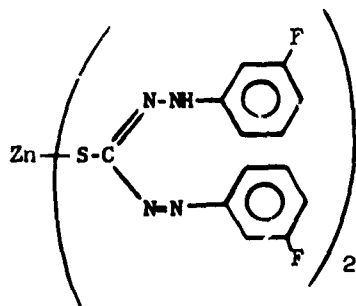
Spectral Data

| | Color | λ_{Max} | ϵ | Thermal Return, Half Life: |
|--------------|--------|-----------------|------------|--|
| Unirradiated | Yellow | 265 | 28,300 | % Conversion: 81 (Cary 14 NIR Source) |
| | | 305 (sh) | 14,600 | |
| | | 485 | 56,300 | |
| Irradiated | Blue | 590 | | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks: Purification solvent: chlorobenzene followed by trituration with methanol.



Compound No.: 56 Name: Zinc bis[1,5-di(m-fluorophenyl)thiocarbazonate]



Mol. Wt.: 647.83 M.P.: 244.5-245(d)

Appearance: Maroon solid

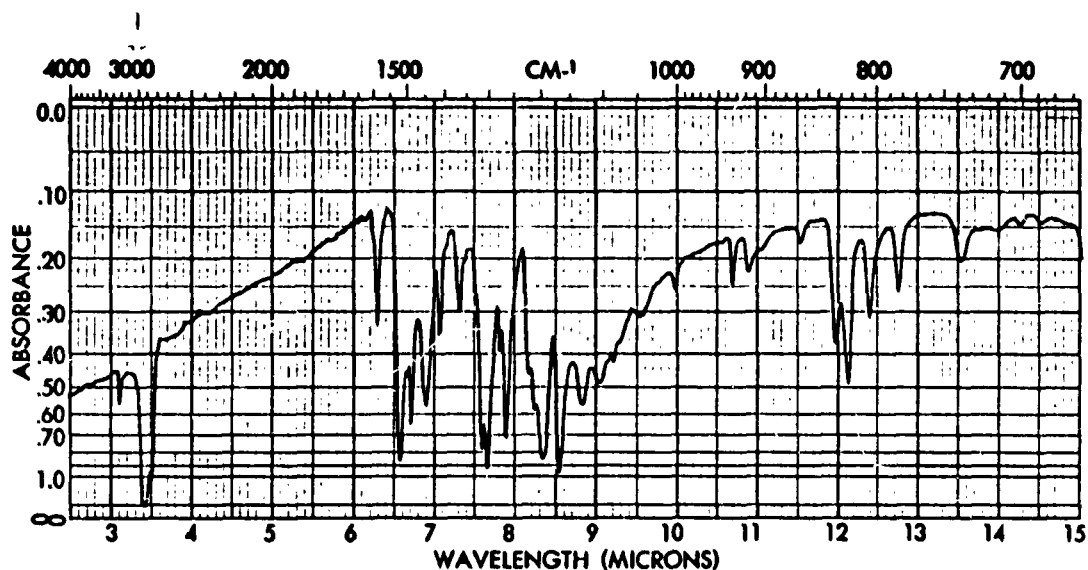
Synthetic Procedure: 1 % Yield: 23

| Analysis: | C | H | N | S | F | Zn |
|-----------|------|------|------|------|------|------|
| Found | 48.4 | 3.05 | 17.3 | 10.0 | 11.8 | 9.75 |
| Calc. | 48.2 | 2.80 | 17.3 | 9.98 | 11.7 | 10.1 |

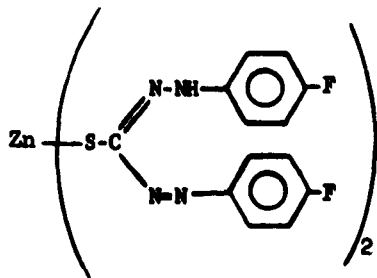
Spectral Data

| Color | $\lambda_{Max.}$ | ϵ | Thermal Return, Half Life: 26 sec. |
|--------------------------|------------------|------------|--|
| Unirradiated Red | 275 | 29,400 | % Conversion: 69 (Cary 14 NTR Source) |
| | 360 | 11,500 | |
| | 528 | 89,800 | |
| Irradiated Bluish Red | 680 | | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks: Purification solvent: chloroform-methanol.



Compound No.: 57 Name: Zinc bis[1,5-di(p-fluorophenyl)thiocarbazonate]



Mol. Wt.: 647.83 M.P.: 274-275 (d)

Appearance: Maroon solid

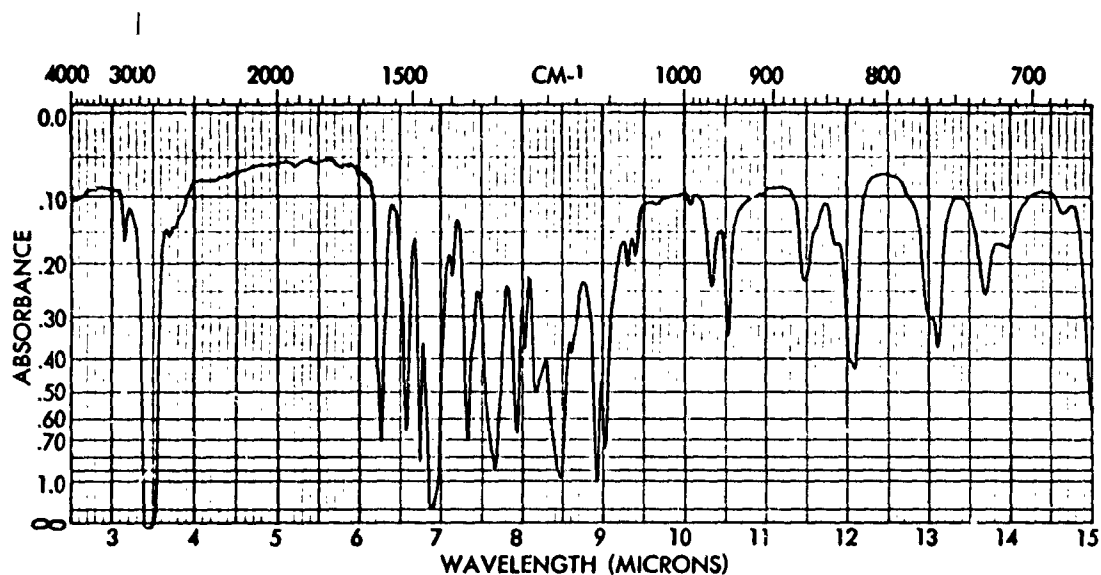
Synthetic Procedure: 1 % Yield: 32

| Analysis: | C | H | N | S | F | Zn |
|-----------|------|------|------|------|------|------|
| Found | 48.2 | 3.08 | 17.3 | 9.88 | 12.3 | 9.6 |
| Calc. | 48.2 | 2.80 | 17.3 | 9.98 | 11.7 | 10.1 |

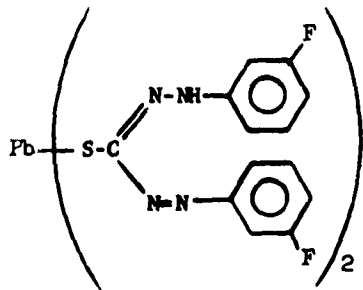
Spectral Data

| Color | λ_{Max} | ϵ | Thermal Return, Half Life: 14 sec. |
|--------------|-----------------|------------|------------------------------------|
| Unirradiated | | | % Conversion: 66 |
| Red | 275 | 27,100 | (Cary 14 NTI Source) |
| | 360 | 10,700 | |
| | 525 | 87,100 | |
| Irradiated | | | Lightfastness in C.A. Film: |
| Bluish Red | 670 | | (Sun hours to 50% fade) |

Remarks: Purification solvent: tetrahydrofuran-methanol.



Compound No.: 58 Name: Lead bis[1,5-di(m-fluorophenyl)thiocarbazonate]



Mol. Wt.: 790.36 M.P.: 216-217

Appearance: Maroon solid.

Synthetic Procedure: 1 % Yield: 30

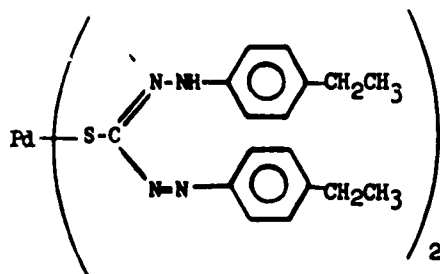
| Analysis: | C | H | N | S | F | Pb |
|-----------|------|------|------|------|------|------|
| Found | 40.0 | 2.62 | 14.2 | 8.14 | 9.87 | 26.1 |
| Calc. | 39.5 | 2.30 | 14.2 | 8.19 | 9.62 | 26.2 |

Spectral Data

| | Color | λ_{Max} | ϵ | Thermal Return, Half Life: |
|--------------|-------|-----------------|------------|--|
| Unirradiated | Red | | | % Conversion: (Cary 14 NIR Source) |
| Irradiated | | | | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks: Limited solubility in CH_2Cl_2 . Purification solvent: tetrahydrofuran-
methanol.

Compound No.: 59 Name: Palladium bis[1,5-di(p-ethylphenyl)thiocarbazonate]



Mol. Wt.: 729.42

M.P.:

Appearance:

Synthetic Procedure:

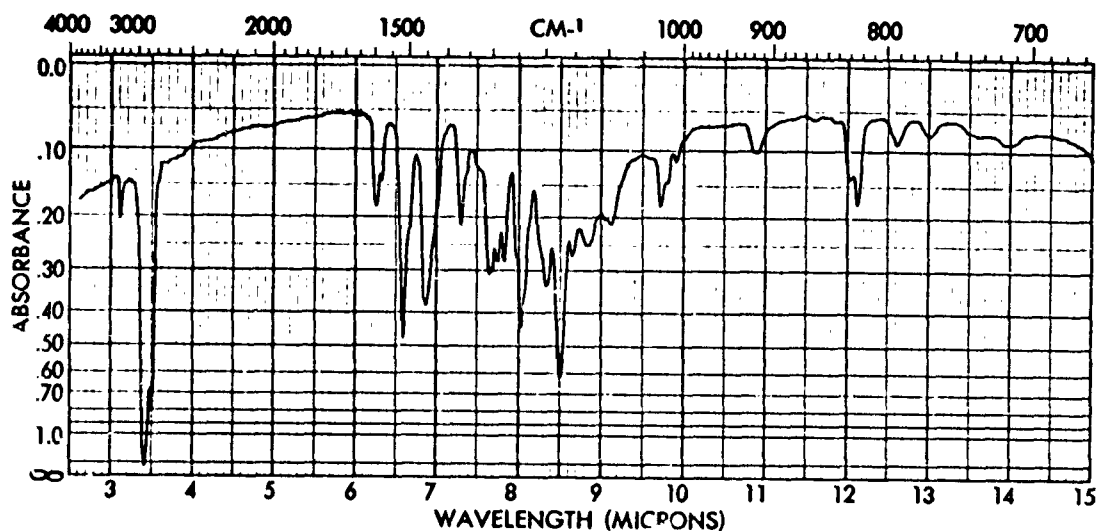
% Yield:

| | | | | |
|-----------|---|---|---|---|
| Analysis: | C | H | N | S |
| Found | | | | |
| Calc. | | | | |

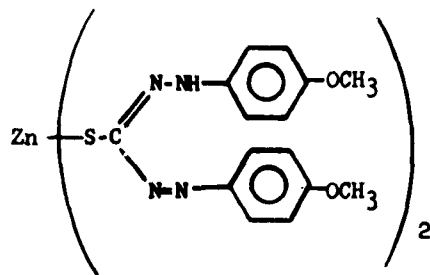
Spectral Data

| Color | λ Max. | ϵ | Thermal Return, Half Life: |
|--------------|----------------|------------|--|
| Unirradiated | | | % Conversion: (Cary 14 NIR Source) |
| Irradiated | | | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks: Product gave very poor analysis, will be resynthesized.



Compound No.: 60 Name: Zinc bis[1,5-di(p-methoxyphenyl)thiocarbazonate]



Mol. Wt.: 696.10

M.P.: 254-254.5

Appearance: Green iridescent solid.

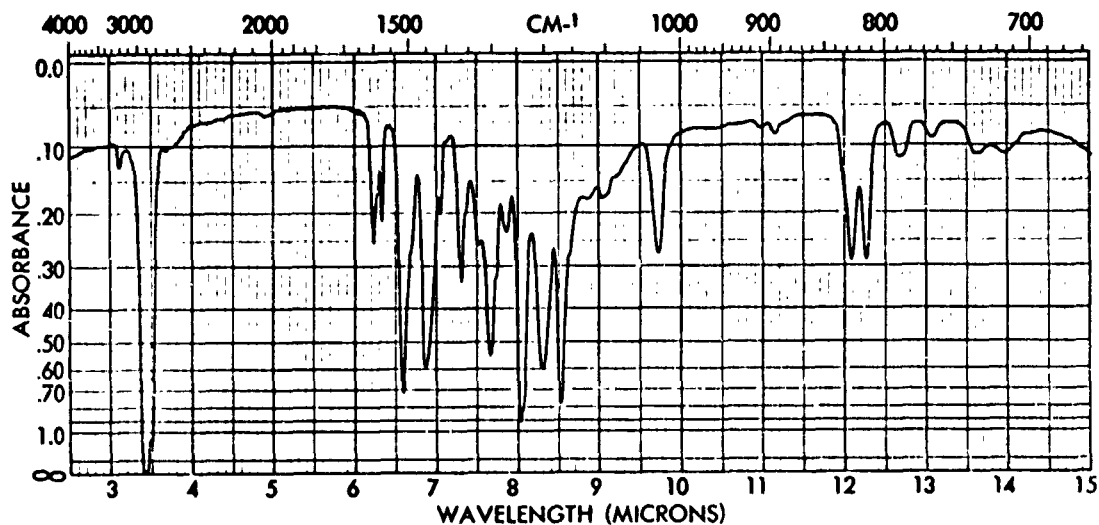
Synthetic Procedure: 1 % Yield: 45

| Analysis: | C | H | N | S | Zn |
|-----------|------|------|------|------|------|
| Found | 51.9 | 4.33 | 16.2 | 9.32 | 9.39 |
| Calc. | 51.8 | 4.34 | 16.1 | 9.21 | 9.39 |

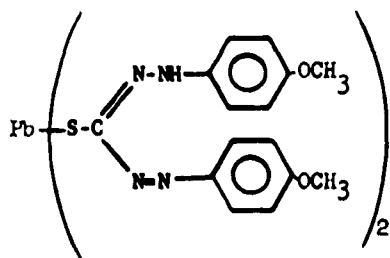
Spectral Data

| | Color | λ Max. | ϵ | Thermal Return, Half Life: |
|--------------|-------------|----------------|------------|---|
| Unirradiated | Pink | 280 | 24,400 | % Conversion: 61 (Cary 14 NIR Source) |
| | | 315 | 17,150 | |
| | | 545 | 93,000 | |
| Irradiated | Bluish Pink | 690 | | Lightfastness in C.A. Film: 45 (Sun hours to 50% fade) |

Remarks: Purification solvent: chloroform-methanol.



Compound No.: 61 Name: Lead bis[1,5-di(p-methoxyphenyl)thiocarbazonate]



Mol. Wt.: 838.67

M.P.: 191-192

Appearance: Maroon solid.

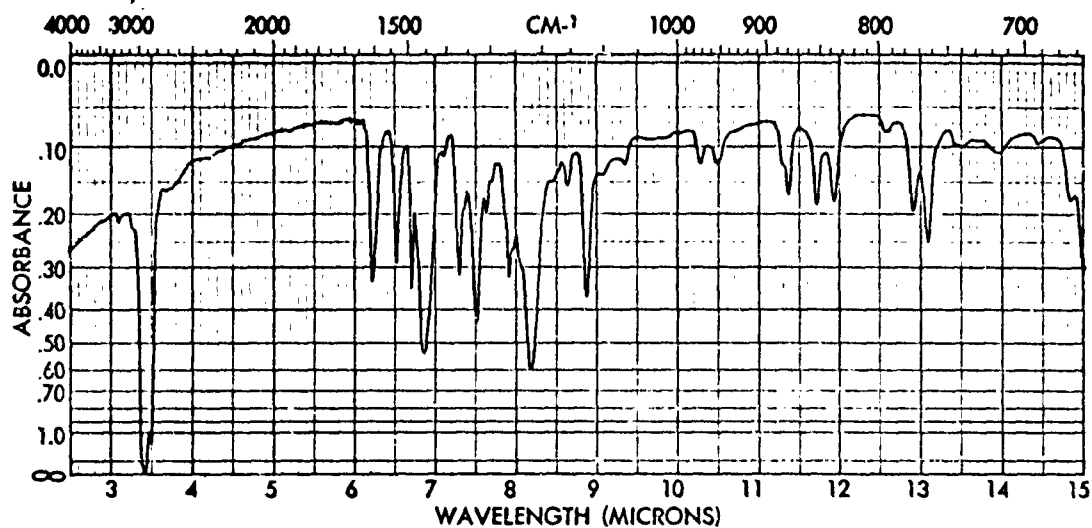
Synthetic Procedure: 1 % Yield: 24

| Analysis: | C | H | N | S | Pb |
|-----------|------|------|------|------|------|
| Found | 42.8 | 3.33 | 13.4 | 8.14 | 24.5 |
| Calc. | 43.0 | 3.61 | 13.4 | 7.65 | 24.7 |

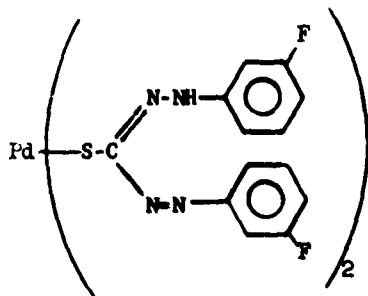
Spectral Data

| | Color | λ_{Max} | ϵ | Thermal Return, Half Life: |
|--------------|-------|-----------------|------------------|---|
| Unirradiated | Pink | 320 (sh) 530 | 21,200 65,400 | % Conversion: Less than 10%. (Cary 14 NIR Source) |
| Irradiated | | 620 (?) | | Lightfastness in C.A. Film: 15 (Sun hours to 50% fade) |

Remarks: Purification solvent: tetrahydrofuran-methanol.



Compound No.: 62 Name: Palladium bis[1,5-di(m-fluorophenyl)thiocarbazonate]



Mol. Wt.: 838.67 M.P.: 285-285.5

Appearance: Dark purple solid

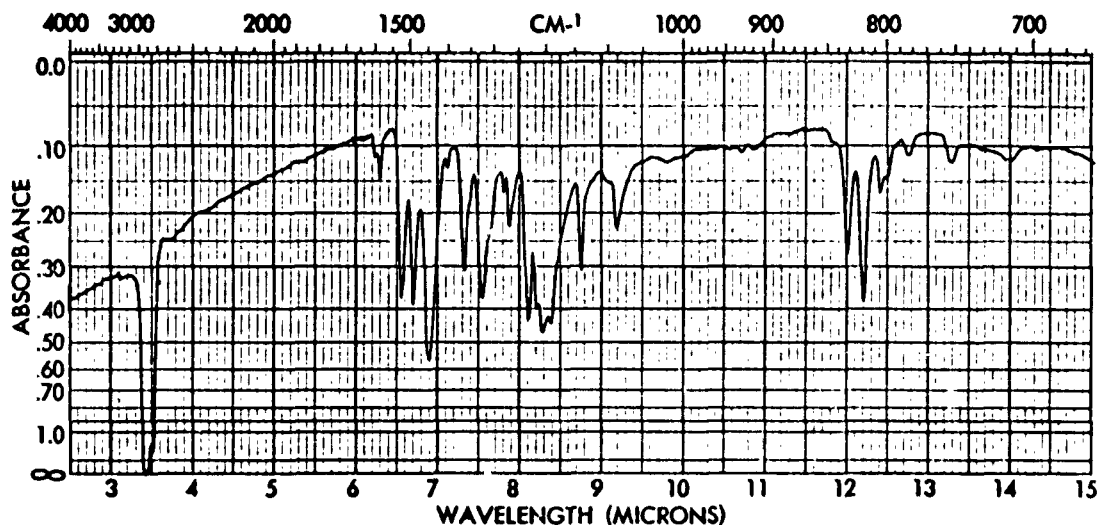
Synthetic Procedure: 2 % Yield: 25

| Analysis: | C | H | N | S | F | Pd |
|-----------|------|------|------|------|------|------|
| Found | 45.6 | 2.87 | 16.2 | 9.06 | 11.5 | 14.9 |
| Calc. | 45.3 | 2.63 | 16.3 | 9.31 | 11.0 | 15.0 |

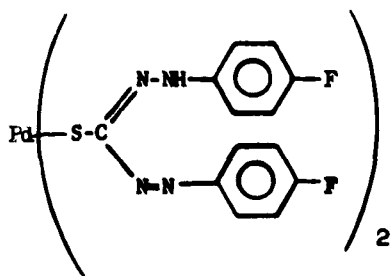
Spectral Data

| | | | |
|--------------|-----------------------|-------|--|
| | Color λ_{Max} | ξ | Thermal Return, Half Life: |
| Unirradiated | Pale Green | | % Conversion: (Cary 14 NIR Source) |
| Irradiated | Yellow | | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks. Poor solubility in CH_2Cl_2 . Purification solvent: tetrahydrofuran-methanol.



Compound No.: 63 Name: Palladium bis[1,5-di(p-fluorophenyl)thiocarbazonate]



Mol. Wt.: 688.99 M.P.: 310-311

Appearance: Dark purple solid.

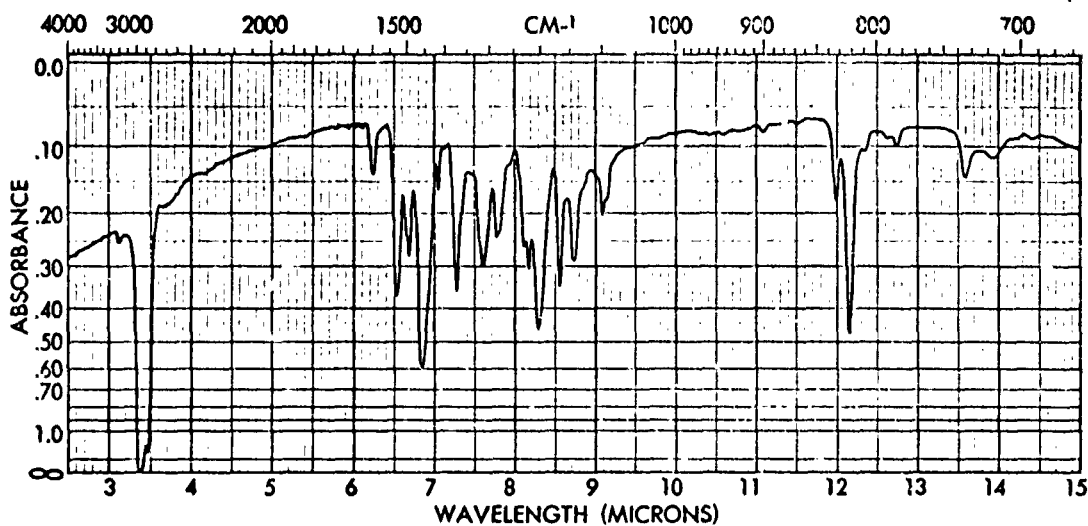
Synthetic Procedure: 2 % Yield: 20

| Analysis: | C | H | N | S | Pd |
|-----------|------|------|------|------|------|
| Found | 45.4 | 2.57 | 16.2 | 9.04 | |
| Calc. | 45.3 | 2.63 | 16.3 | 9.31 | 15.0 |

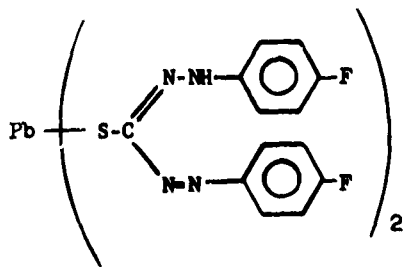
Spectral Data

| | | | | |
|--------------|--------|------------------|------------|--|
| | Color | $\lambda_{Max.}$ | ϵ | Thermal Return, Half Life: |
| Unirradiated | Green | | | % Conversion: (Cary 14 NIR Source) |
| Irradiated | Yellow | | | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks: Poor solubility in CH_2Cl_2 . Purification solvent: chlorobenzene.



Compound No.: 64 Name: Lead bis[1,5-di(p-fluorophenyl)thiocarbazonate]



Mol. Wt.: 789.78 M.P.: 236-237 (d)

Appearance: Maroon micro needles.

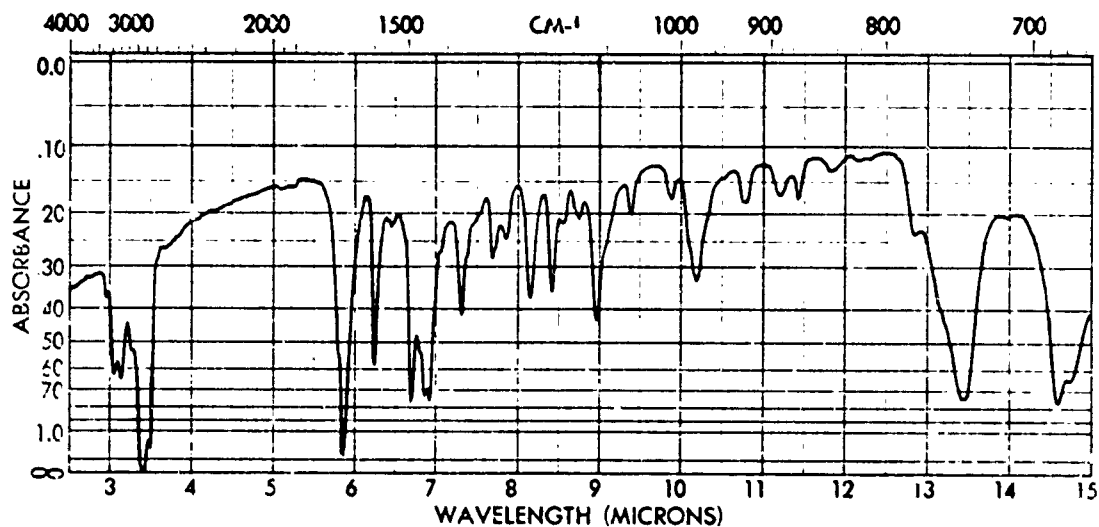
Synthetic Procedure: 1 % Yield: 45

| Analysis: | C | H | N | S | F | Pb |
|-----------|------|------|------|------|------|------|
| Found | 39.8 | 2.59 | 14.4 | 9.02 | 9.79 | 26.5 |
| Calc. | 39.5 | 2.30 | 14.2 | 8.12 | 9.62 | 26.2 |

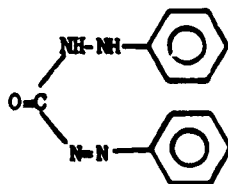
Spectral Data

| | | | |
|--------------|-----------------|------------|--|
| Color | λ_{Max} | ϵ | Thermal Return, Half Life: |
| Unirradiated | Pink | | % Conversion: (Cary 14 NIR Source) |
| Irradiated | | | Lightfastness in C.A. Film: (Sun hours to 50% fade) |

Remarks: Poor solubility in CH_2Cl_2 . Purification solvent: tetrahydrofuran.



Compound No.: 65 Name: 1,5-Diphenylcarbazone



Mol. Wt.: 240.26 M.P.: 126-127

Appearance: Orange-yellow needles

Synthetic Procedure: * % Yield: 50

Analysis: C H N S
 Found
 Calc.

Spectral Data

| Color | λ Max. | ϵ | Thermal Return, Half Life: |
|--------------|----------------|------------|-----------------------------|
| Unirradiated | | | % Conversion: |
| Weak Pink | 455 | 636 | (Cary 14 NIR Source) |
| | 560 | 440 | |
| Irradiated | | | Lightfastness in C.A. Film: |
| Yellow | | | (Sun hours to 50% fade) |

Remarks: *da Silva, J., Calado, J. and de Moura, M. L., *Talanta* 11, 983 (1964).

FIGURES 1 - 10

FIGURE 1

SPECTRAL CURVES OF 2.6×10^{-5} M METHYLMERCURY
1,5-DIPHENYLHICCARBAZONATE IN METHYLENE
CHLORIDE (1-CM. CELL)

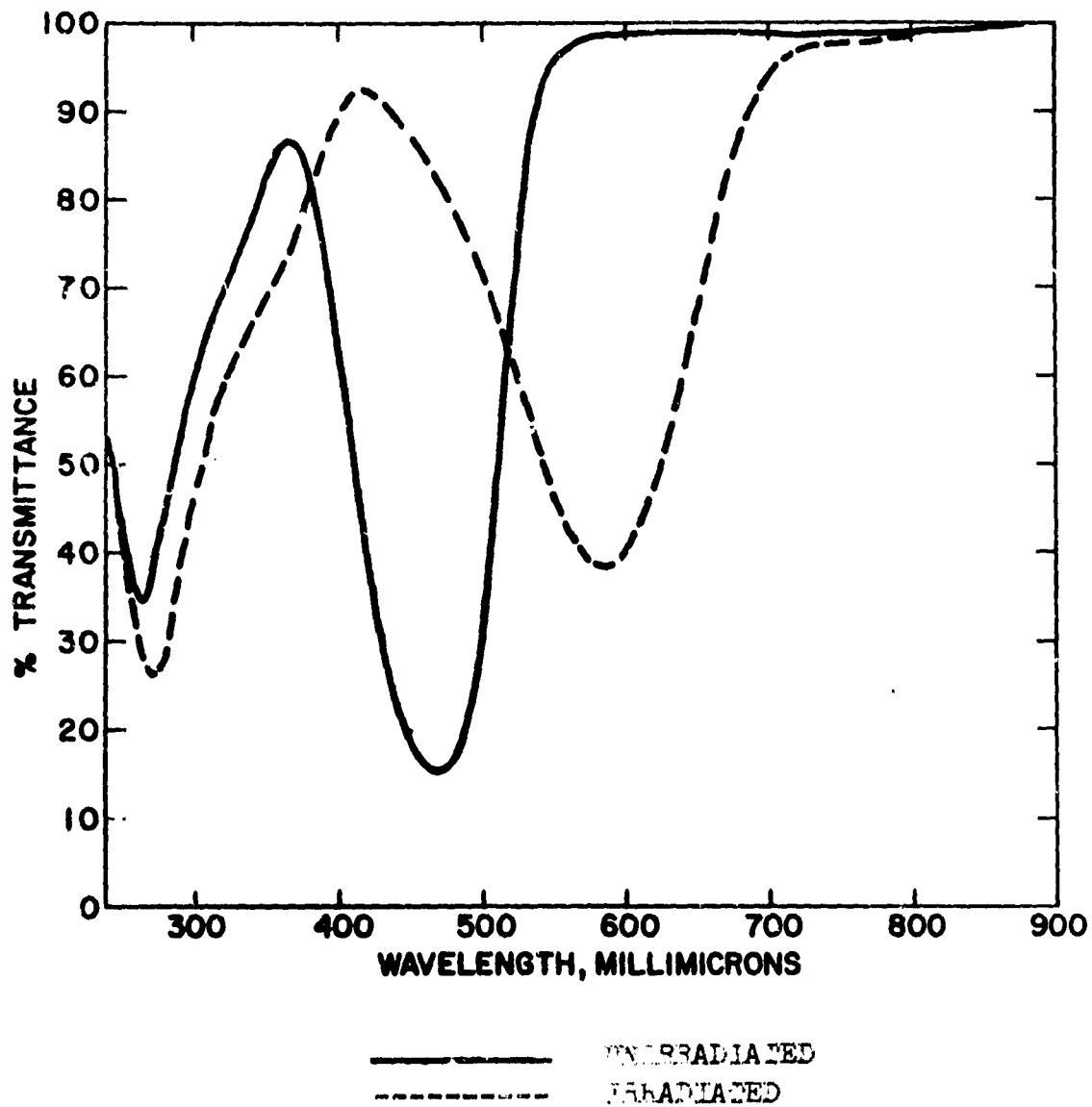


FIGURE 2

SPECTRAL CURVES OF 1.54×10^{-5} M MERCURY
BIS(1,5-DIPHENYLTHIOCARBAZONATE) IN METHYLENE
CHLORIDE (1-CM. CELL)

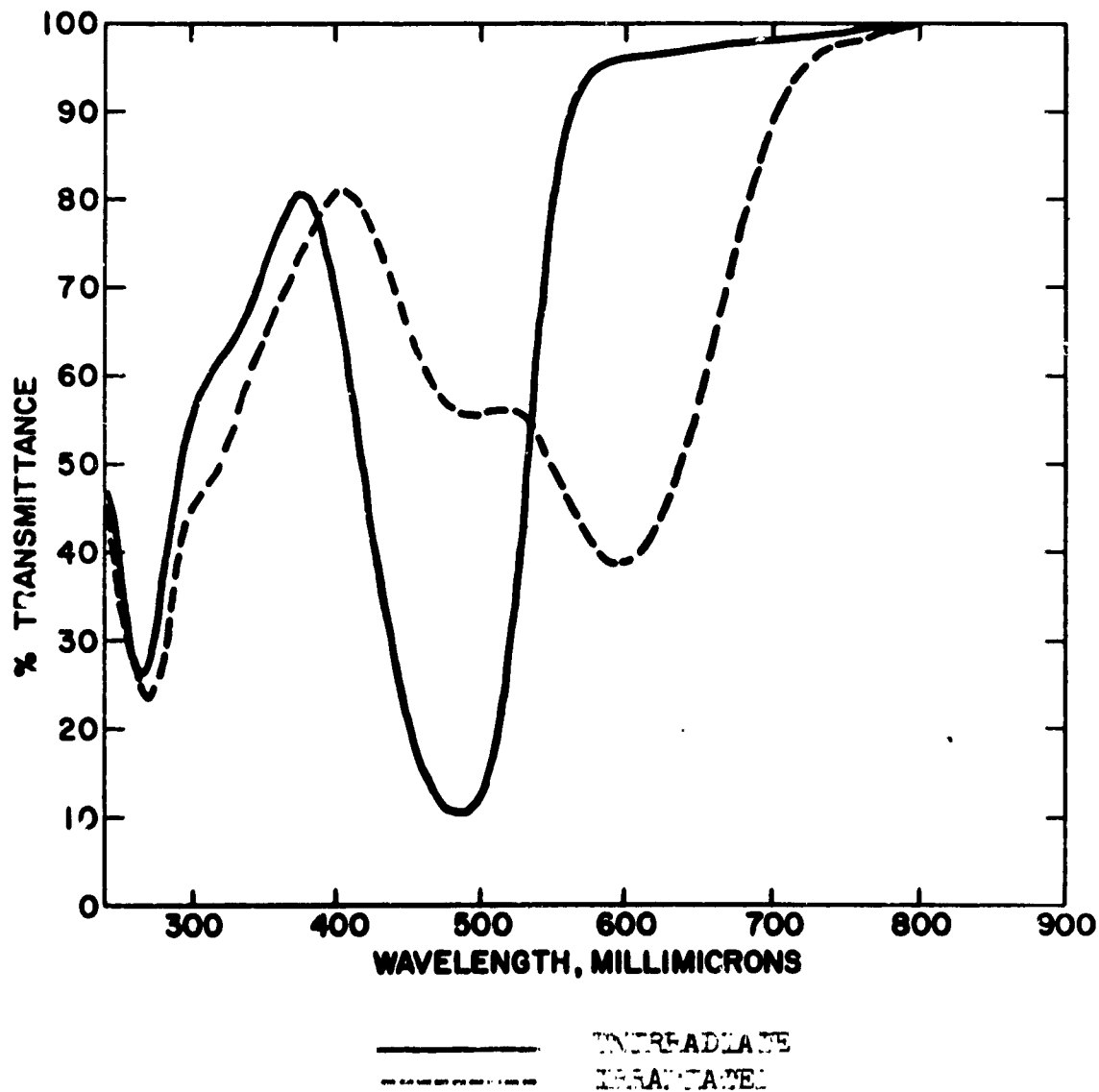


FIGURE 3

SPECTRAL CURVES 1.62×10^{-5} M MERCURY BIS-
[1,5-DI(*o*-TRIFLUOROMETHYLPHENYL)THIOCARBONATE]
COMPOUND 24, IN METHYLENE CHLORIDE (1-CM. CELL)

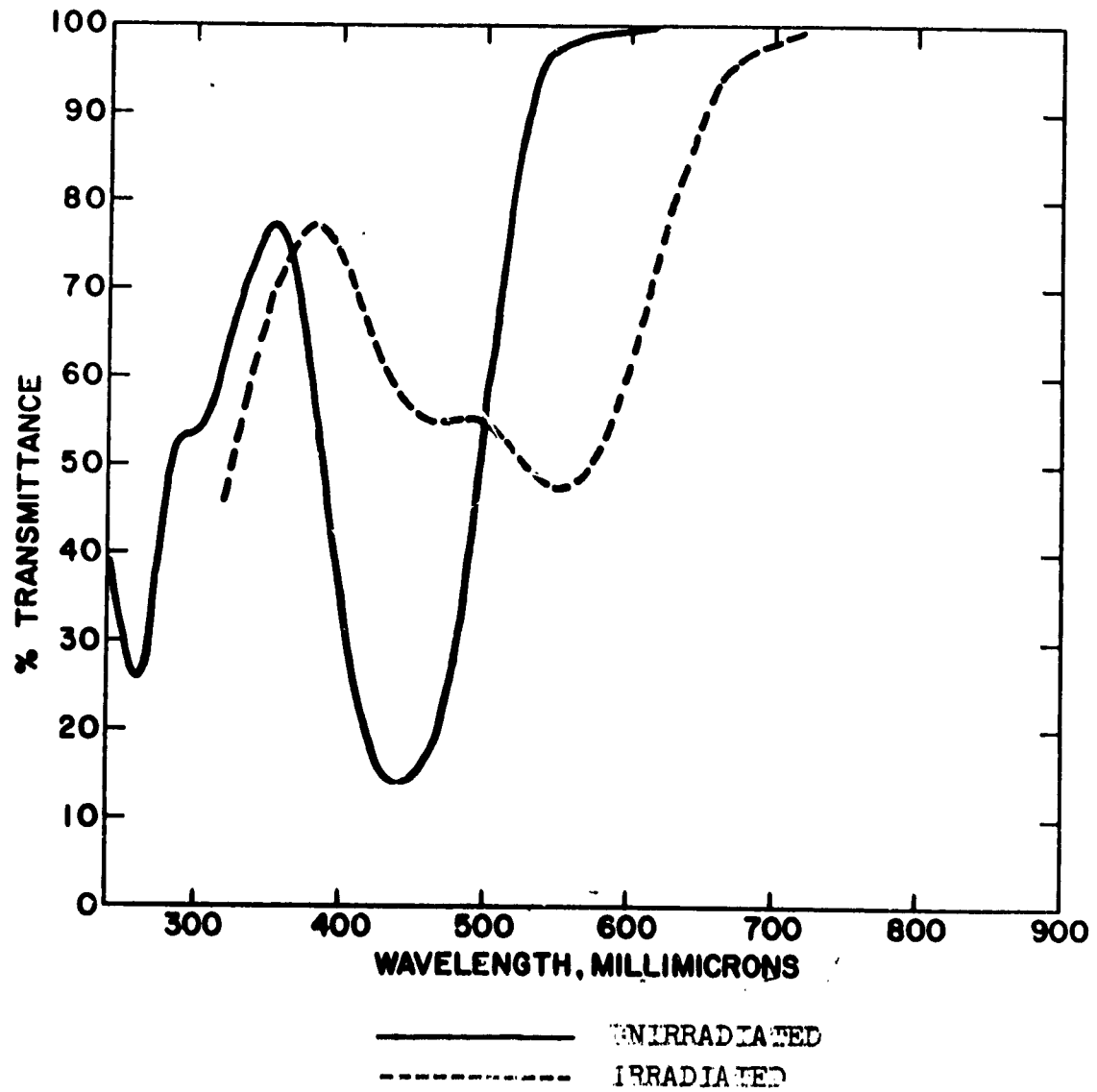


FIGURE 4

SPECTRAL CURVES OF 7.28×10^{-6} M ZINC BIS-
(1,5-DI(3-METHOXYPHENYL)THIOCARBAZONATE)
COMPOUND 3, IN METHYLENE CHLORIDE (1-CM. CELL)

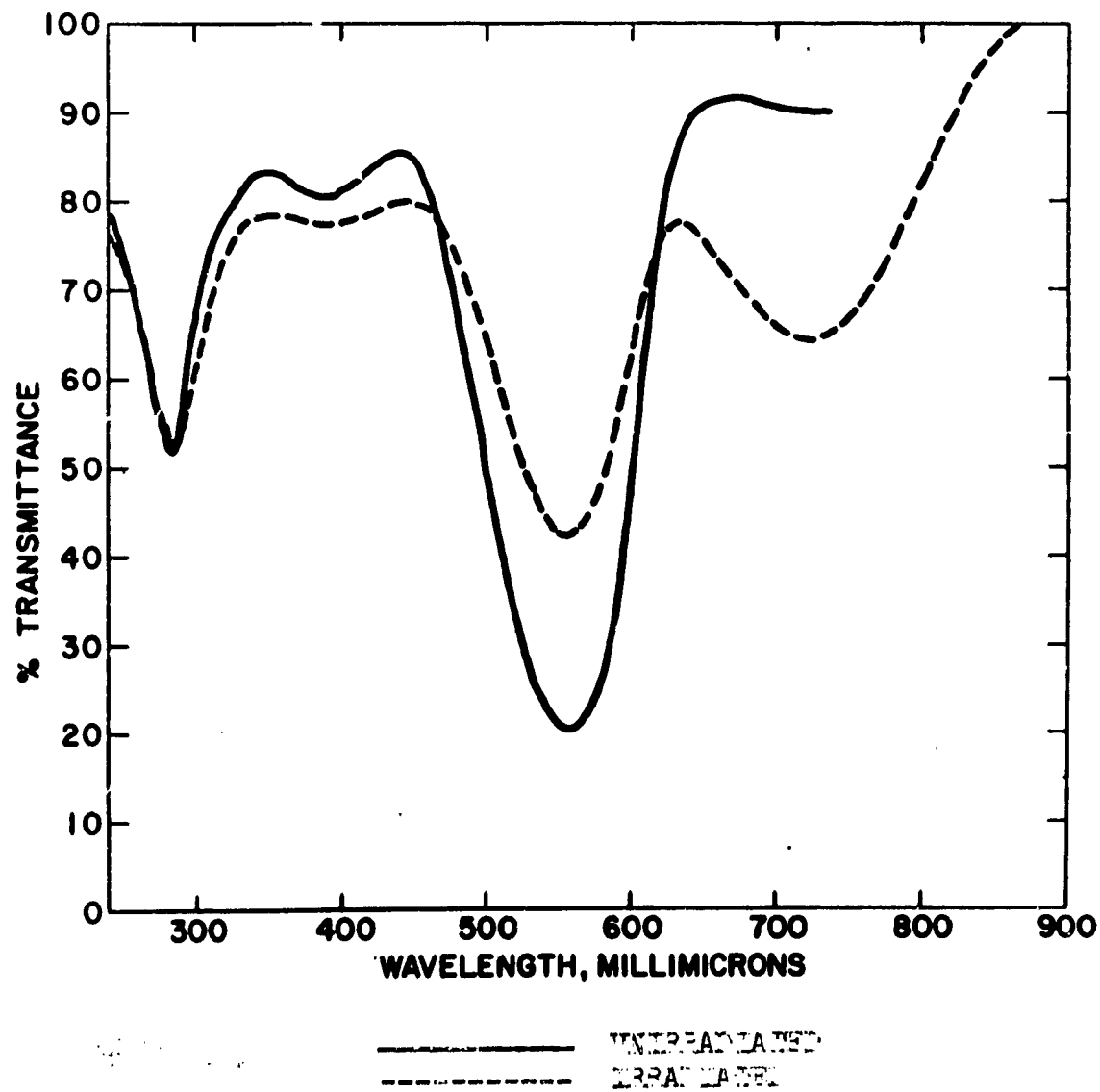


FIGURE 5

SPECTRAL CURVES OF 2.1×10^{-5} M PALLADIUM BIS-
[1,5-DI(o-ETHYLPHENYL)THIOCARBAZONATE],
COMPOUND 8, IN METHYLENE CHLORIDE (1-CM. CELL)

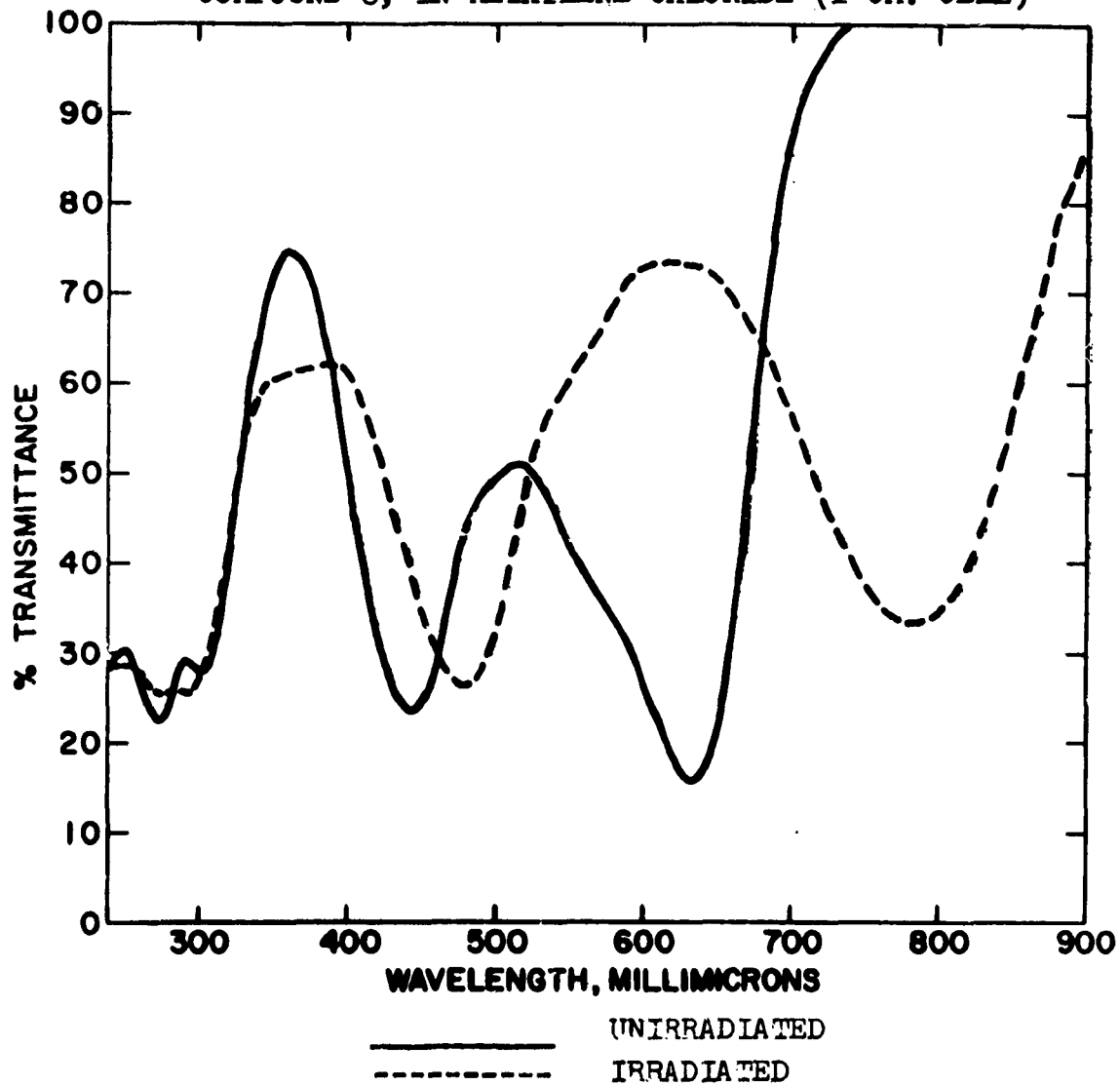


FIGURE 6

SPECTRAL CURVES OF 1.05×10^{-5} M BISMUTH
TRIS[1,5-BI(2-METHOXYPHENYL)THIOCARBAZONATE],
COMPOUND 5, IN METHYLENE CHLORIDE (1-CM. CELL)

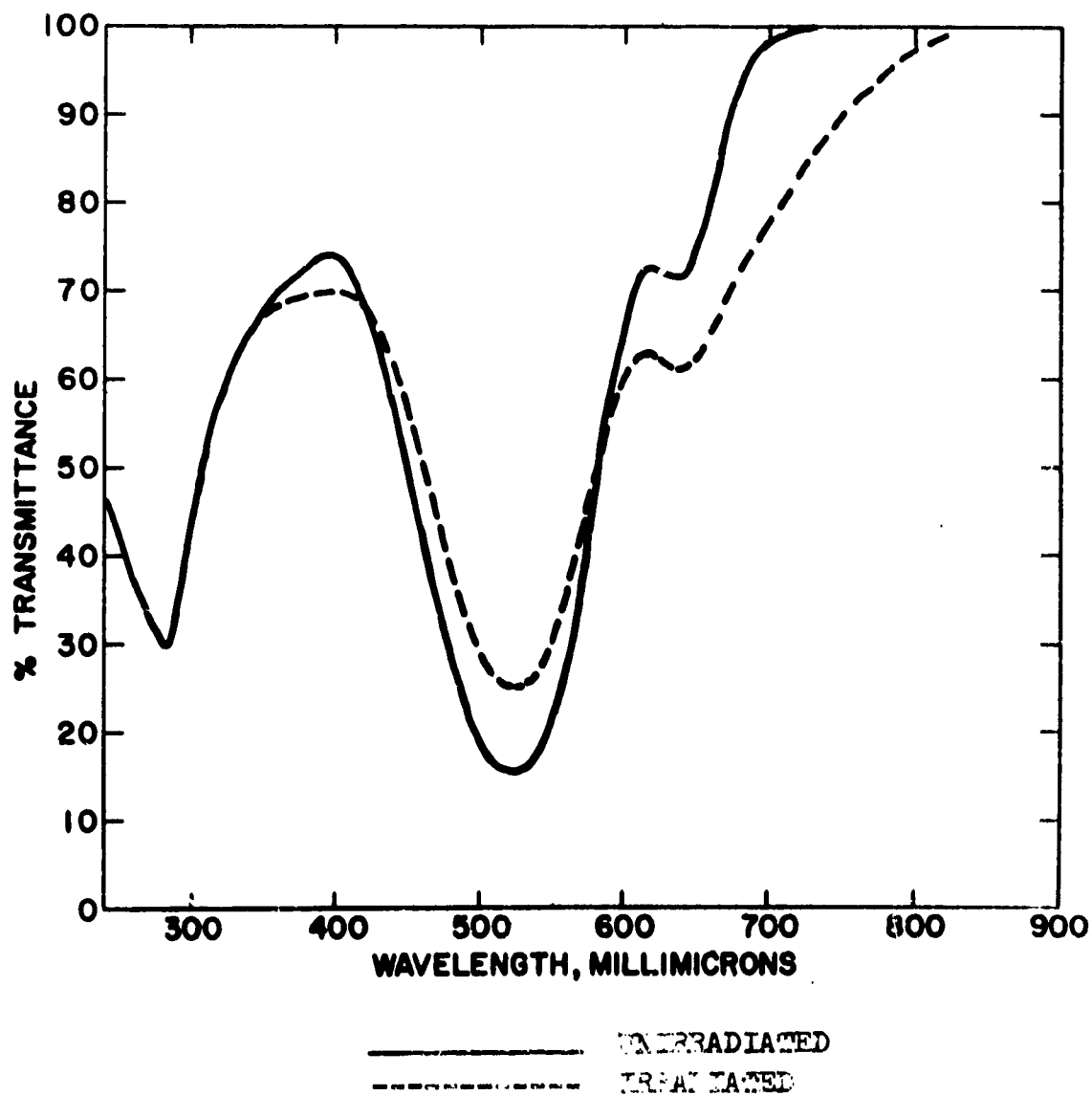


FIGURE 7

SPECTRAL CURVES OF 2.58×10^{-5} M TRIPHENYLLEAD
(1,5-DIPHENYLETHIOCARBAZONATE), COMPOUND 10, IN
METHYLENE CHLORIDE (1-CM. CELL)

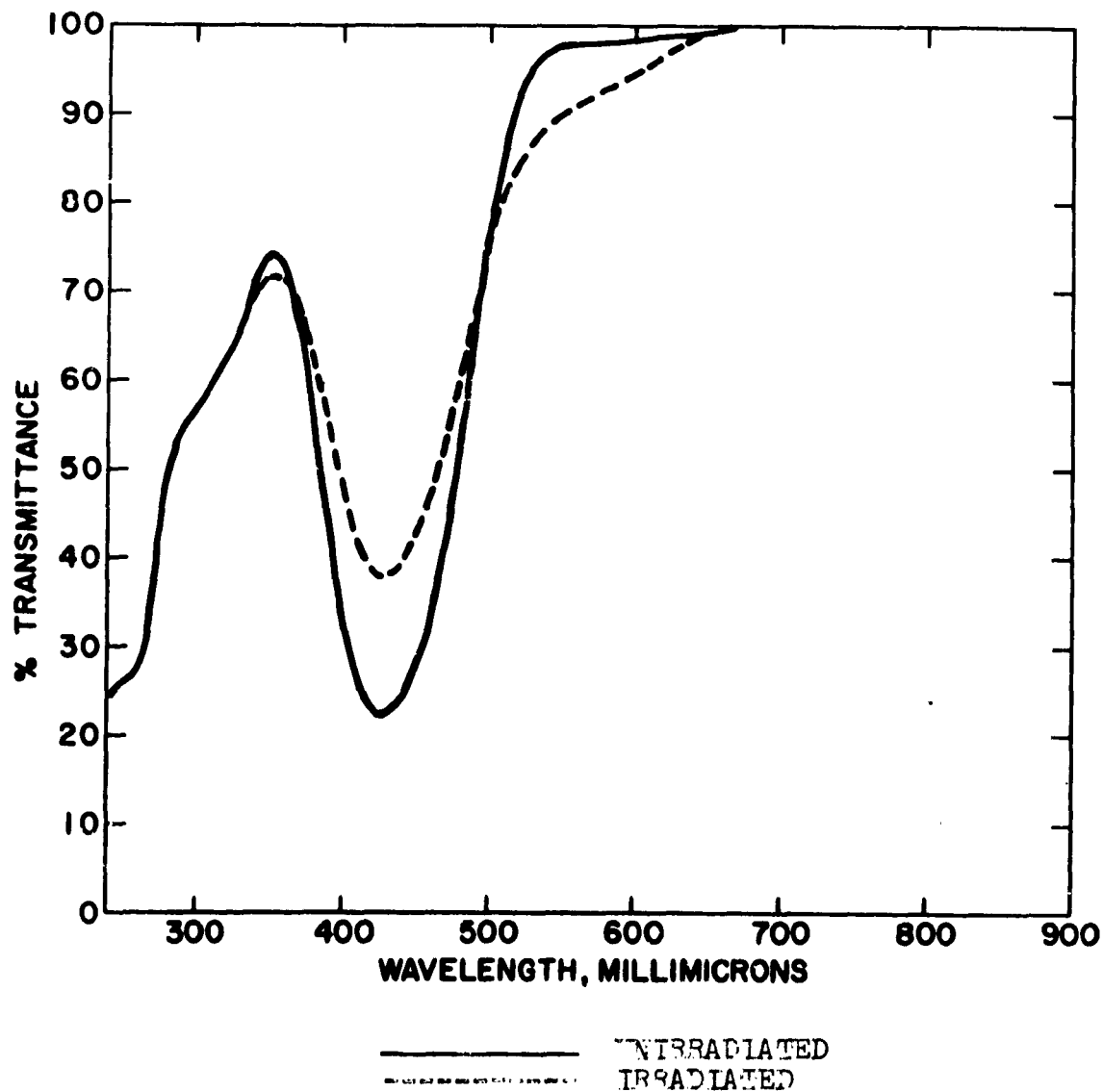
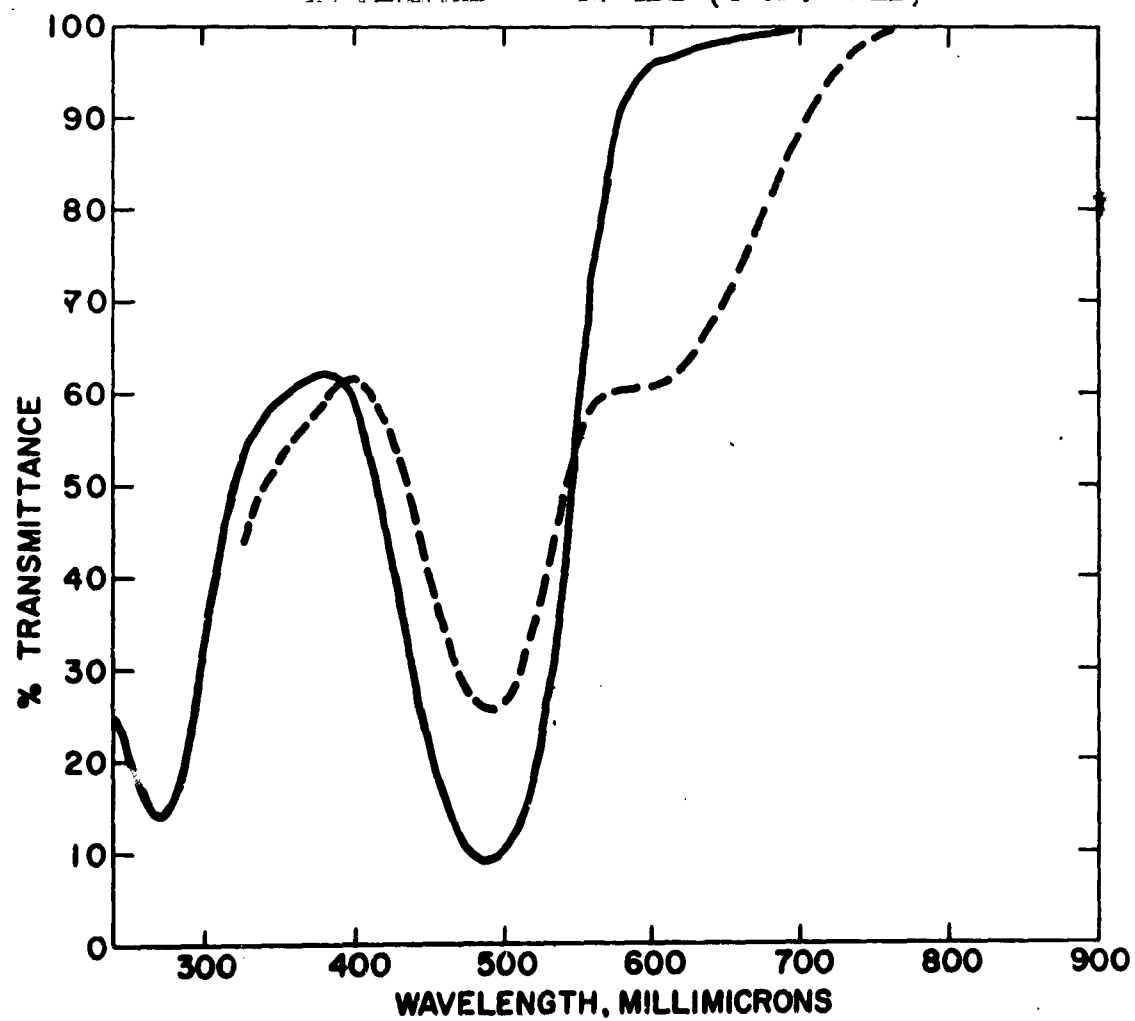


FIGURE 8

SPECTRAL CURVES OF 2.13×10^{-5} M PHENYLBISMUTH BIS
(5-SUBSTITUENT) ARSAZONATE, COMPOUND 13,
IN METHYLENE CHLORIDE (1-CM. CELL)



————— V. RADIATE
- - - - - 13

FIGURE 9

SPECTRAL CURVES OF 2.9×10^{-5} M SILVER
1,5-DI(o-ETHYLPHENYL)THIOCARBAZONATE,
COMPOUND 6, IN METHYLENE CHLORIDE (1-CM. CELL)

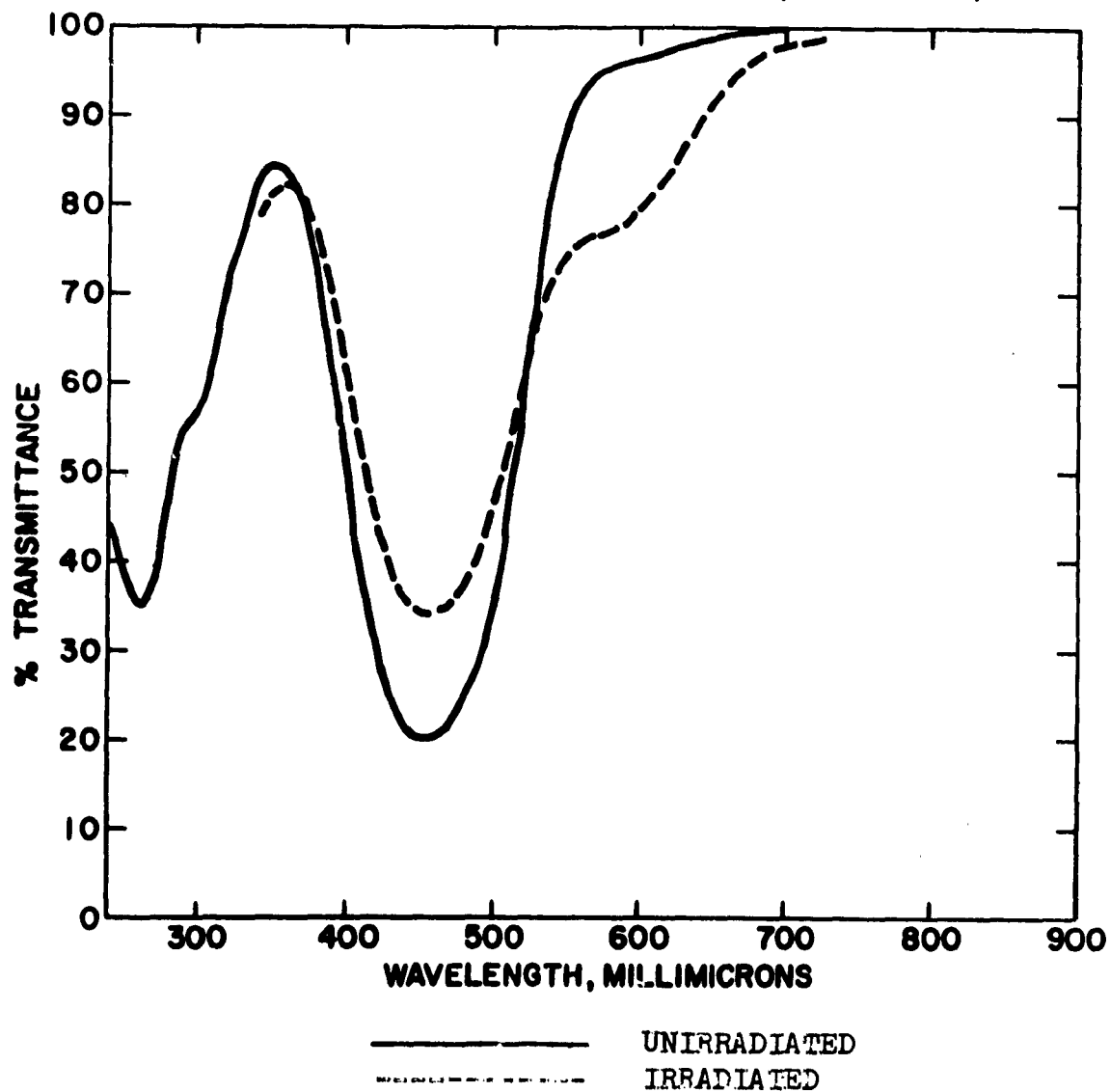
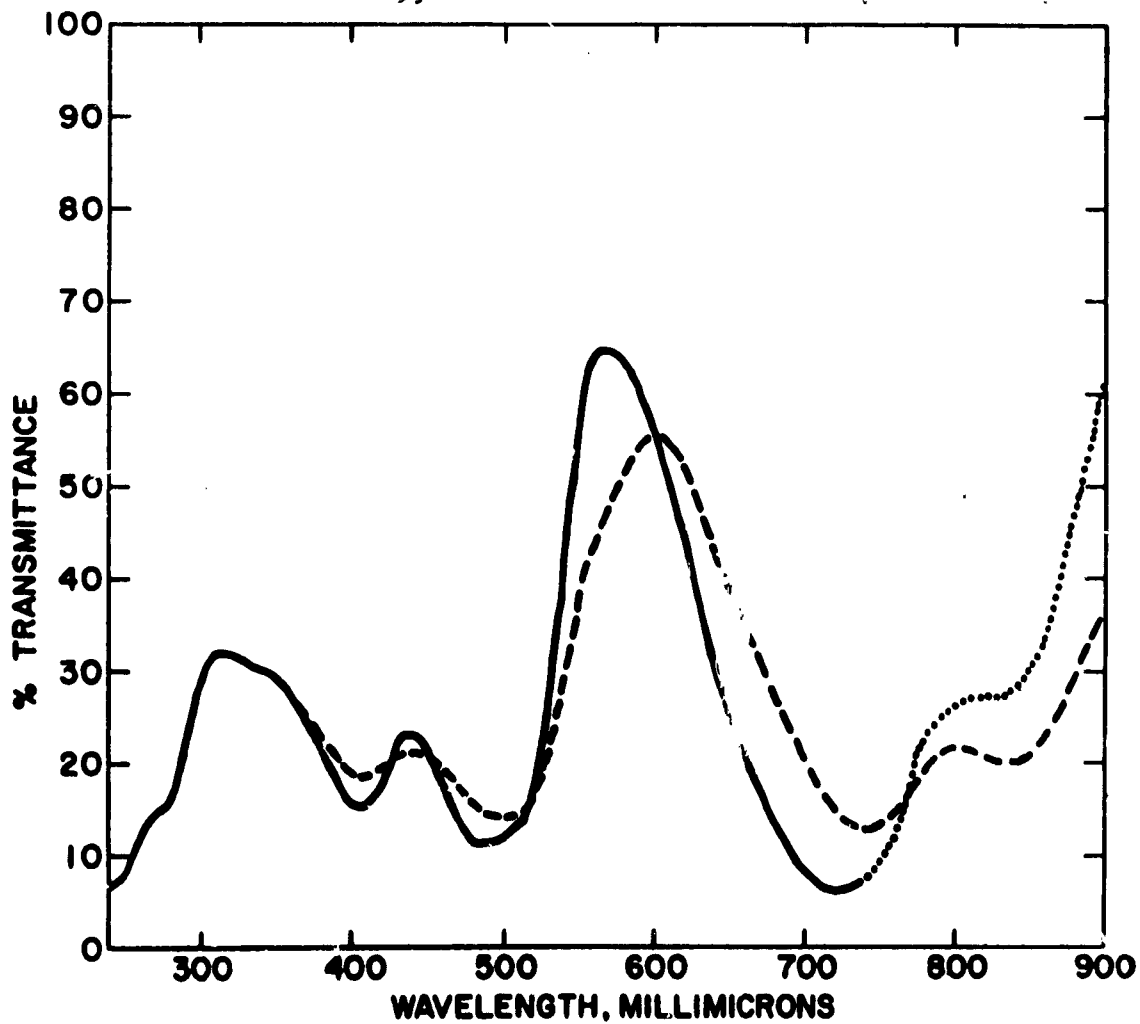


FIGURE 10

SPECTRAL TYPES OF 4.31×10^{-5} M PLATINUM
BIS(THIOCARBAZONATE) (1,2-DI-PHENYL-1,2-DITHIOCARBAZONATE),
COMPOUND 3, IN METHYLENE CHLORIDE (1-CM. CELL)



————— UNIRRADIATED

..... PERIODICALLY UNIRRADIATED SOLUTIONS
BEHAVING AS THE KAMM LAM 2

..... UNIRRADIATED

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

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| 13 ABSTRACT <p>In a study of photochromic colorants potentially useful for a "chameleon" type camouflage system, a number of metal dithizonates have been synthetically modified by introduction of groups in the <u>ortho</u>, <u>meta</u>, and <u>para</u> positions of both phenyl rings of dithizone. The resulting complexes were tested for spectral, photochromic and lightfastness properties. While spectral changes and increases in both solubility and lightfastness were affected by some <u>ortho</u> substituents, the photochromic properties (photostationary conversion and thermal return rate) were only slightly affected by substitution.</p> <p>The complexes of mercury exhibit the best all-round performance, although some zinc complexes approach the performance of mercury. The complexes of palladium exhibit potentially useful spectral and photochromic behavior that is quite different from the mercury type complexes and more application research is recommended regarding the incorporation of these palladium complexes in textile fibers.</p> <p>Fiber reactivity (on nylon) has been introduced into the mercury dithizonate system via a dichlorotriazinyl reactive group. This compound exhibited photochromic properties when reacted with nylon.</p> <p>Recommendations for future synthetic work are presented.</p> | | | |

| 14. KEY WORDS | LINK A | | LINK B | | LINK C | |
|------------------------|--------|----|--------|----|--------|----|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| Synthesis | 8 | | | | | |
| Colorants | 2 | | 9 | | | |
| Chromotropic | 0 | | | | | |
| Photochromic | 0 | | | | | |
| Mercury | 1 | | | | 1 | |
| Zinc | 1 | | | | | |
| Palladium | 1 | | | | | |
| Metalorganic compounds | 1 | | | | 1 | |
| Camouflage | 4 | | 4 | | | |
| Photochromism | | | 8 | | 2 | |
| Chromotropism | | | 8 | | | |
| Nylon | | | | | 1,2 | |
| Fiber | | | | | 1,2 | |
| Chemical reactions | | | | | 8 | |

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